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Low valent coinage metal coordination compounds with group 15, 16 and 17 donors

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Abstract

The advances made during the decade following 1985 in the coordination chemistry of monovalent group 11 metals with ligands possessing donor atoms from groups 15, 16 and 17 is discussed in an abstract manner aiming at the presentation of the main point of each discussed contribution. The classification of the ligands, wherever it was possible to achieve, has been performed with the synthetic inorganic chemist in mind, advancing from the simpler to the more complex ones, placing particular emphasis on the ligating atoms rather than on the overall ligand structure and constitution. The discussion does not include the enormous variety of group 11 metal compounds with metal–metal bonds while only a few compounds with metal–carbon have been introduced. © 1997 Elsevier Science S.A.

Keywords: Coinage metals; Halide; Pnictide; Chalcogenide; Homoleptic complexes; Heteroleptic complexes

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Nomenclature

acac	acetylacetone anion
bpy	2,2′-bipyridine
CD	Circular dichroism
CP MAS	Cross polarization magic angle spinning
COD	1,5-cyclooctadiene
COT	cyclooctatetraene
Cp	cyclopentadienyl ion
Cy	cyclohexyl group
DMF	*N,N*-dimethylformamide
DMSO	dimethylsulfoxide
dpam	1,1-bis(diphenylphosphino)amine
dppb	1,2-bis(diphenylphosphino)benzene
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dppp	bis(diphenylphosphino)propane
DSC	Differential scanning calorimetry
dtc	dithiocarbamate ion
hfac	1,1,1,5,5,5-hexafluoro-pentanedione-2,4 anion
MNT	maleontrile
NQR	Nuclear quadrupole resonance
phen	9,10-phenanthroline
py	pyridine
pytH	pyridine-2-thione
pymtH	pyrimidine-2-thione
pz	pyrazolate ion
TG	thermogravimetric analysis
THF	tetrahydrofuran
THT	tetrahydrothiophene

In most cases, for clarity and brevity, in the complex compounds discussed after the main ligand has been referred to, it is simply represented by L. Homobidentate ligands are represented correspondingly as L–L and in some cases as N–N or P–P to denote the specific donor atom. The widely accepted shortcuts MeOH, MeCN, EtOH, Me_2CO are used for methanol, acetonitrile, ethanol and acetone. Substituted ligands are abbreviated following the above parent ligand notation, i.e. 2,9-dimethyl-9,10-phenanthroline is noted as 2,9-Me_2phen and dimethyldithiocarbamate as dMe_2tc. In cases where the substituent locant is obvious none is inserted, like in 2,4,5-trimethylpyrazolate, which is simply referred to as Me_3pz. The symmetric heteroatomic macrocyclic ligands are abbreviated accordingly, i.e. [9]aneS_3 represents 1,4,7-trithiacyclononane. Considering the bisphosphino ligands, analogous to the above-listed diphenyl substituted ones, is the notation used for the dimethyl counterparts, i.e. bis(dimethylphosphino)methane is dmpm. The well-known techniques of infrared, mass spectrometry, nuclear magnetic resonance, cyclic voltametry and ultraviolet visible are abbreviated as IR, MS, NMR, CV and UV Vis, respectively.

1. Introduction

The chemistry of copper(I), silver(I) and gold(I) is an ever-growing field since there appears to be involved a remarkable versatility of the metals regarding their local environments which range from linear two-coordinate to square pyramidal, whereas the overall structures of the complexes include monomeric and polymeric species. The ligands usually present in such complexes are bearing pnictide, chalcogenide or halogen donor atoms. In the following the chemistry of these metal ions with ligands having as donors group 15, 16 and 17 atoms will be discussed. The discussion is very abstract, dealing only with the main point of interest in every case and does not attempt to compile or discuss spectroscopic information except when this was the only evidence in the original study. The classification followed may not be a typical one, but is consistent with the expectation of the synthetic inorganic chemist who needs information about the nitrogen or sulphur donors which coordinate to low valent coinage metals and the investigations carried out on these complexes. Ligands with donor atoms from each one of the groups 15, 16 and 17 of the periodic table are discussed, followed by presentation of the compounds where mixed ligands are observed in the chromophore, belonging to pairs of or all three groups investigated. Within each category, care has been taken to group analogous donor atoms, and the general point was to proceed from the more simple to the more complex ones. Unavoidably, in some cases, reference to analogous compounds had to be made for comparison, or in discussing the reactivity of some complexes, therefore deviating somewhat from the above criterion of chromophore constitution. The time domain covered is the decade following 1985; for the previous period, an excellent and extensive work has been published [1], while recently an updated but abstract summary of the elements' chemistry has been compiled [2]. In such a vast number of citations that are related to the above topics during this period, a few may have been, inadvertently, omitted or overlooked but we hope that the major interesting points have not been missed.

2. Complexes with single group donor atoms

2.1. Complexes with group 15 donors

2.1.1. Nitrogen donors

2.1.1.1. Copper complexes. Copper(I) acetate in the presence of formamide and acetic anhydride forms, in refluxing MeCN, a series of products with the general formula $[Cu_n(CN)_m(MeCN)_x]$ depending on the reactant ratio. The green $[Cu_3(CN)_4(MeCN)_4]$ possesses IR spectrum similar to that of the structurally determined $[Cu(NH_3)_4][Cu(CN)_3]$ and therefore is formulated accordingly [3].

Secondary ion mass spectrometry for both free $[Cu(MeCN)_4][PF_6]$ and in a graphite matrix proved the existence of CuL_3^+ and CuL_2^+ species, whereas for $[Cu(NCR)_4]^+$ ($R = Bu^t$, Cy), only fragments up to CuL_3^+ were obtained [4].

The interaction of gaseous NO has been investigated towards several mono- or binuclear copper complexes where copper is bound to three nitrogen atoms, either pyridinic or pyridinic and amino in nature. The process leads to evolution of N_2O and oxidation of the complexes to bridged oxo- or peroxo- species [5]. Reactions with nitrosonium ion in acetonitrile afforded the corresponding divalent copper complexes, with coordinated acetonitrile, while for the 1,3-bis((pyridylethynyl)-ethylamino)-2-hydroxybenzene, the final complex incorporates a bridging NO unit [6]. The closely related 1,3-bis((pyridylethynyl)ethylamino)benzene also produced a dicopper complex for which the kinetics of oxygen uptake revealed an initial reversible step leading to a dioxygen adduct before resulting in the final hydroxylated product [7]. The reaction of $[\{Sb_2(NCy)_4\}_2Li_4]$ with four equivalents of CuCl in toluene yielded $[\{Sb_2(NCy)_4\}_2Cu_4]$ with a Cu_4 core and linear CuN_2 environment for each copper [8].

$M(NBu^t)_2(NHBu^t)_2$ ($M = Mo$, W) treated with methyllithium produced $Li_2M(NBu^t)_4$ which, in toluene at −78°C, reacted with $[Cu(MeCN)_4][BF_4]$ to give the cluster $[M_2Cu_4(NBu^t)_2(\mu\text{-}NBu^t)_6(\mu\text{-}NHBu^t)_2][BF_4]$ [9]. Oligomeric complexes $[Cu\{N(SiMe_2Ph)_2\}]_4$ and $\{Cu_3N(SiMePh_2)_2\}_3$ have been formed by the reaction of bulky $NH(SiR_3)_2$ with CuBr in the presence of Butyllithium [10]. The reaction of copper(I) halides with lithiated amines in THF produced the tetrameric $[Cu(NRR')]_4$ ($NRR' = NMe_2$, $MeN(CH_2)_2NMe$, $N(CH_2CH_2)_2$) which appear to be inert to PPh_3, while dppm and dppe gave rise to $[Cu_3(dppm)_3]$ and $[Cu_2(\mu\text{-}PPh_2(dppe)_2]$ [11]. Treatment of bis(2-pyridylethyl)(4-vinylbenzyl)amine with $[Cu(MeCN)_4][PF_6]$ in acetonitrile afforded monomeric $[Cu(L)][PF_6]$, which, upon treatment with ethylene glycol dimethylacrylate in acetonitrile, produced a macroporous polymer to which CO was found to bind reversibly. The corresponding silver polymer did not reveal any such reactivity [12]. Two- three- and four-coordinated copper being present in complexes $[Cu(L)]^+$ with tris[2-(3,4,5-trimethylpyrazolyl)ethyl]amine, bis[2-(1-pyrazolyl)ethyl]amine and 1,3,5-trimethylpyrazole, respectively, gave rise to clearly distinct absorption and resonance Raman spectra which can be used as coordination environment probes [13]. Analogous studies were carried out for the complexes of [2-

1-methylimidazolyl)]methoxymethane and the emitting state was identified as well as that of the corresponding $[Cu(L)(CO)]^+$ [14].

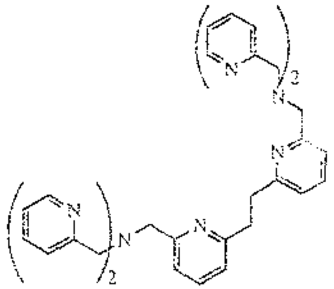
The relative Cu(I) ion affinities of 20 common amino acids were determined in the gas phase based on the unimolecular dissociations of their copper-bound heterodimers which fall within 20 kcal mol^{-1} [15].

The lithium salt of [2-(6-methyl)pyridyl]trimethylsilylamide reacted in Et_2O with CuCl to give the dimeric $Cu_2(L)_2$ compound, which, upon reaction with two equivalents of CuCl, gave $[Cu_6(L)_4Cl_2]$ [16]. Reaction of the dimer with excess PMe_3 gave the product $[Cu(L)(PMe_3)_2]$. Crystal structure determination and investigation of the ground state electronic energy in *N,N'*-di-*p*-tolylformamidato dicopper by spectroscopic and theoretical means concluded that despite the short Cu–Cu distance [2.497(2) Å], there is no direct metal–metal interaction [17].

Digonal copper environment is observed in $[Cu(cimetidine)]_2$, an extremely stable complex oxidized at +0.47 V [18], $[Cu_2(1,8\text{-naphthyridine})_2][ClO_4]_2$ [19]. $[Cu(S\text{-alkylthiophene-2-carbaldehydeimine})_2][CF_3SO_3]$, where Cu–S are extremely weak, form a pseudo tetrahedral environment [20]. The chelating 2-(*tert*-butyl)acetamido-6-(bis(pyridylethynyl)ethylamino)pterin reacted with monovalent copper to yield in CH_2Cl_2–hexane a mononuclear perchlorate [21].

The reaction of 2,6-dimethylphenyl isocyanide with reduced dopamine-*β*-monooxygenase initially forms monoisocyanide complexes finally leading to a species containing multiple isocyanide ligands. Compound $[Cu(2,6\text{-}Me_2py)(L)][ClO_4]$ is also described and whose crystal structure reveals identical isocyanide-binding in analogy with protein systems and its conversion to a trisisocyanide complex is demonstrated by IR and Raman spectroscopy [22]. 2,5-Dimethyl-2,5,-di-isocyanohexane and the corresponding 1,2-ethane give with CuX_2 the mixed valence $[Cu_2(L)_3][Y]_3$ and $[Cu(L)_2][Y]$ ($Y = CF_3SO_3$, ClO_4, BF_4) [23]. $Cu_2(PhN_3Ph)_2$ excited states were studied by both experimental techniques and by semi-quantitative molecular orbital methods [24].

In MeCN–py $[Cu(bpy)_2]^+$ activated HOOH and *t*-BuOOH for the selective ketonization of methylenic carbons in Cy and $PhCH_2CH_3$ groups [25]. Reaction of $[Cu(MeCN)_4][Y]$ with excess pyridine or 4-methylpyridine leads to acetonitrile substitution by the pyridine base. Cu NQR studies of several mononuclear alkylpyridine complexes of the type $[Cu(L)_3][Y]$ ($Y = PF_6$, ClO_4) have been reported [26], while analogous compounds in acetonitrile reveal no interaction of $[Cu(MeCN)_4][BF_4]$ with C_6H_6 and NEt_2Ph, and a only weak interaction with haloarylazo compounds [27]. Cationic complexes of the formula $[Cu(L)]^+$ are obtained with 4-methyl-4-[6-(1-((2-imidazol-4-yl ethyl)imino)ethyl)pyrid-2-yl]-4,5,6,7-tetrahydro-*1H*-imidazo[4,5-c]pyridine and 2,6-bis[1-(2-imidazol-4-ylethyl)-imino)ethyl]pyridine with flattened tetrahedral and five-coordinate copper environments respectively. The latter is readily oxidized by dioxygen with subsequent partial oxygen recovery [28]. Several substituted pyridines or ligands with pyridine-like nitrogen atoms have produced Cu(I) compounds. 2,6-Dimethyl and 2,4,6-trimethylpyridine form two-coordinate cationic units with Cu(I). The structures and the Cu NQR spectra of several such compounds bearing BF_4, PF_6, $CuCl_2$ and ClO_4 as counteranions have been investigated [29]. Forms α- and γ- of the 2,4-dimethylpyridine perchlorate and the 2,4,6-trimethylpyridine dichlorocuprate have coplanar ligand rings, while in the rest, complex dihedral angles of approximately 70° were observed. 2,6-bis(1-Phenyl(-1-(pyridin-2-yl)ethyl)pyridine in acetonitrile formed $[Cu(L)(MeCN)][CuCl_2]$ and $[Cu(L)(MeCN)]_2[Cu_2X_4]$ (X = Br, I) [30]. In these compounds, the Cu–py distances are fairly standard ranging from 2.07 to 2.08 Å while the Cu–NCMe ones are 2.00(2), 1.90(2) and 1.94(3) Å for X = Cl, Br and I, respectively. In a conformational polymorph of $[Cu(2,6\text{-}Me_2py)_2][ClO_4]$, the linear CuN_2 environment is present with pyridine planes at 56.2° [31]. 2-Aminomethylpyridine and 2-hydrazinopyridine form monomeric compounds of the formula $[Cu(L)_2]X$ where $Cu\text{-}NH_2$ are naturally longer than $Cu\text{–}N_{ar}$, and strong intermolecular hydrogen bonds are formed [32]. Dimethylaminophenyl pyridines and phenanthrolines produced tetrahedral $[Cu(L)_2][PF_6]$ complexes where the copper metal resists chemical and electrochemical oxidation [33]. The reactivity of [Cu{Tris((2-pyridyl)methyl)amine}(MeCN)][PF_6] with benzyl and allylhalides led to copper oxidation with concomitant dibenzyl and diolefin products [34]. Nitromethane and metallic copper react in pyridine to give [Cu(CN)(PY)2] and [Cu(NCO)(PY)2]2 with bridging NCO ligands and Cu–N distances of 1.97(2)–2.26(2) Å for NCO and 2.03(1)–2.09(2) Å for pyridine [35]. The CuN_2 environment is identified in $[Cu\{di(2\text{-}pyridyl)amine\}_2]^+$ salts where the anion is either Cl or $[Cu(L)X_2]$ for X = Cl, Br [36]. In the case of CuI, the final product is of the formula $[Cu_2(L)_2(\mu\text{-}I)_2]$. EXAFS studies revealed that in excess pyridine, $Cu(py)_4^+$ is formed and nowater coordination is evident [37]. 2,2′:6′,2″:6″,2‴-Quarterpyridine forms double helical complexes of the formula $[Cu_2(L)_2][PF_6]_2$ with pseudo tetrahedral CuN_4 environment [38]. *Trans*-12-bis(2-pyridyl)ethylene formed polymeric $\{Cu(L)(PF_6)\}_n$ with Cu–N distances ranging between 1.878(6) and 1.890(6) Å. Terminal pyridyl and quinolyl ligands form $[Cu(L)]^+$ complexes which readily uptake dioxygen to form $(CuL)_2O_2$ (tripyridyl, dipyridylquinolyl) or $Cu(L)O_2^-$ (pyridyldiquinolyl), while



I

triquinolyl is unreacive [39]. The polypyridyl ligand I in EtCN formed $[Cu_2(L)(EtCN)_2]^{2+}$ and oxidized faster than the monomeric $[Cu(EtCN)(L')]^+$ (L′ = Tris(2-pyridyl)ethyl)amine) with the initial step being the formation of an $\text{–}O_2\text{–}$ bridge between the copper atoms [40]. Electrochemical reduction of Cu(II) complexes with di-2-pyridylamine appears to be more favorable (−0.36 V in DMSO. −0.29 V in DMFI and −0.11 V in acetonitrile relative to $Fe(Cp)_2$ than for the corresponding bipyridine and phenanthroline [41]. Absorption and emission studies at room temperature and at 77 K were carried out for $[Cu(polypyridyl)][ClO_4]$. e.g. 1,2-bis(9-methylphenanthrolin-2-yl)ethane. 1,2-bis(6′-methylbipyrid-6-yl)ethane and 5,5′.3′.5″-tetramethyl-2.2′:6′.2″:6″.2‴-quartepyridine [42]. Ethyl bridged bipyridine and phenanthroline give $[Cu_2(L)_2]^{2+}$ complexes with a double helical structure assigned by ^1H NMR. The compounds are oxidized reversibly at higher voltage than the monomeric $Cu(bpy)_2^+$ [43]. Reaction of 2.6-bis(2-pyridylethynyl)pyridine with $[Cu(MeCN)_4][PF_6]$ in MeOH. yielded the trimer $[Cu_3(L)_3][PF_6]_3$ and dimer $[Cu_2(L)_3][PF_6]_2$; the latter was found unstable in CD_3NO_2 solution [44]. Mononuclear copper(I) complexes containing the N_4-tripodal tetradentate tris[(2-pyridyl)-methyl]amine and the corresponding ligands with one. two, or three 2-quinolyl substituents were studied. Only the last ligand formed a $[(L)Cu(MeCN)]^+$ complex unreactive to dioxygen. All three reacting complexes follow the same reaction mechanism. involving the initial reversible formation of 1:1 $Cu:O_2$ adducts which react reversibly with starting Cu(I) species to form 2:1 complexes, although considerable differences exist in detail. depending on the ligand [45]. The binuclear complexes $[Cu_2(L)(BF_4)_2(MeCN)_4]$ and $[Cu_2(L)(BF_4)_2(CH_2Cl_2)_{0.5}]$, which were readily prepared from 2.6-bis[*N*-(2-pyridylethyl)formimidoyl]-1-methoxybenzene in the appropriate solvents. and the helical $\{Cu(L)(BF_4)\}_n$ have been studied as models for monooxygenase reactivity [46]. 2.6-bis(1-Methylimidazol-2-yl)pyridine formed $[Cu_2(L)_2][ClO_4]_2$ the bis-coordinated ligand forming the strands of a helix [47]. A variety of homometallic copper(I) complexes of ligands containing two (2.2′-bipyridin-6-yl)methyl moieties linked via 1.4.10.13-tetraoxa-7.16-diazacyclooctadecane. 1.4.10.13-tetrathia-7,16-diazacyclooctadecane. 4.4′-bipyridinediium. *N.N′,N″*-tritosyldiethylenetriamine and toluene-*p*-sulfonamide spacer units have been isolated. FAB MS investigations suggest that most of the complexes are of the formula $[Cu_2(L)_2][PF_6]_2$. Solution ^1H NMR spectra imply the existence of additional complex components of 1:1 L:copper(I) ratio [48]. The copper(I) complex $[Cu_2(L)_2]$ and its 1:1 adduct with CuX. $[Cu_6(L)_4X_2]$ (X = Cl, Br) have been prepared from lithium reagents and the appropriate metal halide and [2-(6-methyl)pyridy]ltrimethylsilylamide and have been characterized crystallographically. In the dimer. the ligands span the two metal centers with Cu···Cu 2.420(1) Å, while in the clusters, they span three metal centers which are either two- or three-coordinate. The compound $[Cu_2(L)_2]$ reacts with trimethylphosphine to form $[Cu(L)(PMe_3)_2]$ [49]. The MLCT excitation at 465 nm of the complex $[Cu(2,2'\text{-bis}(6\text{-}(2.2'\text{-bipyridyl}))\text{biphenyl})][ClO_4]$.2MeCN was established and its quasi-reversible oxidation in various solvents associated with coordinative changes upon oxidation [50].

The *vic*-dioxime 5.5′-bis[2-(4′-benzylideneamino-benzo-15-crown-5)]dithioglyoxime gives $[Cu(L)_2][PF_6]$ probably with tetrahedral CuN_4 environment [51]. Sodium sulfite treatment of aqueous solutions of CuX_2 and 1-cyanoguanidine resulted in the formation of Cu_2X_2L (X = Cl, Br). $CuBrL \cdot H_2O$ and $[Cu_2(L)_4]^{2+}$ [52]. In particular. the chloride yielded. upon treatment with 0.5 or 1.5 equivalents of sodium sulfite,

$[Cu_2(\mu\text{-}Cl)_2(L)_2][SO_4]$ and $[Cu_2(\mu\text{-}Cl)_2(L)_2][S_2O_6]$, respectively [53]. 2-Cyanoguanidine in THF in the presence of pyridazine formed $\{[Cu(L)\}_3([\mu\text{-pyridazine})_3][BF_4]_2$ and $[\{Cu(L)\}_2(\mu\text{-pyridazine})_3][BF_4]_2$ [54] with trigonal and tetrahedral copper atoms, respectively. Pyridazine reacted with $[Cu(MeCN)_4][PF_6]_2$ in acetone under argon to give $[Cu_2(L)_3(MeCN)_2][PF_6]_2$ while in-situ reduction of $Cu(ClO_4)_2$ in acetone under ethylene or CO gave $[Cu_4(L)_6][ClO_4]_4$ [55].

Pyrazine and tetramethylpyrazine form, in acetone, infinite two-dimensional sheets of $\{[Cu(L)_{3/2}(MeCN)PF_6 \cdot 1.2Me_2CO\}$ where Cu_6 units are observed and $[Cu_2(L)][ClO_4]$ with a zigzag polymeric form respectively [56]. 6,6′-dimethyl-2,2′-bipyrazine, 2,2′-dimethyl-6,6′-diphenyl-4,4′-bipyrimidine form CuL_2^+ complexes while *catena*-poly-[(2,2′-dimethyl-4,4′-bipyrimidine-*N,N′,N″*)(MeCN)$_2$Cu$_2$] have been characterized structurally [57]. 2,3-Dimethylpyrazine produced an interesting product of autoreduction of the perchlorate Cu(II) complex, $[\{Cu(L)\}_2(\mu\text{-}L)]^{2+}$ [58]. 2-Methyl and 2,3-dimethylpyrazine form, in water, $[Cu_2(L)_3][ClO_4]_2$ [59]. Tetranuclear Cu complex has been obtained with 3,6-bis(2-pyridyl)pyridazine possessing a planar Cu_4 core of tetrahedrally coordinated metal atoms [60].

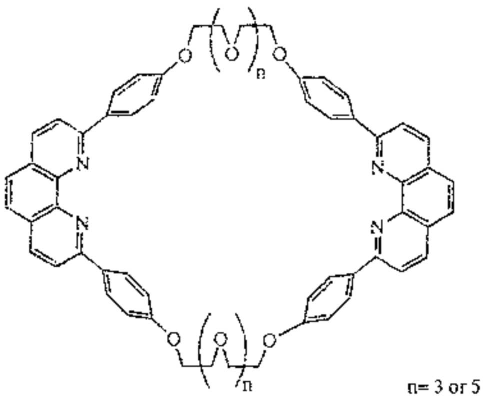
The crystal structures of the polymeric pyrazolates α-$[Cu(L)]_n$ and the 1:1 mixed metal phase, $[(Cu,Ag)(L)]_n$, have been determined by X-ray powder diffraction data and compared with that of β-$[Cu(L)]_n$. All complexes consist of infinite chains of linearly coordinated metal atoms, bridged by bidentate pyrazolato anions. The α-$[Cu(L)]_n$ and β-$[Cu(L)]_n$ phases differ mainly in the interchain Cu···Cu contacts [61]. Finally, ab initio, all electron Hartree–Fock calculations have been utilized to investigate the reactivity of pyrazole and pyrazolate anion towards Cu^+ and $Cu(NH_3)^+$ [62]. Several substituted polypyrazoles afford $[Cu(L)]^+$ with metal-to-ligand-charge-transfer (MLCT) bands in the UV region and emission resulting from $3d \rightarrow \pi^*$. Their phenolate counterparts show lower absorption and emission transitions. The reaction of the complexes with CO produces new compounds with higher absorption and lower emission energies [63]. No π-back donation was observed in $Cu_3(\mu\text{-}P_2)_3$ contrary to their Au counterparts [64]. The structure of the 3,5-dimethylpyrazolate compound reveals a symmetric trimeric unit with very weak Cu···Cu interactions [65]. The analogous structure of the product with 3,4,5-trimethylpyrazole is reported along with that of the mixed valence product $[Cu(3\text{-}CO_2\text{dimethylpyrazole})(Me_3pz)]_2Cu$ [66]. IR and DSC studies are reported for a series of trimeric pyrazolate complexes of the formula $[Cu(4\text{-}Y,3,5\text{-}Me_2pz)]_3$ where Y = H, Cl, Br, I and CH_3 [67]. The tetrameric cluster $[Cu(3,5\text{-}Ph_2pz)]_4$ acts as catalyst with 100% selectivity in the oxidative coupling of amines to azobenzenes and uptakes CyNC to form dimeric $[Cu(L)(CyCN)]_2$ [68]. The hindered 3,5-diphenyl and 3-*tert*-butyl Tris(pyrazolyl)borates yield complexes of the formulas $[Cu(L)]_2$ and $[Cu(L)(MeCN)]$, which generally dissociate in solution due to the lability of the pyrazolate ligands. For the diphenyl-substituted ligand, a complex involving both its neutral and deprotonated forms has been obtained [69].

The first well-characterized mononuclear copper nitrosyl complexes are of the formula $[Cu(L)(NO)]$, (L = tris(3-R,5-R′-pyrazolyl)hydroborate, $R = Bu^t$, $R' = H$; $R = R' = Ph$). NO binding was found to be weak, reversible and temperature dependent. Irreversible displacement of the nitrosyl ligand was effected by addition of excess acetonitrile or CO to yield the respective Cu(I) adducts [70].

Photoelectron spectroscopy of imidazole bound to Cu(I) sites at single crystal surfaces has been used as model of the blue copper protein bonding and correlated to SCF–Xa calculations [71]. The reaction of 1,2-dimethylimidazole with $[Cu(MeCN)_4][PF_6]$ formed the two-coordinate complex $[Cu(L)_2][PF_6]$ and the T-shaped three-coordinate $[Cu(L)_3][PF_6]$ the structures of which have been studied by X-ray absorption spectroscopy. The latter is reactive toward dioxygen contrary to the former which is unreactive toward O_2 and CO [72]. *N*-methyl-3-ethylimidazolate–CuCl melts show oxygen uptake to a variable degree with the best results (80 O per Cu atom) being observed for $Cu_3(L)_2$, while imidazolate itself is not at all reactive [73]. *N,N,N′,N′*-Tetrakis(2-benzimidazolylmethyl)-1,2-ethanediamine formed, in $EtOH/Et_2O$, $[Cu_2(L)][ClO_4]_2$ from which the metal was extracted by KCN in DMSO leaving the ligand intact as its ability to recoordinate revealed [74]. The compound was also found to reversibly oxidize in DMSO, the oxidation proceeding through an initial Cu–O–Cu step as surface-enhanced Raman scattering showed [75]. The ligand 1,3-bis(1-methylbenzimidazol-2-yl)benzene reacts with copper(I) to give $[Cu_2(L)_2][ClO_4]_2$, the crystal structure of which shows a dinuclear nonhelical structure with each copper linearly coordinated to a benzimidazole group of each ligand. The structure is retained in polar aprotic solvents [76]. The reaction of the polydentate ligand 1,4-bis[*N,N*-bis-(2-benzimidazolylmethyl)amino] butane with $[Cu(MeCN)_4][BF_4]$ in MeCN/MeOH at 3 C produced $[Cu(L)][BF_4]$, which takes up O_2 to produce the corresponding Cu(II) complex after 24 h [77]. Complexes of the tridentate tris(1-ethyl-4-*R*-imidazolyl)phosphine ($R = Me, Pr_i$) of the formula $[Cu(L)][Y]$ ($Y = PF_6, ClO_4, CF_3SO_3$), were prepared. The adducts $[Cu(L)(MeCN)][Y]$ were obtained by crystallization from acetonitrile. Oxygen reacts with these species giving peroxodicopper(II) complexes providing useful models for the spectroscopic, magnetic, structural and functional properties of the dicopper site in hemocyanin [78]. The analogous reaction of bis(bis(2-pyridyl)ethyl)amino)*m*-xylene in DMF yielded, besides the formation of the corresponding phenoxy-bridged cupric dimer, the hydrolyzed DMF [79]. The dinucleating bis-bidentate ligand bis[5-(1-methyl-2-(6-methyl-2′-pyridyl)benzimidazolyl)] methane and its mononuclear analog 6-methyl-2-(1-methylbenzimidazol-2-yl)pyridine form $[Cu_2(\mu\text{-}L)_2][ClO_4]_2 \cdot H_2O$ and $[Cu(L)_2][ClO_4]$ respectively with pseudotetrahedrally coordinated Cu. Conductivity measurements and UV–Vis spectra show that the dinuclear structure is maintained in solution in polar aprotic solvents, and ^1H NMR measurements unambiguously establish a double-helical structure for this complex [80].

The reaction of 6-diphenylphosphino-2,2′-bipyridyl with $[Cu(MeCN)_4]^+$ and $[Cu(bpy)(MeCN)_2]^+$ gives dimeric compounds of the formula $[Cu_2(\mu\text{-}L)_2(MeCN)_2]^{2+}$ and $[Cu_2(\mu\text{-}L)_2(bpy)]^{2+}$ with head-to-tail and head-to-head coordination of the ligands, respectively [81]. Linking two bipyridine units with a 1,3-phenylene spacer has provided a novel class of ligand which promotes the spontaneous self-assembly of double helicates upon reaction with transition-metal ions. Interaction with copper(I) resulted in dinuclear double-helical complexes with the metal ions occupying pseudo-tetrahedral coordination sites [82]. The reaction kinetics of $[Cu(phen)_2]^+$, $[Cu(5\text{-}NO_2phen)_2]^+$ and $[Cu(bpy)_2]^+$ with O_2^-, O_2 and H_2O_2 in the presence of thymus DNA have been evaluated and the corresponding oxidation mechanisms proposed [83].

Substituted phenanthrolines react with $[Cu(MeCN)_4][BF_4]$ in CH_2Cl_2–MeCN to produce the bis-complexes which are oxidized to the corresponding Cu(II) species in the region of −1.64 to −1.76 V [84]. A general discussion of the energies, intensities and lifetimes of the luminescent states of several $Cu(2.9\text{-}R_2phen)_2^+$ complexes has been published [85], but specific studies are missing, especially with respect to their absorption and emission properties. The photochemical oxidation in CH_2Cl_2 of $Cu(2.9\text{-}Me_2phen)_2^+$ was attributed to outer sphere electron transfer from solvated CH_2Cl_2 [86]. Resonance Raman studies of the excited states revealed that for R = Me and Ph, the 360 nm band is an MLCT one and the 540 nm band is $\pi \rightarrow \pi^*$ [87]. Laser-excited resonance Raman of the ground and first MLCT excited state of the 2.9-dimethylphenanthroline compound is in contradiction to the prediction of the state to be $[LCu^{II}(L^{\cdot -})]^+$ [88]. Hydrostatic pressure affects the emission from the MLCT excited state via an associative mechanism [89]. The MLCT excited states for $Cu(2.9\text{-}Me_2phen)_2^+$ and $Cu(2.9\text{-}Me_2\text{-}4.7\text{-}Ph_2phen)_2^+$ produced by flash photolysis in CH_2Cl_2 are quenched by MeCN, Me_2CO and *p*-dioxane [90] through exciplex formation, while the corresponding complexes with 2.9-dimethyl- and 2.9-diphenylphenanthroline quenching is achieved by $Cr(acac)_3$ and $Cr(hfac)_3$ as well as by Lewis bases, e.g. DMF, DMSO, THF and MeCOOEt, again through exciplex formation [91] or by anthracene [92]. The activation volume for the energy transfer quenching of the MLCT excited state of the diphenylphenanthroline complex has also been determined [93]. Several $Cu(2.9\text{-}R_2phen)_2^+$ quench uranyl phosphate and arsenate photoluminescence. A product with the stoichiometry $[NBu_4]_{0.6}[Cu(2.9\text{-}R_2phen)_2^+]_{0.4} \cdot UO_2EtO_4 \cdot 2H_2O$ is reversibly oxidized and reduced by Br_2 and N_2H_4 vapors [94]. A study of $Cu(2.9\text{-}Ph_2phen)_2^+$ and the related copper catenate of **II** indicate that they possess low symmetry, which is retained in solution [95]. $Cu(phen)_2^+$, $Cu(2.9\text{-}Me_2phen)_2^+$ and $Cu(2.9\text{-}Me_2\text{-}4.7\text{-}Ph_2phen)_2^+$ react with natural DNA fragments and synthetic oligonucleotides revealing hypsochromic absorptions. The last reveals luminescence even at room temperature [96]. The electron transfer rate from $[Cu(2.9\text{-}Me_2phen)]_2[Y]$ was studied by ^1H NMR in water (X = Cl) and acetonitrile and acetone ($X = CF_3SO_3$). The final Cu(II) species were shown to contain coordinated solvent molecules [97]. The formation constant and oxidation potential for $Cu(2.9\text{-}Me_2phen)_2^+$ were calculated from electrochemical measurements. It is predicted that this compound is the primary O_2 reductant in solutions where it is adsorbed on electrodes [98]. 2.9-Dianisylphenanthroline forms the ionic compound $[Cu(L)_2][BF_4]$ in which copper is tetrahedrally coordinated. The corresponding Cu(II) compound was also studied by ESR while dopped into the above complex: the study showed that divalent copper compound adopts a five-coordinate conformation [99]. Multiply substituted 2.9-R-4.7-R′-phenanthroline complexes reveal charge transfer absorptions in the visible region in MeOH–EtOH at 90 K and emission at room temperature in the region 710–770 nm, while unsubstituted phen complexes do not [100]. The equilibrium between $Cu(R_2phen)Cl$ and



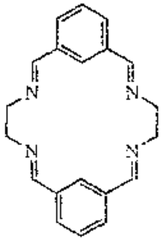
II

$[Cu(R_2phen)_2][CuCl_2]$ has been confirmed by ^1H NMR studies in solution [101]. Copper complexes with several substituted phenanthrolines react with $Cu(PPh_3)_2(BH_4)$ to form $Cu(L)(BH_4)$ for 4,7-, 5,6- and 3,4-dimethyl-3,4,7,8-tetramethylphenanthroline with a unique CuN_2H_2 environment while for 2-, 4- and 5-methylphenanthroline mixed-ligand products. $Cu(L)(PPh_3)(BH_4)$ are obtained [102]. 2,9-Me_2phen in MeOH in the presence of excess COD forms the Y-shaped complex $[Cu(2,9\text{-}Me_2phen)(MeCN)]X$ ($X = ClO_4$, PF_6) [103]. 2,9-bis((2'Alkylphenyl) aminomethyl) phenanthrolines form mononuclear $[Cu(L)]^+$ with distorted tetrahedral environments and were characterized by IR ($\nu_{C=N}$) and UV spectra [104]. 2-(2-Alkylphenyl) substituted phenanthrolines and 2,9-dimethyl, 2,9-dimethoxy and 2,9 diethoxyphenanthroline form $[Cu(L)_2][BF_4]$, which are oxidized electrochemically in the region -1.64 to -1.76 V [84]. An analogous compound with 2,9-bis(*p*-carboxyphenyl)phenanthroline has been studied with respect to its action in photoelectrochemical cells [105]. Reaction of 2,9-bis(*N*-pyrazolylmethyl)-1,10-phenanthroline with Cu^+ produced stable compounds in solution, provided the molar ratio was 2:1, whereas for 1:1 mixtures, the solutions oxidized within 1 h [106]. The quenching of emission from the MLCT state of the complex $Cu(2,9\text{-}Ph_2phen)_2$ by Tris(*β*-dionato)Cr(III) complexes and several organic substrates has been investigated in CH_2Cl_2 as a function of hydrostatic pressure and the results are interpreted in terms of the McMillin proposal of competitive energy and electron transfer quenching for these complexes [107]. The synthesis of $[Cu(L)_2[BF_4]$, where L = 2,9-disubstituted phenanthrolines bearing one or two acylaminopyridine binding sites, has been carried out. Their complexation to dicarboxylic acids is analyzed by NMR and UV-Vis. The chromogenic effect is explained by a conformational change in the receptors resulting from hydrogen bond formation with the substrate [108]. Inert atmosphere conditions in the CH_2Cl_2/MeCN solution were needed for 1,4,5,8,9,12-hexa-azatriphenylene and its

2,3-diphenyl 2,3,7-trimethyl, 2,3,7-triphenyl and 2,3,6,7,10,11-hexaphenyl analogs to form complexes with the formula $[Cu(L)_2]\,[BF_4]$ [109].

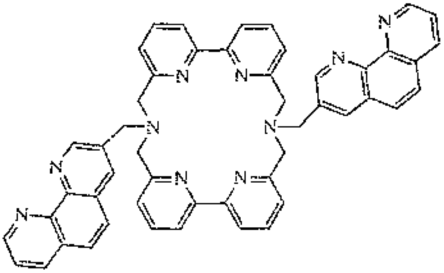
In an interesting sequence of reactions, $[Cu(phen)(PPh_3)(BH_4)]$ in aqueous methanol yielded $[Cu(phen)(PPh_3)(HOCO_2)]$ which, upon treatment with an additional equivalent of phenanthroline or two equivalents of cyclohexylnitrile, formed the ionic compounds $[Cu(phen)_2][HCO_3]$ and $[Cu(phen)(CyCN)_2][HCO_3]$, respectively [110]. Treatment of $[Cu(phen)(PPh_3)(HCO_3)]$ with pyrazole in acetone produced a red solution and deposition of polymeric copper pyrazolate. Treatment of the mixture with CO_2 led to pyrazolate carboxylation and formation of $[Cu(phen)(PPh_3)(CO_2\text{-}pz)(H_2O)]$, which was reversed under nitrogen, while treatment with excess CO_2 recovered the initial pyrazole [111].

The addition of two equivalents of the Schiff base derived from 1,2-diaminoethane 2-(phenylethylthio)benzaldehyde to copper(I) perchlorate resulted in formation of



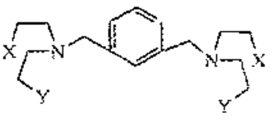
III

$[Cu(L)_2][ClO_4]$ within a tetrahedral CuN_4 environment [112]. The Schiff base **III** formed $[Cu_2(L)][BF_4]_2$, which is oxidized in MEOH through a peroxo-intermediate to give the hydroxylated ligand [113]. Macrocyclic ligands derived from thiophene- or pyridine-dicarbaldehyde react in refluxing MeOH MeCN to give $[Cu_2(L)(MeCN)_2][ClO_4]_2$ or in the presence of NaX $[Cu_2(L)Y][ClO_4]$ (Y = NCS, N_3, NCSe, Cl, Br, I). A study of their UV Vis spectra indicated that they retain their solid-state structure (determined for SCN) in solution as well [114]. The furan-based analogous macrocycle 23,24-dioxa-3,7,14,18-tetraazatricyclo-$[18.2.1.1^{9,12}]$tetracosa-1(22),2,7,9,11,13,18,20-octaene and its 5,5,16,16-tetramethyl derivative gave $[Cu_2(L)(MeCN)_2][ClO_4]_2$ which, in DMF, experienced partial oxidation to the mixed valence $[Cu_4(L)_2(OH)_2][ClO_4]_3$ [115]. The crystal structure of $[Cu_2(L)(MeCN)_2]^{2+}$ with the above macrocycles as well as the 23,24-dithia- analog were studied [116]. Molecular mechanics calculations on the above ligands have been carried out as well as on their dicopper complexes and metal parameters elucidated [117]. The reaction of $[Cu_2(L)(MeCN)_2]^{2+}$ (L is the above dioxa unsubstituted macrocycle) with pyridazine substitutes the MeCN molecules withpyridazine and catalyses hydrazobenzene dehydrogenation with a specificity for *trans*-azobenzene, but at a slower rate than simple Cu(I) salts [118]. Tetraethyleneglycol bis(-2,2′-bipyridin-6′-yl)methyl ether and its 4,4′bis(4-methoxyphenyl)-substituted analog, as well as the corresponding tri- and pentaethyleneglycol. encapsulate both Cu$^+$ and alkali metal ions in a sort of polycrown-ether, thus affording allosteric regulation of alkali metal recognition by heterotropic cooperativity [119]. The reaction of [Cu(MeCN)$_4$][Y] (Y = ClO$_4$, PF$_6$, CF$_3$SO$_3$) with 1,4,8,11-tetrakis(2′-pyridylemethyl)-1,4,811-tetraaza-cyclotetradecane in acetonitrile at 60°C produced [Cu$_2$(L)][Y]$_2$, which reacted with O$_2$ in a quasi-reversible manner [120]. If the reaction is carried under CO, then polymeric {[Cu(L)(CO)(MeCN)][BF$_4$]}$_n$ is obtained with Cu–N ranging between 2.057(3) and 2.083(4) Å, Cu–NCMe equal to 1.075(4) Å and Cu–C of 1.835(4) Å [121]. The electrochemical reduction of the CU(II) complexes with the hydrophobic ligands 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane, 2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecan and 2,6,9,13-tetramethyl-2,6,9,13-tetraazatetradecane in deaerated aqueous solutions yields the corresponding thermodynamically stable copper(I) complexes. The bascicity constants of the ligands were determined potentiometrically [122]. The macrocyclic bis(1,10-phenanthroline)-[2,1,10,9-bcdef:2′,1′,10′,9′–ijklm[1,8]dithia[3,6,10,13]tetraazacyclotetradecine with its two phenanthroline sites binds Cu(I) to form Cu(L) which, in turn, binds to DNA by an intercalative mode. UV–Vis and CD measurements support a constrained distorted square planar geometry for the complex [123]. The bipyridine-



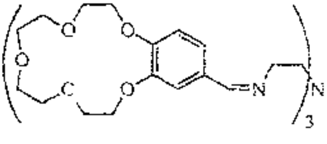
IV

based hexa-aza macrocycle **IV** produced helicates with Cu(I) and Ag(I) in MeOH/CH$_2$Cl$_2$. The structure of the copper complex revealed a distorted tetrahedral coordination [124]. 3,6,9,16,19,22-hexaazatricyclo[22.2.1.1^{12,14}]azaoctacosa-1(26)12,9,11,13,15,22,24-octaene in MeCN/MeOH forms [Cu$_2$(L)][ClO$_4$]$_2$, which oxidized to [Cu$_2$(μ-OMe)(μ-OL)][ClO$_4$]$_2$ reversibly until full oxidation occurs, after which it does not reduce back [125]. The macrocyclic ligand 1,4,8,11-tetrakis(2′-pyridylmethyl)-1,4,8,11-tetraazacyclo-tetradecane coordinated in hot acetonitrile to give the dimeric [Cu$_2$(L)]X$_2$ (X = ClO$_4$, PF$_6$, CF$_3$SO$_3$) which is quasi-reversibly oxidized to the cupric compound [120]. A distorted tetrahedral core is observed in [Cu$_2$(L)(pyridazine)$_2$[ClO$_4$]$_2$ formed by pyridazine and [Cu$_2$(L)(H$_2$O)$_2$][ClO$_4$]$_2$ (L, the Schiff base derived from the condensation of 2,5-diformylfuran and 3-oxapentatne-1,8-diamine) in acetonitrile, as well as in [Cu$_2$(L)(MeCN)$_2$][BPh$_4$]$_2$, which is more stable than the former with respect to electro-oxidation [126]. The step oxidation of [Cu$_3$(1,3-bis[bis(2-pyridinemethyl)amino]benzene)]$^{2+}$ is strongly solvent dependent [127]. The tripodal ligands (bis((2-pyridyl)methyl)(1-methylimidazol-2-yl)methyl)amine and (bis((1-methylimidazol-2-yl)methyl)((2-pyridyl)methyl)amine in acetonitrile form solvated $[Cu_2(L)_2]^{2+}$, which electro-oxidize at approximately −0.6 V and uptake O_2 to form $\{Cu(L)\}_2O_2$ [128]. Polydentate (tris(bis(2-(2-pyridyl)ethyl)ethylamino)amine formed, with $[Cu(MeCN)_4][PF_6]$ and PPh_3 in CH_2Cl_2 $[Cu_3(L)(PPh_3)_2][PF_6]_3 \cdot 2MeCN$ where both CuN_4 and CuN_3P environments are observed [129], while the macrocyclic tetra-Schiff base derived from the 2:2 condensation of isophthalaldehyde with diethylenetriamine gave $[Cu_2(L)]$ $[ClO_4]$ which, upon oxygen uptake, yielded the hydroxylated-pro [130]. Analogous hydroxylation occurs with the tripodal ligand V [131] and the Schiff-based 1,3-bis(*N*-(2-(1-methyl-2-imidazolyl)ethyl)formimidoyl)benzene [132] and polydentate *m*-xylene(bis(2-(2-pyridyl)ethyl)amino)diamine and its 5-ethylpyridyl derivative, but not with the 6-methyl substituted one [133]. Tripodal ligands with central nitrogen atoms react with cuprous salts to form mononuclear cationic complexes. Such ligands are $N(CH_2CH_2N{=}CBPh)_3$ which utilizes a trigonal pyramidal copper environment in $[Cu(L)][BPh_4]$ with $Cu–N_{ap} = 2.232$ and $Cu–N_{ap}$ ranging between 2.004 and 2.019 Å [134]. In the analogous complex of the closely related $N(CH_2CH_2N{=}CH(thiophene\text{-}2\text{-}yl))_3$, the closest Cu–S distance is 3.344 Å, too long to suggest any Cu–S interaction [135]. The tripodal Schiff base IV derived from Tris(ethylamino)amine and [3,4]crown-benzaldehyde also presents a four coordinate CuN_4 center [136], while a CuN_3 center is observed in the cationic complexes with the Schiff bases derived from 2,6-diacetylpyridine and phenylalanine methyl and tyrosine ethylesters, respectively [137]. In general, 2,6-diacetylpyridine Schiff bases form either $[Cu(L)]^+$ or $[Cu_2(L)_2]^{2+}$ complexes, which react reversibly with CO and irreversibly with dioxygen, the latter reaction being more easy in MeCN–MeOH [138]. 1,2,4,5-tetramethylsulfonyl-1,4-benzoquinonediimine-1,2-diamine reacted in pyridine with cupric acetate to produce a dimeric compound with local tetrahedral CuN_4 environment. The complex has the formula $[Cu_2(\mu\text{-}L)(py)_4]$ and readily substitutes pyridine with PPh_3 to give $[Cu_2(\mu\text{-}L)(py)_2(PPh_3)_2]$ [139]. An analogous CuN_4 environment was observed in



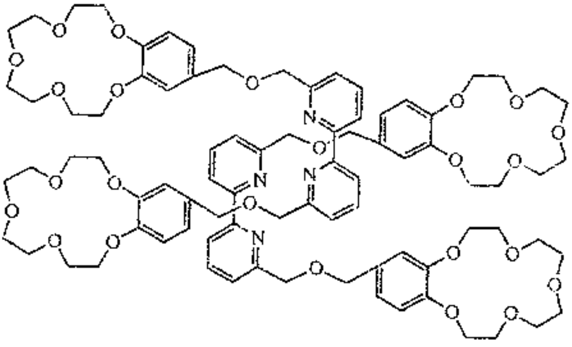
X, Y = py, pz, imz

V



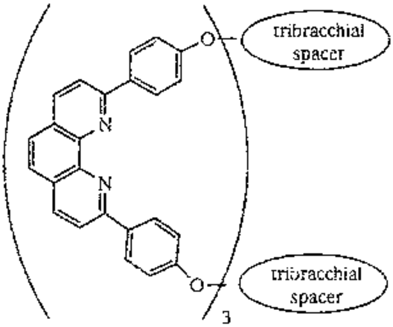
VI

the complex $[Cu_2(2,7\text{-diphenyl-azo-1,8-naphthyridine})_3][BF_4]_2$ [140] as well as in



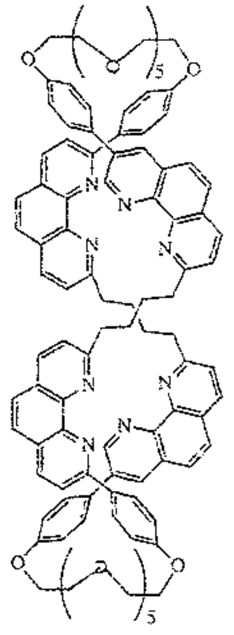
VII

bipyridine-based catenands of the formula **VII** for which dipotassium and tetrasodium hexafluorophosphates have been isolated [141]. Trigonal CuN_3 was observed in the complexation of the tripodal Tris[4,4-dimethyl-2-(4,5-dihydro-oxazolyl)]methylamine in the dimeric $[Cu(L)]_2[BF_4]_2$ [142] and CuN_3 in $[Cu_2\{1,4\text{-di}(2'\text{-pyridylthio})\text{-phthalazine}\}_2][ClO_4]_2 \cdot 2MeCN$ [143]. 2,5-Bis[*N*,*N*-bis(2'-pyridylethyl)aminoethyl]pyrazine produces $[Cu_2(L)Cl_2][ClO_4]_2$ which is reduced in two steps at 0.04 and −0.07 V to the corresponding Cu(I) compound. The final product is also obtained by in-situ reduction of cupric perchlorate in refluxing acetonitrile [144].



VIII

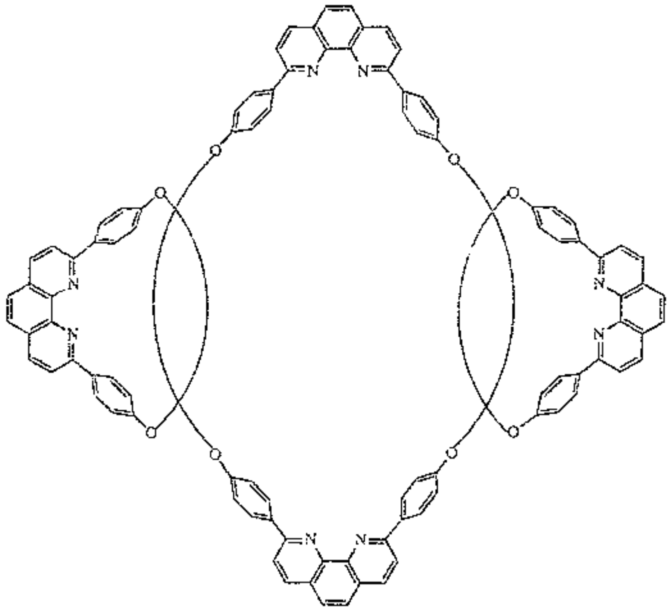
The new *endo* **VIII** with its three phenanthroline sites reacts with three equivalents of $[Cu(MeCN)_4][BF_4]$ in the presence of three equivalents of phen in DMF producing a trinuclear complex which reveals UV excitation and emission almost identical to those of $[Cu(phen)_2]^+$ [145]. The macrocyclic compound **IX**, in its knotted structure, coordinates to copper, binding it with the two intramole phenanthroline-



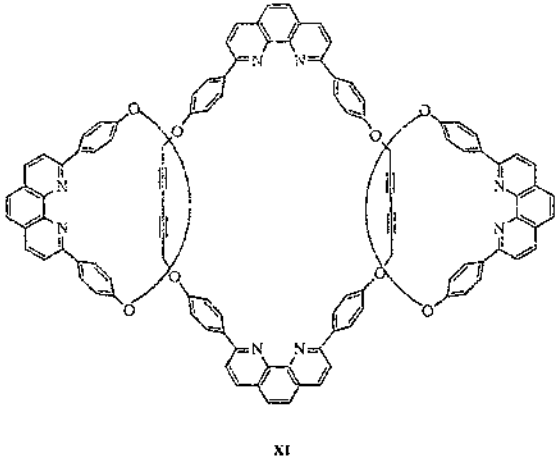
IX

bearing arms as well to give an overall tetrahedral coordination [146]. The crystal structure and solution NMR studies of a dicopper [3]-catenate composed of two peripheral 30-membered rings interlocked with a central 44-membered one has been reported [147]. The absorption, emission and excitation spectra, and the luminescence quantum yields and lifetimes of the emitting excited states of the [3]-catenand **X** and some of its metal complexes have been investigated. In $[Cu_2(L)]^{2+}$, the ligand-centered luminescence bands are completely quenched and as in the $[Cu(L)]^{+}$, due to the presence of a catenate-type moiety. In $[Ag_2(L)]^{2+}$, a strong phosphorescence is present at 77 K. In $[(Cu,Ag)(L)]^{2+}$, only the copper MLCT emission is present [148]. The luminescence of the catenand **XI** its mono- and bis- copper catenates have been reported both in CH_2Cl_2 and in an MeOH/EtOH/CH_2Cl_2 rigid matrix at 77 K [149]. Five new dicopper(I) "knots" ranging from 80- to 90-membered rings have been synthesized, their yields depending on methylene fragments linking the two chelating units and the length of the unit used in the cyclization reaction. The face-to-face isomers were in the major products. In CH_2Cl_2 solution, both isomers exhibit MLCT absorption bands in the visible and emission bands in the red spectral region. The profile of the absorption spectra and the luminescence properties depend on the length of the connectors [150].

A set of rotaxanes has been constructed consisting of a 30-member macrocyclic ring, incorporating two threaded 2,9-diphenylphenanthroline residues, coordinated



X



XI

to Cu(I) with gold-(III) and zinc(II) porphyrins as terminal stoppers. The rates of the various electron transfer processes markedly depend on the molecular geometry which is affected by the coordinated metal [151].

The interactions of Cu(L), (L = the deprotonated form of *meso*-tetrakis(4-(*N*-methylpyridiniumyl))porphyrin) to different types of DNA samples have been studied by electronic absorption and CD as well as luminescence spectroscopy at pH 7.8. The nucleotide type and the nucleotide-to-copper ratio affects the type of the interaction and the site to which it occurs [152].

2.1.1.2. Silver complexes. Secondary ion MS for both free $[Ag(RCN)_4][Y]$ (R = Me, Bu^t, Cy; Y = ClO_4, PF_6) and in a graphite matrix proved the existence of fragments up to AgL_3^+, the gas phase stability of AgL_2^+ being large with respect to AgL_3^+ [4]. Reaction of $AgAsF_6$ or $AgSbF_6$ with cyanogen halides in liquid SO_2 produced the first complexes of the formula $[Ag(NCX)_2]^+$ and the structure of the chloro compound with hexafluoroantimonate was solved [153]. Dicyanopolysulfanes $S_n(CN)_2$ ($n = 2,3$) react with $AgAsF_6$ in liquid SO_2 to form $[Ag\{S_n(CN)_2\}_2]_x[AsF_6]_x$ with bridging ligands and each silver coordinated to four nitrogen atoms from four different ligands [154].

The crystal structure determination of $[Ag_2(1,8\text{-naphthyridine})_2][ClO_4]_2$ revealed a digonal AgN_2 environment around the silver atoms [19]. The thermochemical data associated with the complexation of several amines to silver in DMSO at 298 K have been studied and compared with those in water [155]. The stability of silver complexes with 1,2-diaminoethane, 1,3-diaminopropane and diethylenetriamine in DMSO at 298 K was also studied potentiometrically with the diaminopropane forming witht the monomeric and polymeric complexes as well [156]. Potentiometric studies revealed that ethylenediamine and five of its *N*-methyl and two of its C-methyl derivatives coordinate to Ag^+ in 1M KNO_3 with the C-Me ligands showing a higher stability for the AgL_2 species [157].

Mixed nucleobase silver complexes with 1-methylcytosine or 9-methyladenine, and 7,9-dimethylguanine have been prepared and studied. Silver appears in a distorted trigonal-planar environment with both nucleobases and a water molecule virtually coplanar. Intramolecular hydrogen bonding is observed. An alternative model to existing hypotheses on Ag–DNA interactions was put forward which considers the "insertion" of a metal-aqua entity into an existing base pair [158]. Only when 9-ethyl guanine solution in ethanediol was solidified and layered with $AgNO_3 \cdot H_2O$ did a clear reaction occur to affording $[Ag(L)_2][NO_3]$ where the ligand coordinates through its N-7 atom. The optimal reaction conditions for 1,9-dimethyl guanine are in aqueous medium at pH ≈ 4 [159]. The structures of several *N*-((alkylamino)carbonyl)-4-substituted benzenesulfonamide complexes with silver, of the general formula $K[Ag(L)_2]$, prepared in alkaline aqueous ethanol were proposed, on the basis of spectroscopic evidence, to be analogous to the corresponding Mg^{2+} complexes, i.e. involving linear AgN_2 coordination to the urea nitrogen atoms [160]. Several imides form anionic AgL_2^- complexes, which oxidize irreversibly in acetonitrile to afford the parent ligands (succinimide, tetramethylsuccinimide, phthalilmide, *p*-CN-formanilide) or hydrazine derivatives through N–N coupling (formanilide) [161]. Crystal structure determination and investigation of the ground state electronic energy in *N*,*N*′-di-*p*-tolylformamidato disilver by spectroscopic and theoretical means concluded that besides the short Ag–Ag distance [2.705(1) Å] there is no direct metal–metal interaction [17].

A flattened tetrahedral silver is obtained in bis(4,4′,6,6′-tetramethyl-2,2′-bipyridine)silver tetrafluoroborate, which is isomorphous and isostructural to the corresponding copper perchlorate [162]. Reflux of $AgClO_4$ with terpy in acetonitrile yielded a double salt of the formula $[Ag_3(terpy)_4][Ag(terpy)(MeCN)][ClO_4]_4$ where a collinear Ag_3 array with digonal central and tetrahedral terminal Ag atoms is realized in the polynuclear cation [163]. Several 2-arylazopyridines are found to chelate in $[Ag(L)_2][NO_3]$ compounds [164], while 2,6-diacetylpyridine, bis(6-chloro-2-pyridyl)hydrazone are wrapped around the binuclear core of $[Ag_2(L)_2][PF_6]_2$ giving rise to a short Ag···Ag contact of 3.141(1) Å [165]. Compounds $[Ag(L)_2]^+$ are formed by several pyrido[1,2-*a*]pyrimidine derivatives with two coordinate silver [166].

The tetrameric complex $[Ag_4(L)_4]$ has been prepared from lithium reagents, silver(I) halides and [2-(6-methyl)pyridyl]trimethylsilylamide, and has been characterized crystallographically. The ligands link four silver atoms in a plane [49]. (4R,5R)- and (4S,5S)-4,5-bis(2-(2-pyridyl)ethyl)-1,3-dioxolane react with silver in MeOH to afford $\{[AgL][CF_3SO_3]\}_\infty$ which, in the solid state, reveal a helical structure, while in solution their spectra are identical and indistinguishable from the spectra of $[Ag_2(rac\text{-}L)_2][CF_3SO_3]_2$ indicating that they do not retain their solid-state structure [167].

Piperazine and pyrazine react with $AgBF_4$ and $AgPF_6$, respectively, in a 2:1 ratio to yield two-dimensional polymeric chains of $[Ag(L)_2][Y]$ with four-coordinated silver atoms [168]. The polytopic ligand 6,6′-bis[2-(6-methylpyridyl)]-3,3′-bipyridazine formed $[Ag_9(L)_6]^{9+}$ where a 3 × 3 grid of tetrahedral AgN_4 units is observed in accordance with the ^{109}Ag NMR spectra [169]. The reactions of $AgBF_4$ with pyrazine in EtOH have led to the isolation of four polymeric coordination products. Using a 1:1 molar ratio, the one-dimensional linear polymeric $\{[Ag(L)][BF_4]\}_\infty$ was obtained, while with a 1:2 ratio, two polymorphs of $[Ag_2(L)_3](BF_4)_2$ were obtained, an air stable two-dimensional and a decomposing-in-air three-dimensional polymer were obtained. With higher metal-to-ligand ratios, the unstable one-dimensional zigzag polymer $[Ag(L)_3][BF_4]$ was obtained [170].

IR and UV data are reported for $[Ag_2(L)_x][CrO_4]$ and $[Ag(L)_x(NO_3)]$ where L = bpy, 4,7-Ph_2phen, 4,4′-bpy and hexamethylenetetramine, supporting for the last two ligands, CrO_4 coordination [171]. Linking two bipyridine units by a 1,3-phenylene spacer has provided a novel class of ligand which promotes the spontaneous self-assembly of double helicates upon reaction with transition-metal ions. Interaction with silver(I) resulted in dinuclear double-helical complexes with the metal ions occupying pseudo-tetrahedral coordination sites [82].

The reaction of $AgPF_6$ with pyrazole in EtOH/CH_2Cl_2 gave among others $[Ag(L)_2][Ag_2(L)_5][PF_6]_3$ while $AgSbF_6$ gave $[Ag(L)_3][SbF_6]$. The former was obtained as stacks of two different two-dimensional layers with both square planar and square pyramidal silver atoms, whereas in the latter only octahedral coordination was observed [172]. $AgNO_3$ and sodium 3,5-diphenylpyrazolate in THT give rise to trimeric $Ag_3(\mu\text{-}L\text{-}N,N')_3$ with a nonplanar Ag_3N_6 core, while $Ag(PhCO_2)$ affords hexameric $Ag_6(\mu\text{-}L\text{-}N,N')_6$ with a two-bladed propeller shape [173]. The crystal structures of the polymeric pyrazolates $[Ag(L)]_n$ and the trimeric $[Ag(L)]_3$, have been determined by X-ray powder diffraction data. The polymeric complex consists of infinite chains of linearly coordinated metal atoms, bridged by bidentate pyrazolato anions [61]. The stability constants of silver complexes with 3-methylpyrazole 3,5-dimethylpyrazole, 1,2,4-triazole, 4-amino-1,2,4-triazole, thiazole, 4-methylthiazole and 2-aminothiazole were determined potentiometrically in water and the ligand π-acceptor capacities derived [174]. Bis(pyrazolyl)alkanes give 1:1 ionic compounds with NO_3, CH_3SO_3 and 2:1 with ClO_4 silver salts, the crystal structure of the latter being reported. The compounds are stable in acetone but in DMSO the ligands are partially substituted by the solvent [175]. Two-, three- and four-coordinated copper being present in complexes $[Ag(L)]^+$, where L is Tris[2-(3,4,5-Me_3pz)ethyl]amine, bis[2-(1-pyrazolyl)ethyl]amine and 1,3,5-trimethylpyrazole, respectively, gives rise to clearly distinct absorption and resonance Raman spectra which can be used as coordination environment probes [13]. Analogous studies were carried out for the complexes of [2-(1-methylimidazolyl)]methoxymethane and the emitting state was identified as well as that of the corresponding $[Ag(L)(CO)]^+$ [14].

Silver imidazolate has been synthesized in water by addition of ammonia to a solution of $AgNO_3$ and imidazole. X-ray powder diffraction revealed polymeric chains, containing linearly coordinated silver atoms joined by imidazolate fragments and short interchain Ag···Ag contacts. The compound readily reacts with Lewis bases to form compounds of the formula $\{Ag_2(L)_2(base)_m\}_n$ ($m=2$, 3) [176]. 1,1′-dimethyl-2,2′-bis(6-methylpyrid-2-yl)-5,5′-[pyridine-2,6-diylbis[(1-methyl-*1H*-benzimidazol-2,5-diyl)-methylene]]bis[*1H*-benzimidazol] self assembles with a mixture of bivalent iron and monovalent silver in acetonitrile to afford $[FeAg_2(L)_2]^{4+}$ with silver pseudotetrahedrally coordinated to two bidentate ligands [177].

Several 2-arylpyridine carboxaldimines form $[Ag(L)_2][ClO_4]$, unstable in acetonitrile but stable in MeOH and $CHCl_3$, undergoing transmetallation with MCl_2 ($M=Fe$, Co, Ni) [178]. Silver complexes have been prepared with 1,1′-(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-dimethyl)ferrocene, *N,N*′-bis(ferrocenylmethyl)diaza-18-crown-6, bis[*N,N*′-bis(cyclopentadienyl-methyl)-4,13-diaza-18-crown-6]di-iron and with their amide precursors. The solid-state structure of the former with $AgClO_4$ has been obtained and revealed an Fe–Ag interaction which was further confirmed by ^1H NMR, UV–Vis spectroscopy, stability constant measurements in MeOH and acetonitrile, while a positive shift of the redox potential was also observed [179]. The synthesis and X-ray crystal structure of a disilver complex $[Ag_2(L)][BF_4]_2$ of a bibracchial tetraimine Schiff-base macrocycle derived from the silver-templated cyclo-condensation of 2,6-diacetylpyridine and Tris(2-aminoethyl)amine are reported [180]. The crystal structure of $[Ag_2(L)][ClO_4]_2$ complexes is reported with the bibracchial tetraimine Schiff-base macrocycles derived from the condensation of 2,6-diacetylpyridine with *N,N*-bis(2-aminoethyl)-2-(aminomethyl)pyridine, *N,N*-bis(3-aminopropyl)-

2-(aminomethyl)pyridine, *N,N*-bis(3-aminopropyl)-2-methoxyethylamine and *N,N*-(3-aminopropyl)-2-methoxylbenzylamine [181]. Reaction of Ag^+ in acetonitrile with 1,4,7-triazacyclononane and the 1,4,7-trimethyl analog and the addition of tetrabutylammonium salts affords the complexes [AgX(L)] (X = Cl, Br, I, CN, SCN) while using a ratio of 2:1 in EtOH yields $[Ag(L)_2]^+$ and in pyridine, $[(L)Ag(\mu\text{-}CN)Ag(L)]PF_6$ has been obtained [182].

Schiff bases derived from *N,N*-bis(2-aminoalkyl-2-phenylethyl)amine form either acyclic mononuclear (alkyl = Et) or macrocyclic dinuclear (alkyl = *n*-Pr) silver complexes with trigonal silver environments as IR and ^1H NMR measurements reveal [183].

Several cryptands form $[Ag_n(L)][Y]$ compounds, with $n = 1$ or 2 and Y being noncoordinating anions; in all these silver is coordinated to three or more N atoms. For example, the triflate salt of the cryptate formed by a 2:3 condensation of tris(2-aminoethyl)amine with *p*-diformylbenzene in MeOH [184] reveals tetracoordinated silver, while in the analogous cryptand obtained from 2,5-dimethoxy-1,3-phenylenedialdehyde, the silver is three-coordinated [185] as in the product of template condensation of tris(3-aminopropyl)amine and 5-R-2-hydroxymethyl-1,3-phenylenediacetaldehyde (R = OH, Me, Et, Br) [186]. Both AgN_3 and AgN_3C environments are present in (1,15-dioxa-4,12,18,26-tetraaza-6;10,20:24-dinitrilo-octacosa-4,7,9,11,18,20,22,25-octene)cyanodisilver(+) [187] and AgN_5 in $[Ag_2(L)_2][BF_4]_2$ where L represents the deprotonated form of 1,11-bis(2′-hydroxyethyl) 4;8,12;16,17:21-trinitrilo-1,2,10,11-tetraazacyclohenicosa-2,4,6,9,12,14,18,20-octaene, owing to a short intradimer Ag···N contact [188].

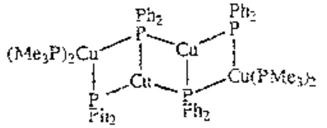
2.1.1.3. Gold complexes. The complexes $[Au(NH_2R)_2]X$ (R = H, Me, Et or Bu^t; X = Br, SbF_6, BF_4) have been synthesized by bubbling gaseous NH_2R through an acetonitrile solution of gold(I) ions [189] and characterized by IR, NMR spectra and TG and DSC techniques; the single-crystal structural determination of $[Au(NH_3)_2]Br$ confirmed the linear coordination about gold. The complex $\{[Au_2(L)_2][BF_4]\}_n$ (L = diethylenetriamine) has been synthesized and characterized by IR and NMR spectroscopy. Its crystal structure revealed that the molecular cation has a ring configuration with local AuN_2 environments and a polymeric structure due to weak interdimer Au···Au contacts [190].

Sodium 3,5-diphenylpyrazolate and Au(THT)Cl afforded, in THT, Tris(μ-L.*N,N′*)trigold with a planar Au_3N_6 core, while reaction with $AuCl(PPh_3)$ gave hexameric $Au_6(\mu\text{-}L.N,N')_6$ with an 18-membered ring [173]. Metathesis reaction between $AuCl_3py$ and sodium 3,5-diphenylpyrazolate in THF affords the mixed valence trimeric compound $[Au^I_2Au^{III}(\mu\text{-}pz)_3]Cl_2$ which, upon reaction with aqua regia, transforms to the 4-chloropyrazolate complex. The XPS spectra of the product show only a broadening on the high-energy side of the Au(I) band [191].

Tetraphenylprophyrinato gold with $[M(mnt)_2]$ anions (M = Ni, Pt) reveals one-dimensional assemblies of gold atoms and no interaction with the anion, as indicated by the findings of magnetic measurements, EPR, Vis and conductance measurements [192].

2.1.2. Phosphorous donors

2.1.2.1. Copper complexes. Crystallographic studies of the ionic compounds $[Cu(PMe_3)_4]X$ revealed distorted tetrahedral copper environments with mean Cu–P distances of 2.270, 2.271 and 2.278 Å for X = Cl, Br, I. The trigonal pyramidal environment in $[Cu(PPh_3)_4][PF_6]$ presents an axial and a mean off-axial Cu–P length of 2.465(2) Å and for Cu–P of 2.566(2) Å [193]. Several complexes of the formula $[Cu(L)_4][BF_4]$ ($L = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_2H, $PPhH_2$) were studied by spectroscopic methods [194]. Dissociation of $Cu(triethylphosphite)_3Cl$ in solution led to the formation of $[Cu(triethylphosphite)_4]Cl$ and several low-coordination Cu(I) compounds, the concentration of which depends upon the polarity of the solvent [195]. High-resolution solid-state ^{31}P NMR spectra of Cu(I)-phosphine complexes show field-dependent, distorted quartets in which the line separations are not constant due to the combination of scalar J_{PCu} coupling with incompletely averaged dipolar and anisotropic J interactions. The quartet distortion is related to structural data, ^{63}Cu quadrupole coupling constants and anisotropy in the P–Cu scalar coupling constant. This information is discussed in light of a simple EFG analysis for the copper atom based on s–p hybridization schemes involving its vacant 4p orbitals [196]. Computational studies by LGTO-local density functional theory are reported on the electronic structure of $[Cu_nP_m]^{x-}$ clusters [197]. Neutron diffraction studies on $H_6Cu_6\{P(p\text{-tolyl})_3\}_6$ verified the existence of an octahedral copper atom cluster and face-capping hydrides in accordance with previous theoretical predictions [198]. Reaction of $[CuCl(PPh_3)]_4$ with $[MCo_3(CO)_{12}]$ (M = Fe, Ru) in toluene yielded $[MCo_3(CO)_{12}\{\mu_3\text{-}Cu(PPh_3)\}]$ to which triphenylphosphine added to form the ionic $[Cu(PPh_3)_3][MCo_3(CO)_{12}]$ [199].



XII

Phosphide complexes $[Cu(PPh_2)_2]_2$ react with PMe_3 to form **XII** complexes with eight-membered rings and both digonal and tetrahedral copper atoms. The same reaction in the presence of CuCl affords $Cu(PPh_2)_3Cl(PMe_3)_2$ with trigonal and tetrahedral copper atoms [200].

Reaction of copper tetrafluoroborate or perchlorate with dppm in refluxing acetone produced the dimer $[Cu_2(\mu\text{-dppm})_2]^{2+}$. Analogous compounds were obtained with 2-(diphenylphosphino)pyridine, while upon recrystallization of $[Cu_2(\mu\text{-}L)_3]^{+}$ from acetonitrile, a product incorporating an MeCN molecule as was produced as shown by ^{31}P NMR measurements [201]. *Cis*-bis(diphenylphosphino)ethylene formed $[Cu(L)_2][PF_6]$ which was studied crystallographically and by solid-state ^{31}P NMR [202]. *N*,*N*′-bis[2(diphenylphosphino)ethene-1,2-diamine and the corresponding 1,3-propanediamine give complexes $[Cu(L)][BF_4]$ with distorted tetrahedral copper environment [203]. The asymmetric diphosphine $Ph_2PCH_2CH_2PEt_2$ produced water-soluble air-stable complex of the formula $[Cu(L)_2]Cl$ on which ^{31}P and ^{63}Cu NMR studies discussed the inversion process at the metal center which is in a CuP_4 environment [204]. The synthesis and structural and solid-state ^{31}P CP/MAS NMR characterization of *cis*-bis(diphenylphosphino)ethylene and the complexes $[Cu(L)_2][PF_6]$ have been carried out. Solution and solid-state ^{31}P NMR chemical shift parameters are similar, supporting the hypothesis that the tetrahedralbis(chelated) cations are also stable in solution [205]. 1,2-bis[bis(2-diphenylphosphino)ethyl)amino]ethane produced a $[Cu_2(L)]$ complex where both crystal structure and ^{31}P NMR revealed equivalent phosphorus atoms [206]. α,α′-bis[bis(2-diphenylphosphino)ethyl)amino]ethane, the corresponding diphenylarsino and the diphenylphosphino *m*-xylene finds coordination to two copper atoms forming Cu_2L^+ and Cu_2L^+, which show quasi-reversible one-electron redox couples [207]. The highly symmetric compound $[Cu_2(dmpe)_2(\mu\text{-dmpe})][BF_4]$ shows ^{63}Cu NMR signal and does not dissociate at the NMR time scale [208]. (R^*,R^*)-(±) or (R^*,S^*)-1,2-phenylenebis(methylphenylphosphine) formed $[M(L)_2]^+$ compounds with the copper triad metals and appear to rearrange in solution by intermolecular ligard redistribution (rate $Au<Cu<Ag$) and inversion at the metal centers (rate $Ag<Au<Cu$) [209]. A highly distorted tetrahedral environment has been observed in the $[Cu(dmpe)_2][Cu\{Co(CO)_4\}_2]$ [210].

1,1′-bis(diphenylphosphino)ferrocene reacts with Cu^+ to give $[\{Cu(L)\}_2(\mu\text{–}L)]^{2+}$ perchlorate and tetrafluoroborate with a trigonal CuP_3 environment [211]. The compound undergoes a single reversible step three-electron oxidation in 1,2-dichloroethane to give the corresponding $[\{Cu(L)\}_2([\mu\text{–}L)]^{5+}$ ion which disproportionates to $[Cu(L)]^{2+}$, ferrocenyl radical and CuL^+ [212].

Complexes of the formula $Cu(P\text{–}P)BH_4$ were proved to photoisomerize *cis*-piperylene to *trans*. Estimation of the triplet excited states of these complexes with a peculiar CuP_2H_2 chromophore are at 60–61 and 66–67 kcal mol^{-1} above the ground state for dppe and dppp, respectively [213]. Analogous environments are present in the products of the reaction of $[nido\text{-}7,8\text{-}C_2B_9H_{10}L]^{n-}$ ($L=H$, $n=2$; $L=$ 4-pyridinemethylcarboxylate, $n=1$) with CuCl both in the presence and in the absence of PPh_3. Boron, phosphorous and hydrogen atoms are present in the copper environment and ^{31}P NMR studies show considerable flexibility of the *closo*-compounds that are formed [214].

Hydrogen was found to be present in the Cu coordination sphere in the CuH reaction products with PPh_3 in THF. A pentameric and a hexameric compound have been obtained with Cu–P bond lengths ranging between 2.16(1) and 2.21(1) and 2.200(5) and 2.246(3) Å, respectively [215].

2.1.2.2. Silver complexes. MAS ^{31}P NMR spectra of $[Ag(PPh_3)_2][NO_3]$, $[Ag(L)_2][NO_3]$ ($L=P(CH_2CH_2CN)_3$ $P(m\text{-tolyl})_3$) are reported and correlated with the determined structures [216]. The structure of $[Ag(PPh_3)_4][PF_6]$ revealed an almost ideal tetrahedral silver with $Ag\text{–}P=2.666(3)$ Å [193]. Potentiometric and calorimetric measurements of the stability of several $[Ag(ER_3)_n][ClO_4]$ in pyridine established the complex stability as varying in the sequence primary < secondary < tertiary phosphine. Among the phosphines used, PBu_3 proved to form three species in solution while for Pcy_2H and Pcy_3 only two species were obtained [217]. An ionic compound with the stoichiometry $[Ag(L)_2]_2[Ag_5I_7]$ was obtained by refluxing in acetonitrile AgI and Tris(2,4,6-trimethoxylphenyl)phosphine [218]. Cyclopentyldiphenyl and dicyclopentylphenyl phosphines form mononuclear gold(I) perchlorate and tetrafluoroborate complexes [219]. The formation of complexes $[Ag(L)_n][PF_6]$ in CH_2Cl_2 were followed by ^{31}P NMR studies at 193 K. At least two species were determined in solution the exchange rate being greater for 5-phenyldibenzophosphole than for triphenylphosphine [220].

The thermodynamics of complex formation between silver(I) and PPh_3, dppm, dppe and dppp has been investigated in propylene carbonate at 298 K by potentiometric and calorimetric techniques. PPh_3 forms three successive mononuclear complexes, dppm only polynuclear species, whereas mononuclear complexes, in addition to polynuclear ones, are formed by dppe and dppp [221]. $^{109}Ag\{^{31}P\}$ INEPT studies on $[Ag(L)_2][NO_3]$, L = dppe, depe, eppe, dppp and 1,2-diphenylphosphinoethylene, are reported to yield values in the range 1378–1468 ppm relative to 4 M $AgNO_3$ in D_2O [222]. ^{31}P NMR studies confirm formation of dimeric cationic units for dppm, dppe, dppp, bis(2(diphenylphosphino)ethyl)phenylphosphine and Tris(2-(diphenylphoshpino)ethyl) phosphine upon reaction with $AgClO_4$. The tendency of dppm to form polymeric compounds is also confirmed [223]. Eight-membered rings were observed in $[Ag_2(dmpm)_2]Br_2$ with bromine links between adjacent units. The solid-state IR and Raman spectra of $[Ag_2(L)_2][PF_6]_2$ and $[Ag_2(dppm)_2][PF_6]_2$ are also reported [224]. Dmpe and dppe react with $AgAsF_6$ in $MeNO_2$ or acetone in a 3:2 ratio to afford $[Ag_2(L)_3][AsF_6]_2$. When a mixture of the ligands is used, ^{31}P NMR reveals the presence of mixed-ligand cations. The observed exchange is faster for dppe involving end-on exchange of a bridging ligand [225]. $[Ag_2(dmpe)_2][BPh_4]_2$ prepared in acetonitrile possesses two bridging and two chelating dmpe ligands [226], while bis[*cis*-1,2-bis(diphenylphosphino)ethylene]silver nitrate is monomeric and capable of transferring the nitrate to organotin(IV) compounds forming ionic species of the formula $[AgL_2][Y]$, ($Y = SnPh_2(NO_3)_2$, $SnPh_3(NO_3)_2$ or $SnPh_2Cl_2(NO_3)$). ^{31}P NMR measurements reveal identical P environments in both the initial and the final compounds [227]. Analogous is the reaction of bis(diphenylphospino)methane silver nitrate with $SnPh_2(NO_3)_2$ in MeCN–Me_2CO resulting in formation of $[Ag(L)_2][SnPh_2(NO_3)_3]$ studied by IR and ^{31}P and ^{119}Sn NMR [228].

The reaction of $HC(PPh_2)_3$ with $Ag(CF_3SO_3)$ in CH_2Cl_2 afforded $[Ag_3(L)_2Cl]^{2+}$ consisting of a central triangular metal core and UV–Vis spectrum in acetonitrile virtually identical to that of the free ligand [229]. 1,8-bis(Diphenylphosphino)-3,6,-dithiaoctane and its 3,6-di(phenylphosphino) counterpart form $[Ag(L)][BF_4]$ Complexes in acetone and ^1H, ^{31}P and ^{109}Ag NMR studies predict AgS_2P_2 and AgP_4 environments, respectively [230]. The thioether moieties in Ph_3PCH_2SR (R = Me, Ph) and $Ph_3PCH_2CH_2SR$ (R = Me, Et, Ph), however, did not appear to coordinate to silver; neither do they alter significantly the phosphino group's donor ability as studies in DMSO reveal. Thermodynamic studies establish the complex stability sequence as Ph < Me < Et [231].

Trans coordination by dppf in cationic AgL^+ complexes with ClO_4 and CF_3SO_3 anions has been observed [232]. The dimetallic complex $[Pt(CN)_2(\mu\text{-dppm})_2Ag][ClO_4]$ undergoes electron transfer in photoreactions with halocarbons. Its emission quenching by pyridinium acceptors was also studied [233].

2.1.2.3. Gold complexes. Electrospray MS of mixtures of $Au(PPh_3)Cl$ and PR'_3 (R,R′ = phenyl, *p*-Cl, and *p*-methyl phenyl) verifies the existence of mixed ligand cations of the general composition $Au(PR_3)_2^+$ and $Au(PR_3)$ [234]. The strong enthalpy stabilization of PPh_3 and PCy_3 upon ligation to Au has been verified by potentiometric and calorimetric measurements in pyridine [235].

Electronic absorption and MCD spectra of $[Au\{P(Bu^t)_3\}_2][ClO_4]$ in acetonitrile helped in the identification of the MLCT d→p transition [236]. $Au(PEt_3)(CN)$ although normally linear in the solid state, disproportionates in solution to $[Au(PEt_3)_2][Au(CN)_2]$ like the corresponding triphenylphosphino complex which is in fast equilibrium even at 200 K [237]. The ligand scrambling in $Au(PR_3)(CN)$ to yield $[Au(PR_3)_2][Au(CN)_2]$ (R = Me, Et, *i*-Pr, Ph, Cy) is studied by ^{13}C and ^{31}P NMR. The K_{eq} values vary as Cy > Me > *i*-Pr > Et > Ph. The PCy_3 and $P(i\text{-}Pr)_3$ are new complexes [238]. Reaction of Tris(2-cyanoethyl)phosphine with Au(THT)Cl in CH_2Cl_2/MeCN afforded Au(L)Cl and $[Au(L)_2]Cl$, the latter encapsulating gold within the cyano- arms. Its reaction with H_2SO_4/H_2O at 120 °C results in the formation of $Au\{CH_2CH_2COOH)_3\}_2Cl$ [239]. Luminescence studies are reported for $AuCl(PPh_3)_2$, $[Au(PPh_3)_3][BPh_4]$ and Au(THT)Cl. Titration of $[Au(THT)_2][PF_6]$ with PPh_3 in acetonitrile reveals that the luminescence depends on the phosphine molar fraction, the emitting species being either AuP_2^+ or AuP_3^+. For Trisalkylphosphines, emission was found to occur only for ratios P:Au > 3 [240]. Cyclohexyldiphenyl and dicyclohexylphenyl phosphines form mononuclear gold(I) perchlorate and tetrafluoroborate complexes [219].

The electrochemical reduction of $[Au_9(PPh_3)_8]^{3+}$ and $[Aug_9(P(p\text{-}OMeC_6H_4)_3\}_8]^{3+}$ in CH_2Cl_2, Me_2CO, MeCN and PhCN is studied by normal and differential pulse and CV revealing two distinct peaks almost solvent independent [241]. Reversible isomerization between the normal-pressure green "part of eicosahedron" $[Au_9(PPh_3)_8][PF_6]_3$ and the high-pressure brown D_{4d} centered-crown one is achieved in the range up to 80 kbar, with the most marked changes observed in the range 45–60 kbar [242]. Magnetic circular dichroism measurements of $Au_9(PPh_3)_8^{3+}$ with NO_3 and ClO_4 counterions are reported in acetonitrile [243].

Treatment of *o*-tolylphosphine with Tris(triphenylphosphineaurio)oxonium tetrafluoroborate in THF afforded $[(o\text{-tolyl})PAu(PPh_3)_3][BF_4]$ with noninteracting Au centers. The compound further reacted with $[AuPPh_3][BF_4]$ to afford $[(o\text{-tolyl})P(AuPPh_3)_4][BF_4]_2$ with a square pyramidal central phosphorous atom and the four Au ones on the basal plane. Analogous reactions are realized with the corresponding arsine [244]. Analogous reaction with *p*-phenylenediphosphine yielded $\{(AuPR_3)_3(\mu\text{-}L)(AuPR_3)_3][BF_4]_2$ (R = Ph, Bu^t) while if the 1:1 stoicheiometry is applied and a further equivalent of $Au(PR_3)(BF_4)$ is used,

$[(AuPPh_3)_4(\mu\text{-}L)(AuPPh_3)_4][BF_4]_4$ is formed as ^1H and ^{31}P NMR indicate [245]. The corresponding *tert*-butyl oxonium salt upon reaction with $P(SiMe_3)_3$ in THF at −78°C yielded $[P\{AuP(Bu^t)_3\}_4][BF_4]_2$ a tetrahedral gold cluster [246] while the extremely bulky (2,4,6-tris-*tert*-butyl)phenylphosphine formed $[(AuPR_3)_3(L)][BF_4]$ (R = Ph, *t*-Bu), and addition of $[Au(L)][BF_4]$ yielded $[L(AuPPh_3)_4][BF_4]_2$ and $[Au(PBu^t)_3][BF_4]$, respectively [247].

The synthesis, structural and solid-state ^{31}P NMR characterization of *cis*-bis(diphenylphosphino)ethylene and the complexes $[Au(L)_2][PF_6]$ has been carried out. Solution and solid-state ^{31}P NMR chemical shift parameters are similar, supporting the hypothesis that the tetrahedral bis(chelated) cations are also stable in solution [205]. A short Au···Au interaction has been observed in $[Au_2(\mu\text{-}dmpm)_2][PF_6]_2$. Solid-state IR and Raman spectra are reported as well as for $[Au_2(L)_n][PF_6]_2$ ($n=2, 3$) and $[Au(L)_2]Cl_2$ [224]. ^{31}P NMR studies in solution verify that $[Au_2([\mu\text{-}dppe)_3]^{2+}$ is converted to $[Au(dppe)_2]^+$ by β-D-thioglucose and reduced glutathione in aqueous methanol. The product is kinetically stable, producing $[\{Au(L)\}_2(dppe)]$ [248]. Excited tris[bis(dicylcohexylphosphino)ethane]digold(2+) has proved capable of electron transfer to alkylpyridinium acceptors in acetonitrile and the effective rates of this transfer are reported [249]. Intense $d\sigma^* \rightarrow p\sigma$ transition in absorption and MCD spectra of $Au_2(dmpm)_3^{2+}$ in water and acetonitrile are reported [250]. The UV spectra of $[Au(dmpm)]_2X_2$ (X = Br, ClO_4) and $[Au(dmpe)]_2X_2$ (X = Cl, Br, I, ClO_4) do not obey the Beer law, therefore predicting X-association to yield $[Au_2L_2X]^+$. Bands attributed to Au_2 $d\sigma \rightarrow p\sigma$ transitions underline the importance of Au···Au interactions [251]. Luminescence at 593 nm in solution of $[Au(dppm)]_2[BF_4]_2$ is attributed to $^3Au(\sigma^*)(\sigma)$ emissive state and a Au_2 σ^* HOMO on the basis of Xα studies [252]. The electrochemical behavior of several bis(diphenylphosphino) gold(I) complexes was studied by cyclic voltametry [253]. Absorption and emission properties have been reported for the mixed metal complex $[Ir(CO)ClAu(AuCl)_2(\mu\text{-}L)][PF_6]$ prepared by the reaction of $[Ir(L)_2(CO)][PF_6]$ with three equivalents of $Au(Me_2S)Cl$ (L = bis(diphenylphosphinomethyl)phenylphosphine) as well as of $[Au_2Ir(CN)_2(\mu\text{-}L)_2][PF_6]$ which was the product of the treatment of the former with KSCN and $Au(Me_2S)Cl$[254].

The reaction of $[Au(THT)_2][ClO_4]$ or $[Au(acac)(PPh_3)]$ with $CH(PPh_2)_3$ led to dinuclear complexes, $[Au_2(\mu\text{-}CH(PPh_2)_3)_2][ClO_4]_2$ or $[Au_2(\mu\text{-}C(PPh_2)_3)_2]$, respectively, which react further with $[Au(acac)(PPh_3)]$ and $[Au(THT)(PPh_3)][ClO_4]$ to afford the tetranuclear complex $[(Ph_3P)AuPPh_2C(PPh_2AuPPh_2)_2CPPh_2Au(PPh_3)][ClO_4]_2$. Trinuclear complexes were also realized and the compounds studied by NMR and X-ray diffraction techniques [255].

The reaction of secondary phosphines with several gold compounds is shown to produce either ring- or chain-structured polymers of $[Au(\mu\text{-}PR_2)]_n$ (R = Et, Ph, p-MeC_6H_4, p-$Bu^tC_6H_4$), probably through the intermediacy of $[AuX(PHR_2)]$ compounds, a few of which were also isolated and analyzed. In nonpolar solvents complexes $[Au(PHPh_2)_2]^+$ were also realized [256].

Bis(diphenylarsino)methane reacted with either $Au(THT)_2^+$ or $Au(C_6F_5)(THT)$ in CH_2Cl_2 to form $[Au_2(L)_2]^{2+}$ or $[AuL(C_6F_5)]^+$, respectively [257]. Reaction of $K[AuCl_4]$ with bis(dimethylphosphinomethyl)methylphosphine in MeOH yielded

$[Au_3(\mu\text{-}L)_2]^{3+}$, the crystal structure of which has been determined. The nonlinear metal chain [Au–Au–Au angle 136.26(4)°] experiences intramolecular Au···Au contacts of 2.981(1) and 2.962(1) Å. The complex revealed phosphorescence in acetonitrile solution [258]. Tris(2-(diphenylphosphino)ethyl)amine forms Au(L)Y, monomeric with three-coordinate gold for Y = PF_6, NO_3 and dimeric for Y = BPh_4 [259]. The reaction of $HC(PPh_2)_3$ with $K[AuCl_4]$ in the presence of 2,2′-thiodiethanol in MeOH yielded $[Au_3(L)_2Cl]^{2+}$ consisting of a central triangular metal core [229]. The gold(I) complex with 1-diphenyphosphino-2-(2-pyridyl)ethane exhibited a digonal structure with monodentate *P*-bound ligands. NMR studies revealed that the species, besides ligand exchange, rearranges in solution by inversion at the tetrahedral metal center [260]. Bis((diphenylphosphino)methyl)phenylarsine reacted with AuCN in toluene and upon recrystallization from $CHCl_3$–Et_2O yielded $[Au(L)_2][Au(CN)_2]$ [261]. The complex cation $[Au_2(L)_3]^{2+}$ [L = 2,6-bis(diphenylphosphino)pyridine] revealed an intramolecular Au···Au separation of 4.866 Å as determined by X-ray crystallography and displayed photoluminescence at 520 nm in fluid solutions at room temperature [262]. Bis(diphenylphosphino)amine replaced THT from $[Au(THT)_2][ClO_4]$ to form dimeric $[Au_2(\mu\text{-}L)_2][ClO_4]_2$ which upon treatment with halogens forms the corresponding Au(II) species $[(AuX)_2(\mu\text{-}L)_2][ClO_4]_2$ [263]. Emission and absorption spectra in acetonitrile have been measured for $[Au_2(L)_2][PF_6]_2$, $[Au_2(L)_3][PF_6]_2$ and $[AuL_2](PF_6)$ for L = 1,2-bis(dicyclohexylphosphino)ethane [264]. The ^{197}Au Mössbauer spectrum of the bis(diphenylphosphino)amine complex $[Au_2(\mu\text{-}L)_2]^{2+}$ has been obtained at liquid helium temperature [265]. Reaction of $[Au_3(L)_2][ClO_4]_3$ with an excess of the ligand bis(dimethylphosphinomethyl)methylphosphine in methanol yielded $[Au_3(L)_3][ClO_4]_3$ intensely phosphorescing in acetonitrile [266]. The chloro-ylide gold complex $[AuCl(CH_2PPh_3)]$ reacted in acetone with dppm or bis(diphenylphosphino)amine to afford derivatives $[Au_2(\mu\text{-}Ph_2PYPPh_2)_2]$ (Y = CH, N), the latter also being produced by addition of bis(diphenylphosphino)amine to the former. The two complexes further react with silver or gold complexes giving tetranuclear ring systems [267].

$Mn_2(\mu\text{-}H)(\mu\text{-}PCyH)(CO)_8$ reacts with $AuCl(PR_3)$ in THF (R = Cy, Ph, *p*-FC_6H_4, *p*-$OMeC_6H_4$) to give mono- and diaurated polymetallic compounds which are characterized by IR, Vis, ^{1}H and ^{31}P NMR [268]. Auration of primary phosphines PRH_2 by $[\{(PPh_3)Au\}_3O][BF_4]$ in THF at RT afforded $[RP\{Au(PPh_3)\}_3][BF4]$, while $P(SiMe_3)_3$ yielded the hypercoordinated $[P\{Au(PPh_3)\}_5][BF_4]_2$ [269]. The complexation of dendrimers with as many as 3072 terminal phosphino groups to gold has been studied by ^{1}H, ^{13}C and ^{31}P NMR measurements [270].

2.1.3. Arsenic, antimony and bismuth donors

Several complexes of the formula $[Cu(L)_4][BF_4]$ were studied, where L is a tertiary ligand with group 15 donor atoms (EMe_3, EMe_2Ph, $EMePh_2$, EPh_2H, $EPhH_2$, E = As, Sb) as well as $[Cu(L\text{-}L)_2][BF_4]$ with the bidentate ligands $R_2E(CH_2)_nER_2$ (R = Me, Ph; E = As, Sb and *n* = 2, 3) or 1,2-bis$(SbMe_2)C_6H_4$ [194]. Tricyclopentyl arsine formed $[M(L)_2]$ perchlorates and tetrafluoroborates, the former revealing weak anion coordination [219].

A series of $[Cu(L)_2][Y]$ and $[Cu(L)_n][Y]$ ($n=3$ or 4: $Y = ClO_4$, BF_4) were obtained where $L = EPh_3$, EPh_2Ar, $EPhAr_2$, ($E = P$, As, Sb, $Ar = p$-substituted phenyl) and the structure of $[Cu\{SbPh_2(P\text{-}FC_6H_4)\}_4]^+$ has been solved [271]. Several ionic stibine complexes have been studied. The spectral data of $[Cu(SbR_3)_4][BF4]$ ($R = Me$, Et, Ph) and of $[Cu(Me_2SbCH_2CH_2SbMe_2)_2][BF_4]$ and $[Cu(Ph_2SbCH_2CH_2CH_2SbPh_2)_2][BF_4]$ along with $[Cu(PMe_3)_4][BF_4]$ and $[Cu(AsMe_3)_4][BF_4]$ have been reported. The high symmetry of the metal center allowed ^{63}Cu NMR measurements to be carried out [272].

The dimesityl stibine lithium salt added to a cooled THF solution of CuCl and PMe_3 yielded the first Cu(I) antimonide $[(\mu\text{-}Mes_2Sb)Cu(PMe_3)]_2$ with a central Cu_2Sb_2 core [273]. Both (R^*,R^*)-(±) and (R^*,S^*)-1,2-phenylenebis-(methylphenylarsine) form $[ML_2]^+$ compounds with the copper triad metals and appear to rearrange in solution by intermolecular ligand redistribution (rate $Au < Cu < Ag$) and inversion at the metal centers (rate $Ag < Au < Cu$) [209].

Bis(diphenylarsino) methane silver nitrates reacted with $SnPh_2(NO_3)_2$ in $MeCN\text{-}Me_2CO$ resulting in the formation of $[Ag(L)_2][SnPh_2(NO_3)_3]$ studied by IR and ^{31}P and ^{119}Sn NMR [228]. The strong enthalpy stabilization of group 15 donors upon ligation to Au has been verified by potentiometric and calorimetric measurements on several EPh_3 ligands ($E = As$, Sb) in pyridine [235].

2.1.4. Mixed group 15 donors

2.1.4.1. Copper complexes. Several complexes have been isolated, with phosphine and MeCN molecules attached to the metal atom. The effect of the phosphene ligands on the stabilization of $[Cu(MeCN)_n(PR_3)_{4-n}]^+$ ($n = 0$–4) has been expressed in relation to their ^{31}P NMR chemical shifts and electrochemical data [274]. $[Cu(PPh_3)_2(MeCN)_2][ClO_4]$ reacted with terpy in CH_2Cl_2 to displace MeCN forming a five-coordinate copper center which was shown by spectroscopic measurements to retain it in solution [275]. The 6-diphenylphosphiao substituted bipyridine forms $[Cu(\mu\text{-}L)_2(MeCN)_2]^{2+}$ complex where a local $CuPN_3$ environment is present. The complex reveals oxidation peaks at −1.35 and −1.53 V in MeCN, while it reduces CO_2 to CO with concomitant carbonate formation as solution IR studies predict [276]. $[Cu(MeCN)_2$ (*o*-(dimethyalinino)methyl- diphenylphosphinobenzene)$][BF_4]$ and $[Cu(MeCN)_n(PPh_3)_{4-n}][BF_4]$ were studied as catalyst in *trans*-stilbene cyclopropanation with $N_2 = CH(CO_2Et)$ where alkene intermediate presence was proposed to account for the activity of the latter in the case of $n=2$ [277].

Several *N*-heterocylces reacted with $Cu(NO_3)_2$ in the presence of triarylphosphines to give compounds of the formula $[Cu(PPh_3)_2(L)_2][NO_3]$ ($L =$ pyrazine, 1,2,4-triazole, 2-methylimidazole), $[Cu(PAr_3)(pyrazole)_3][NO_3]$ ($Ar = m$-, p-$CH_3C_6H_4$) or $[Cu(ONO_2)(PPh_3)L]$ (3,4,5-trimethylpyrazole, 4-phenylimidazole, bis(pyrazol-1-yl)methane, bis(3,5,-dimethylpyrazine)methane, bis(1,2,4-triazole)-methane), the latter showing fluxional behavior above 240 K [278]. Several 5,6-disubstituted 2,3-bis(2′-pyridyl)pyridazines react in CH_2Cl_2 with

$[Cu(PPh_3)_2(MeCN)_2][BF4]$ displacing MeCN to form $[\{Cu(PPh_3)_2\}_2(\mu\text{-}L)][BF_4]_2$, the excitation spectra of which are interpreted in terms of the π^* energies of the ligands. The complexes react with excess triphenylphosphine to yield $[Cu(PPh_3)_2(L)][BF_4]$ [279]. Reaction of the potassium salts of tetrakis(1*H*-pyrazol-yl)borate and dihydrobis(1*H*-pyrazol-1-yl)borate with $Cu(PAr_3)_2(NO_3)$ yielded compounds $Cu(PAr_3)_2(L)$ which were studied by ^1H and ^{31}P NMR studies [280]. The coordinated 4,5-dicyanoimidazole in $Cu(L)(PPh_3)_2$ undergoes rapid alcoholysis in the presence of CO, being transformed to imino-methylester. The structure of the final product reveals a CuP_2N_2 environment, the N atoms being imino and an imidazolo, respectively [281]. The structures of $[Cu(L)_n(PPh_3)_2][BF_4]$, with 2,2′-biimidazolate, bibenzimidazolate, tetramethylbiimidazolate ($n=1$) and imidazole and pyrazole ($n=2$) have been elucidated utilizing ^1H and ^{31}P NMR [282].

Reaction of cyanoacetic acid and $MeCu(PPh_3)$ in THF at -78 C gave rise to $(PPh_3)_2Cu(LH)(L)$ where a highly distorted tetrahedral CuN_2P_2 environment is observed and hydrogen bonding through the coordinated acid ligand forms loosely connected dimeric units [283]. Reaction of $CuCl(PPh_3)_2$ with $Na(CN)_2BH_2$ in acetonitrile yielded $(PPh_3)_2Cu(CN)_2BH_2$, a linear polymer with bridging dicyanodihydroborate ions [284]

Electrospray MS revealed the existence of $[Cu(PR_3)_2(phen)][BH_4]$ (phen = several substituted phenanthrolines) and all possible cationic units when two different phosphines are present in solution, therefore confirming the rapid ligand exchange in solution [285]. Bulky phosphines enhance the reactivity of electron transfer from [Co(EDTA)] to $[Cu(phen)(phosphine)_2]^+$ {phosphine = PPh_3, PPh_2Cy, PCy_3, $P(p\text{-}MeOC_6H_4)_3$ and anions ClO_4, NO_3} [286]. The reduction of methylviologen by a variety of $[Cu(N\text{-}N)(PPh_3)_2]^+$ complexes in aqueous ethanol has been studied and the efficiency was found to vary in the sequence 2,9-Me_2phen > 4,4′,6,6′-Me_4bpy > 4,4′-Me_2bpy > phen > bpy > 4,7-Ph_2phen, the last two being practically inactive [287]. Photoreduction of methylviologen was effected by the 2,9-Me_2phen complex with PPh_3, PPh_2Cy and $P(p\text{-}OMeC_6H_4)_3$ and the corresponding quatum yields discussed in terms of the excited state lifetimes [288] The emitting ability of the above complexes was studied in methanol, where the dimethyl-substituted phenanthrolines appear to be stronger emitters probably due to the absence of solvent-induced exciplex quenching. Correspondingly, in CH_2Cl_2, the emission increase with temperature indicates significant thermal population of the excited singlet state [289]. The triphenyiphosphine and the *p*-methyl and *p*-chloro- substituted ones give complexes with dimethylphenanthrolines, which show emission in mixed methanolethanol environment at 77 K [290]. Ab initio calculations on the model compound $Cu(HN{=}CHCH{=}NH)(PH_3)_2^+$ are in support of a pseudotetrahedral ground state and planar MLCT excited state easy for water coordination [291]. Absorption and emission maxima of the $[Cu(PPh_3)_2$-(di-2-pyridylketone)]$[NO_3]$ compound in CH_2Cl_2 were reported as well as its catalytic activity in the photochemical transformation of NBD to QDC with a quantum yield of 0.17 (irradiation at $\lambda > 320$ nm for 12 h) [292]. The central pyridyl nitrogen of terpy and two phosphorus atoms define the equatorial plane. ^1H and ^{13}C NMR spectra show that the five-coordinate nature of the compound is also retained in solution [293]. $Cu(PCy_3)_2(FBF_3)$ reacted with NaX in water to give the metathesis products $Cu(PCy_3)_2Y$($Y = SCN, N_3$). The crystal structure of the azido complex reveals a trigonal planar copper environment [294]. Displacement of acetonitrile from $[Cu(PPh_3)_2(MeCN)_2[BF_4]$ by *N*-(2-pyridinylmethylene)phenylamine and *N*-(2-pyridinylmethylene)-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclodecin-16-ylamine yielded complexes $[Cu(L)(PPh_3)_2][BF_4]$ which emit even in methanolic solutions [295].

Reaction of copper tetrafluoroborate or perchlorate with dppm in CH_2Cl_2 at room temperature gave rise to $[Cu_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ and $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$ [296], identified by their ^{31}P NMR shifts. Photoluminescence of $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$ and its reactivity towards benzylchloride, 1-bromopentane in catalytic amounts is reported [297]. In CH_2Cl_2 substitution of acetonitrile with PPh_3, pyridine and 4-substituted pyridines occurs, the products being studied by IR, UV and X-ray diffraction [298]. Reaction between $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$ and substituted pyridines or triphenylphosphine in CH_2Cl_2 gave products $[Cu_2(\mu\text{-dppm})_2(L)_2]^{2+}$ which possess long-lived emissive electronic excited states in fluid solution at room temperature [299]. The bidentate ligands 6-methylpyridone, dimethylpyrazine, *N*(*N*(*p*-tolyl))$_2$, $MeCO_2^-$ dppm reacted with $[Cu_2(MeCN)_2(\mu\text{-dppm})_2][BF_4]_2$ to give $[Cu_2(\mu\text{-dppm})_2(\mu\text{-L})][BF_4]$ for 1:1 and $[Cu_2(\mu\text{-dppm})(\mu\text{-L})_2]$ for 2:1 ratio [300]. Analogous complexes were obtained with 3,6-bis(3,5-dimethylpyrazoly-1-yl)pyrazine and dppm, dppe or 2-(diphenylphosphino)pyridine. The structure of the dppm compound was reported [301]. Reaction of $[Cu(MeCN)_4]^+$ with 1.5 equivalent of dppe and sodium arenylcyanamides in $Me_2CO{\cdot}EtOH$ afforded $[Cu_2(\mu\text{-dppe})_2(dppe)(L)_2]$ with one bridging and two chelating dppe ligands. When the reaction was carried out in EtOH with $Cu(PPh_3)_2(NO_3)$, the product was $[Cu(PPh_3)_2(L)]_2$ [302]. The reaction of $Ni(CO)_2(dppm)_2$ with $[Cu(MeCN)_4][ClO_4]$ in acetonitrile under CO, followed by recrystallization of the solid product from dichloromethane, yielded $[Ni(CO)_2(\mu\text{-dppm})_2Cu(MeCN)_2][ClO_4]$ which readily exchanges the anion for PF_6 or BF_4 and upon treatment with $NaBH_3CN$ under CO afforded $[Ni(CO)_2(\mu\text{-dppm})_2Cu(BH_3CN)]$ [303].

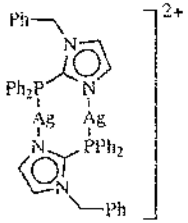
1,2-bis(2-diphenylphosphinoethyl)amino)ethene and the corresponding *m*-xylene and the diphenylarsino analog react in $Me_2CO{\cdot}C_6H_6$ with $[Cu(PPh_3)Cl]_n$ to give $Cu_2L(PPh_3)_2Cl_2$ and with $[Cu(MeCN)_4][ClO_4]$ to give $[Cu_2(L)][ClO_4]$ which readily exchanges anions with NaX to form $Cu_2(L)X_2$ with tetrahedral copper ($X = N_3$, NCS, OH, BH_4) [304]. With the *m*-xylene ligand $Cu_2(L)Cl_2$ has also been observed. The copper(I) hexafluorophosphate with 1-diphenyphosphino-2-(2-pyridyl)ethane has been prepared. The tetrahedral geometry around the metal atom was verified, while NMR studies show that the species, besides ligand exchange, rearranges in solution by inversion at the tetrahedral metal center [260]. ^1H and ^{31}P NMR studies in acetonitrile verified that the complexes $[Cu(L)]^+$ produced in methanol by $[Cu(MeCN)_4]^+$ and 1,10-bis(dimethylphosphino)-4,7-dimethyl-4,7-diazadecane and its dicyclohexyl- and diphenylphosphino- analogs are monomeric, with both nitrogen and phosphorous atoms coordinated to the metal [305].

The tripodal tetradentate ligand Tris(2-pyridylmethyl)amine formed stable cationic complexes $[(L)Cu(L')]^+$ (L' = RCN, CO, or PPh_3) of which the X-ray structures of $[(L)Cu(PPh_3)]^+$ and $[(L_1)Cu(MeCN)]^+$ (L_1 = bis(2-pyridylmethyl)-(5-carbomethoxy-2-pyridylmethyl)amine) were reported. The former reveals a pseudotetrahedral CuN_3P environment with an uncoordinated pyridine site, while the latter possesses a distorted pentacoordinate structure. The reversible oxidation of the complexes was studied [306].

The luminescence of $[\{Cu(L)\}_2(\mu\text{-}2,2'\text{-bipyrimidine})][BF_4]_2$ (L = PR_3, PR_2R', P–P) was found to correlate with the orientation of the phosphine ligand especially since this may or may not promote π-coordination of the bipyrimidine ligand to the metal center [307].

2.1.4.2. Silver complexes. Reaction of $[Ag(PPh_3)(NO_3)]n$ with di-imines in MeOH and subsequent treatment with salts of noncoordinating anions Y (BF_4, PF_6) afforded $[Ag(PPh_3)(L)][Y]$ where L = bpy, phen or *trans*-1,2-bis(4-pyridyl)ethylene. Only the bpy complex reveals resolved ^{31}P NMR spectra (J_{AgP} = 640 Hz) at r.t. in MeCN. For the bis-pyridyl ethylene, a dimeric compound of the formula $[Ag_2(PPh_3)_2(\mu\text{-}L)](NO_3)_2$ was also obtained while with pyridine $[Ag(PPh_3)_3](NO_3)$ is produced through ligand scrambling [308].

Tris(2-(diphenylphosphino)ethyl)amine formed monomeric Ag(L)X complexes, with three-coordinate metal center for X = PF_6, and four-coordinate when X = NO_3 [259]. Both nitrogen and phosphorous were found to coordinate in $[Ag\{(1\text{-benzyl-2-imidazolyl})diphenylphosphine\}_2]^{2+}$ nitrate and tetrafluoroborate **XIII** [309]



XIII

Five-coordinate $[Ag(PPh_3)_2(terpy)][CLO_4]$ has been prepared by the reaction of terpy with $[Ag(PPh_3)_2][ClO_4]$. The metal atom is coordinated to the distal terpyridine pyridyl rings in axial sites. The coordination spheres are completed by the binding of the central pyridyl nitrogen atoms and two phosphorus atoms, which together define the equatorial planes. ^1H and ^{13}C NMR spectra show that the five-coordinate nature is also retained in solution [293].

Silver(I) hexafluorophosphate with 1-diphenyphosphino-2-(2-pyridyl)ethane has been prepared. The tetrahedral geometry around the metal atom has been verified while NMR studies revealed that the species, besides ligand exchange, rearrange in solution by inversion at the tetrahedral metal center [260].

The chiral ferrocene [Fe{1-diphenylphosphino-2-((*R*)-$\mathrm{CHMeNHMeCH_2CH_2NMe_2)C_5H_3}$}{$\mathrm{C_5H_4PPh_2}$}] formed a 2:3 product with $\mathrm{Ag(CF_3SO_3)}$ with two terminal trigonal $\mathrm{AgP_2N}$ and one central bridging $\mathrm{AgP_2}$ atom. Application of a 70-fold excess of $\mathrm{CNCH_2CO_2Me}$ forms [(ferrocene)Ag(isonitrile)$_2$]($\mathrm{CF_3SO_3}$) where "chelating" ferrocene is present [310]. Multinuclear (H, C, N, P, Ag) NMR studies revealed fluxional behavior in (η^5-$\mathrm{C_5Me_5}$)Ir(pz)Ag($\mathrm{PPh_3}$), [{(η^5-$\mathrm{C_5Me_5}$)Ir(μ-pz)$_3$$\mathrm{AgPPh_3}$}$_2$][$\mathrm{BF_4}$] and [($\eta^5$-$\mathrm{C_5Me_5}$)Ir($\mathrm{PPh_3}$)($\mu$-pz)$_2$$\mathrm{AgPPh_3}$][$\mathrm{BF_4}$], associated with argentotropism. The low-temperature Ag–P splitting is related to the dynamic properties of the complexes [311].

2.1.4.3. Gold complexes. Reaction of solid [Au($\mathrm{PPh_3}$)($\mathrm{NO_3}$)] with CO in the solid-state produced, through a series of successive reductions, the compound [Au($\mathrm{PPh_3}$)(NCO)], a product not realized in the outcome of the reaction in $\mathrm{CH_2Cl_2}$ solution [312]. The treatment of *tert*-butylamine and benzylamine with [Au($\mathrm{PR'_3}$)$_2$][$\mathrm{BF_4}$] led to the monoauration products [($\mathrm{R'_3P}$)Au($\mathrm{NH_2R}$)][$\mathrm{BF_4}$] (R′ = Me, R = Bu^t, Bz; R′ = $\mathrm{Ph_2Me}$, R = Bu^t), while [Au($\mathrm{PR'_3}$)$_3$NR][$\mathrm{BF_4}$] (R′ = Me, R = Bu^t, Bz) were obtained using the corresponding oxonium salt [Au($\mathrm{PR'_3}$)$_3$O][$\mathrm{BF_4}$]. Treatment of $\mathrm{NH(SiMe_3)_2}$ with [Au($\mathrm{PR'_3}$)$_3$O][$\mathrm{BF_4}$] afforded both the Tris- and tetra-aurated ammonium salts, [Au($\mathrm{PR'_3}$)$_3$$\mathrm{NSiMe_3}$][$\mathrm{BF_4}$] and [Au($\mathrm{PR'_3}$)$_4$N][$\mathrm{BF_4}$], depending on the reaction conditions [313].

The intensely luminescent [{Au($\mathrm{PPh_3}$)}$_4$(μ-L)][$\mathrm{ClO_4}$]$_2$ and [{Au($\mathrm{PPh_3}$)}$_2$(μ-L)] complexes with L = 2,2′-bibenzimidazolate as bridging ligand have been synthesized and their crystal structure determined revealing short intramolecular Au–Au separations in the former [314].

The mono- and tetra-nuclear 7-azaindolate complexes [Au($\mathrm{PPh_3}$)(L)] and [{Au($\mathrm{PPh_3}$)(μ-L)Cu(μ-L)}$_2$], have been prepared and their crystal structures determined. Short intramolecular Au···Cu and Cu···Cu separations are observed in the latter. In MeCN, both complexes display intense intraligand emission at 510 nm upon UV–Vis irradiation at room temperature while in the solid state only the tetramer is emissive [315]. Reaction of Au($\mathrm{PPh_3}$)Cl with 7-methoxy-1-methyl-9*H*-pyrido[3,4-b]indole or 4,9-dihydro-7-methoxy-1-methyl-3*H*-pyrido[3,4-b]indole afforded Au($\mathrm{PPh_3}$)(L) with the deprotonated indoles, while addition of [Au($\mathrm{PPh_3}$)(MeOH)][$\mathrm{BF_4}$] led to formation of [{Au($\mathrm{PPh_3}$)}$_2$(μ-L)][$\mathrm{BF_4}$] [316]. (1-Benzyl-2-imidazolyl)diphenylphosphine formed [Au(L)$_2$]$^+$ in which both *N* and *P* coordinate to the gold atom [309]. Succinimide reacting with AuCl($\mathrm{PPh_3}$) in MeOH in the presence of NaOH is readily deprotonated and monomeric Au($\mathrm{L^-}$)($\mathrm{PPh_3}$) is formed which is reactive towards $\mathrm{Pr(NO_3)_3 \cdot H_2O}$ in MeOH yielding [Pr{AuL($\mathrm{PPh_3}$)$_2$}($\mathrm{NO_3}$)$_3$]$_n$ the crystal structure of which reveals the existence of AuPN environment [317]. 1,3-dihydro-7-nitro-5-phenyl-2*H*-1,4-benzodiazepin-2-one gives [Au(LH)($\mathrm{PPh_3}$)][$\mathrm{PF_6}$] and in alkaline media Au(L)($\mathrm{PPh_3}$), which upon reaction with [Au($\mathrm{PPh_3}$)(MeOH)][$\mathrm{BF_4}$] forms [{Au($\mathrm{PPh_3}$)}$_2$(μ-L)][$\mathrm{BF_4}$] [318]. Reaction of 1-methylthymine and AuCl($\mathrm{PPh_3}$) in $\mathrm{H_2O}$/MeOH at pH = 11 gives 1-methyl-thyminato-N3-triphenylphosphino gold with a linear AuNP environment [319]. Phthalimide, diphenylhydantoin, saccharin, riboflavin and (tetrahydrosuccinimido) acenaphthenone form Au(L)($\mathrm{PR_3}$) complexes where R = Et, *i*-Pr, Me, Ph, OMe, OPh as well as with PEt_2Ph and $PEtPh_2$. The compounds are studied by ^1H, ^{15}N and ^{31}P NMR and the crystal structure of Au(phthalimide)(PEt_3) confirms the linear AuNP environment present. Reaction with *N*-acetylcysteine proceeds with replacement of the ligands and formation of Au(cysteine)(PR_3) [320].

The 1:1 reaction of $[Au(acac)(PPh_3)]$ with ammonium salts [HL]Y ($Y=CF_3SO_3$, L = 2-nitroaniline, 4-methoxyaniline, $NHPh_2$ or $NHEt_2$; $Y=ClO_4$, $L=NMe_3$) in ether gave complexes $[Au(PPh_3)(L)]X$. The crystal structure of $[Au(PPh_3)(NMe_3)][ClO_4]$ was determined. The gold atom is linearly coordinated with no intermolecular Au···Au contacts [321]. The ligand 1-diphenylarsino-2-diphenylphosphinoethane forms complexes $[(AuCl)_2(\mu\text{-}L)]\cdot 1/2L$ and $[Au(L)_2]Cl\cdot 2H_2O$ in aqueous acetone. Both complexes are kinetically active as ^{31}P NMR studies reveal [322].

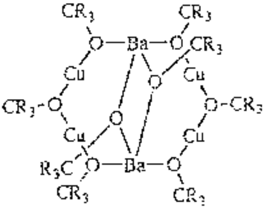
Triorganophosphinegold(I) complexes of the anions derived from pyridine-2-thione and pyrimidine-2-thione, $[Au(PR_3)(L)]$ (R = Et, Ph or Cy), have been prepared and characterized by spectroscopic (IR, ^1H, ^{13}C NMR and FAB MS) methods and for the PPh_3 compounds by X-ray crystallographic techniques. The mononuclear compounds feature linear gold atom geometries defined by *P* and *S* atoms for $[Au(PPh_3)(pyt)]$, $[Au(PPh_3)(pymt)]$ [323].

Reaction of $[(AuNO_3)_2(\mu\text{-dppe})]$ and $[Au(NO_3)(PPh_3)]$ with primary amines in CH_2Cl_2/H_2O yields $[\{Au(NH_2R)\}_2(\mu\text{-dppe})][NO_3]_2$ or $[Au(NH_2R)(PPh_3)][NO_3]$ in which increasing amine bulk drives the ^{31}P signal of the biphosphine to lower field [324]. Tris(triphenylphosphineaurio)oxonium tetrafluoroborate, isostructural to the hydronium ion, was found to be a powerful aurating reagent for primary amines RNH_2 (R = Me, Et, Pr^n, Pr^i, Bu^t, Cy, Bz or Ph). The products have been characterized by analytical and spectroscopic data including ^{197}Au Mössbauer spectroscopy for $[(AuPPh_3)_3NBu^t][BF_4]$ and single-crystal X-ray analysis of this and the compound with R = Cy. The Au···Au contacts near 3.0 Å indicating attractive forces between the gold atoms [325]. Analogous reactions have been reported for $R=p\text{-}FC_6H_4$, $p\text{-}BrC_6H_4$, and $p\text{-}NO_2C_6H_4$). With hydrazines and Ph_2NNH_2, $[\{Au(PPh_3)\}_3NNR_2][BF_4]$ and $[H\{Au(PPh_3)\}_2NNR_2][BF_4]$ were formed respectively (R = Me, Ph). The $[\{Au(PPh_3)\}_3NNMe_2][BF_4]$ compound decomposed in solution to form $[\{Au(PPh_3)\}_6][BF_4]_2$ [326]. Analogous reactions occur also with RNCO [327]. Aminoquinoline yielded $[(\mu_3\text{-}L)(AuPPh_3)_3][BF_4]$, while further addition of $[AuPPh_3][BF_4]$ led to the $[(L)(AuPPh_3)_4][BF_4]_2$ compound where the fourth gold atom was found to bind to the pyridine nitrogen atom of quinoline [328]. Several *para*-substituted anilines (H_2NAr) also reacted with $[\{(PPh_3)Au\}_3O][BF_4]$ in THF to give $[\{(PPh_3)Au\}_3NAr][BF_4]$ which were also obtained by reaction of the oxonium aurate with RNCO [329]. Diamines $Y(NH_2)_2$ (Y = ethyl, *o*-, *m*- and *p*-phenyl) formed bis(imido) species $[(AuPPh_3)_3N\text{-}Y\text{-}N(AuPph_3)_3][BF_4]_2$ characterized by IR, MS, ^1H and ^{31}P NMR studies [330]. $[O(AuPMe_3)_3][BF_4]$ is dimeric with a tetrahedral Au skeleton and Au···Au distances of 3.25 Å [331]. Its reaction with $HN(SiMe_3)_2$ yields $[(AuPMe_3)_3NSiMe_3][BF_4]$ which reacts further with the oxonium gold ion or $AuCl(PMe_3)$ to give $[(AuPMe_3)_5N][BF_4]_2\cdot 2AuCl(PMe_3)$, the first known example of such a cation stabilized probably through Au···Au interactions as the bent environments around the gold atoms reveal [332].

2.2. Complexes with group 16 donors

2.2.1. Oxygen donors

2.2.1.1. Copper complexes. Digonal CuO_2 coordination is observed in the mixed metal alkoxide clusters $Li_4Cu_4(OCMe_3)_8$, $Na_4Cu_4(OCEt_3)_8$ and $Ba_2Cu_4(OCEt_3)_8$. In the first two **XIV**, M_2O_2 puckered rings are bridged with Cu atoms while in the



XIV

latter, **XV** , $Ba_2(OR)_2$ rings are bridged by $Cu_2(OR)_3$ rings and parallel $BaCu_2O_3$ planes are formed [333].

NaOAr react with CuCl in THF to afford the rapidly decomposing $Cu_2(\mu\text{-}OAr)_2(THF)_4$, but in the presence of CO $Cu_2(\mu\text{-}OAr)_2(CO)_2(THF)_2$ is obtained which readily substitutes CO and THF with PPh_3, RCN, while with dppe $[Cu_2(OAr)_2(dppe)_2(\mu\text{-}dppe)]$ is obtained and with di-imines the ionic compound $[Cu(diimine)_2][Cu(OAr)_2]$ is the result [334].

Copper benzoate reacted with RNC to afford $Cu_2(\mu\text{-}PhCO_2)_2(RNC)_2$ in the form of loosely bound dimers in EtOH solvated $[Cu_2(\mu\text{-}PhCO_2)(RNC)_3]$ in THF and with benzo[c]cinnoline and phthalazine $Cu_2(\mu\text{-}PhCO_2)(\mu\text{-}L)]_n$ where planar eight-membered rings involving copper and benzoate are realized [335].

Benzoquinone reacted with $[Cu(MeCN)_4]^+$ in CH_2Cl_2 in the presence of deprotonated $(Cp)Co(OPR_3)_3$ to afford $\{Cu(benzoquinone)(L^-)\}$ which readily dimerizes to $[\{Cu(L)\}_2(\mu\text{-}benzoquinone)]$ and also readily exchanges benzoquinone with CO. The cobalt complex acts as a tripodal ligand with three distinctly different Cu–O bonds ranging from 1.966(2) to 2.184(2) Å [336].

2.2.1.2. Silver and gold complexes. Discrete silver-nitrate anions were realized in *trans*-$[Rh(py)_4Cl_2][Ag(ONO_2)_2]$ [337]. The thermal cyclization of silver amidotriphosphate has been studied in dry and humid air and compared with those of the corresponding ammonium and barium salts [338].

$Ag(hfac)(SEt_2)$ though monomeic in the solid state, upon reaction with Pd(hfac-*C*)(hfac-*O,O*)(SEt_2) in toluene yields $[Ag(hfac)]_4(SEt_2)$, which forms one-dimensional chains with bridging SEt_2 and μ-η-*O*, η^2-*O,O'* and μ_4- conformations for the hexafluoroacetylacetonate anion [339].

The low-temperature (163 K) structure of the silver(I) complex with antimony(III) tartarate has been determined by X-ray methods. The repeating unit is described in terms of an unusual complex tetramer with formula $[Ag_4Sb_4(L)_4(H_2O)_4]$. Two of the four silvers are four-, one is five-, while the other six-coordinate to oxygen atoms [340]. The antimony(III)–silver(I) citrate, $[Sb_2Ag_2(L)_4]$, has been prepared. It has two dimers, each antimony center is in turn linked through one of the carboxylate groups to two silver(I) ions in an asymmetric bis(carboxylato-*O,O'*) bridge. Hydroxyl groups complete the angular three-coordination about each silver, giving a centrosymmetric cyclic dimer structure [341].

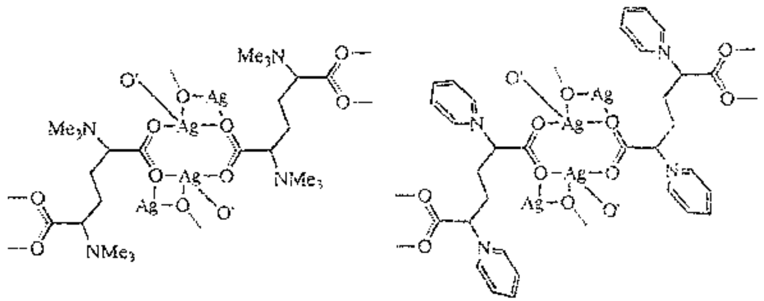
Reaction of $[Ag(NH_3)_2][NO_3]$ with (2-carbamoxylphenoxy)acetic acid in aqueous ethanol afforded dimeric $Ag_2(\mu\text{-}L)_2$, extended to form polymeric chains through Ag–O interactions with amidic oxygen atoms from neighboring units [342]. Analogous was the structure obtained for gycollic acid, with Ag···Ag interactions of 2.8810(9) Å and local AgO_4 chromophore [343]. Polymeric compound was also obtained from the reaction of $AgNO_3$ with 3-carboxylato-1-pyridinoacetate in hot water where both monodentate and bridging carboxylates are present, the basic unit being described as $[Ag_2(L\text{-}O,O')(L\text{-}\mu\text{-}1,1\text{-}O)]$ [344]. A quite stable complex of silver with 2-(8-hydroxyquinolin-5-ylazo)benzoate prepared in aqueous medium at pH 5–6 has been used as a standard for silver determination in geological samples [345]. Reflux of 2,6-pyridinedicarboxylic acid (H_2L) with half equivalents of $AgNO_3$ in MeONa/MeOH afforded $Ag(HL)(H_2L)\cdot H_2O$ with continuous chains of silver atoms each bound to two oxygen atoms of one carboxylate and one of another and weakly interacting with one of a neighboring group [346]. Excess of trimethylaminoacetate monohydrate on $AgClO_4$ in water formed one-dimensional cationic chains of $[Ag_4(L)_6]^{4+}$ units with tetracoordinated silver bonded to two different carboxylates [347].

Several aminopolycarboxylates form silver complexes with 2:1, 1:1 and 1:2 stoichiometries and varying degree of ionization and overall charge, depending on the number of their carboxylate groups. The complex formation was studied potentiometrically at 25°C [348]. Diffusion of silver ions into silica gel adsorbed succinate at pH = 5.6 formed $\{Ag_2(L)\}_\infty$ with planar Ag_4 cores bridged by succinate ions [349].

Deprotonation of 2-pyrrolidinone occurred upon reaction with $AgNO_3$ in the presence of $Hg(MeCO_2)_2$ to afford dimeric $[HgAg(L)_2(NO_3)]_2$ with a central Ag_2O_2 folded ring. Local AgO_3 environments and unusually distorted coordination geometries were observed due to interdimer interactions [350]. Compounds of analogous stoicheiometries were formed by 2-oxazolidone as polymeric sheets of Ag_2O_2 rings linked by twisted HgL_2 bridges [351].

Digonal silver coordination occurs in (β-D-glucurono-γ-lactone)silver nitrate where coordinate nitrate is present as well as in the dimeric lactonate. Interestingly, the use of CO_3^{2-} or $MeCO_2^-$ proceeds to D-glucuronic acid formation [352].

Two flexible double betaines, namely *meso*-2,5-bis(trimethylammonio)adipate and *meso*-2,5-bis(pyridinio)adipate form Polymeric disilver perchlorates and nitrates, the dimeric units extending to step polymers, **XVI**, through silver–oxygen contact to an adjacent dimer. Water molecules are incorporated in the structure of the pyridinio adipates perchlorate salt [353]. Two polymeric silver(I) complexes of betaine and pyridine betaine have been prepared and characterized by X-ray crystallography,



(a) O' from NO_3^- (b) O' from H_2O

XVI

Both complexes are composed of Ag_2(carboxylato-*O,O'*)$_2$ dimers polymerized through coordination to a carboxylate oxygen from an adjacent dimer. In the latter, water coordination is also present and furthermore possesses the shortest [2.814(2) Å] Ag–Ag contact among dinuclear silver(I) carboxylates [354]. Four polymeric silver(I) complexes of the betaine derivatives pyridiniopropionate and trimethylammoniopropionate have been prepared and characterized by X-ray crystallography. The complexes contain bis(carboxylate)-bridged Ag dimers extended into stair-like chains via the coordination of each metal center by a carboxylato oxygen atom from an adjacent unit [355]. Pyridine betaine yields one-dimensional polymeric chains of $[Ag(L)(NO_3)]_n$ with AgO_5 coordination spheres resulting from one nitrate and two carboxylic groups [356] while triethyl betaine gives $[Ag_2(\mu\text{-}L)(ONO_2)_2]$ and $\{[Ag_2(L)_2](ClO_4)_2\}_n$ a stair-like cationic chain with Ag–O interdimer bonds and Ag···Ag bonds of 2.856(2) Å [357]. The AgO_4 environment is present in $\{(NH_4)[Ag(picrate)(H_2O)]\}_n$ with two different types of carboxylato bridged dimers [358], while AgO_3 is reported for $[Ag_2L_2(H_2O)_2]\cdot 2H_2O$ where L = *N*-acetylanthralinate [359] and AgO_2 in $Ag(LH)(NO_3)$ and $Ag(L^-)$, L = D-glucuronic acid, which are polymeric and dimeric respectively on the basis of their IR and ^1H NMR spectral data [360].

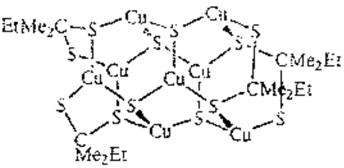
An interesting reaction was that of *cis*-diammine(methyluracilato) (methylcytosine)platinum nitrate with 2 equivalents of $AgNO_3$ in H_2O, which results in the formation of (μ-1-methyluracilato-N^4,O^4)(μ-1-methylcytosine-N^3,O^2)-*cis*-diammineplatinum silver dinitrate silver nitrate · 2 · $5H_2O$ where one silver is O-bonded to the two ligands one water molecule and a nitrate ion, the last two bridging to the next silver atom which may be described as $Ag(OH_2)(OH_2)'(ONO_2)(ONO_2)'$ [361]. The cyclic peptide cyclosarcosylsarcosine formed a 2:1 adduct with Ag^+ where coulombic interactions between silver and nitrate and silver loose coordination to C=O gives rise to an octahedral AgO_6 environment [362]. The dissociation constants of silver complexes with several oxygen-donor cryptands by acid scavenging and their formation constants in DMSO are reported and the equilibria involved discussed [363]. The antiarthritic activity of the $[Au(diferuloylmethane)_2]Cl$ and related compounds has been evaluated [364].

2.2.2. *Sulfur donors*

2.2.2.1. Copper complexes. Sulfur is one of the most suitable donor atoms for complexation to low valent coinage metals. Metal thiolates and thiolate sulfide complexes are numerous and a detailed review has appeared on the subject [365]. Copper ions formed by laser ablation on a FT ion cyclotron forms polysulfanes with stoicheiometries ranging from CuS_4^- to CuS_{12}^- [366].

Reduction of $Cu(NO_3)_2$ in water by *N*,*N*′-dimethylthiurea produces $[Cu(L)_2][NO_3]$ where copper is in a tetrahedral CuS_4 environment, the tetrahedra sharing opposite edges and the chains formed in this way being bridged by nitrate anions [367]. An $[Cu_{10}(L)_9]^-$ aggregate was obtained from the reaction of *N*-(diethoxythiophosphoryl)-*N*′-phenylthiurea with $Cu(ClO_4)_2$ in ethanol at −60°C and its structure determined [368].

Heterocyclic thiones reduce cupric salts and produces either mixed valence or monovalent copper complexes. 1-Methyl-imidazoline-2-thione reacted in $MeCMe_2CO$ with $Cu(BF_4)_2$ to form the dinuclear complex $[Cu_2(L)_6][BF_4]_2$ with two bridging thione ligands and a CuS_4 local environment [369]. Imidazoline-2-thione also formed a $[Cu_2(L)_6][ClO_4]_2$ compound in refluxing MeOH/MeCN [370]. An analogous coordination environment is present in the cluster $[Cu_4(benzimidazoline\text{-}2\text{-}thione)_{10}][ClO_4]_4 \cdot 14H_2O$ which was obtained in aqueous ethanol [371]. A CuS_3 environment was observed in $[Cu_4(3.4.5.6\text{-}tetrahydropyrimidine\text{-}2\text{-}thione)_4][ClO_4]_4$ [372]. Mixed ligand complexes of the formula $Cu_8(thiolate)_4(trithiocarbonate)_4$, **XVII**, have been obtained and their structures solved [373]. The bulky 2-trimethylsilylbenzenethiolate reacts in methanol with Cu(I) to give $[Cu(L)]_{12}$ where half of the coppers are trigonal planar and the other half digonal [374]. Excess 2-triorganosilylpyridine-2-thione in methanol forms trigonal CuL_3^+ [375]. Cuprous thiocyanate refluxed in EtOH/MeCN with 1-methylimidazoline-2-thione produced $[\{Cu_2(SCN)(L)\}_2(\mu\text{-}L)_2]$ with a tetrahedral environment around each copper atom [376]. 4.5-Dimercapto-1.2-dithiole-2-thionate(2-) and its seleno analog forms in MeOH/MeCN the cluster $[NBu^n_4]_2[Cu_4(L)_3]$ which is easily oxidized by ferrocene in Me_2CO/MeCN [377]. *N*-(diethoxy-



XVII Single S's represent thiolate $SCMe_2Et$

thiophosphoryl)-*N*′-phenylthiurea reacting with $Cu(ClO_4)_2$ in ethanol at −60 °C undergoes deprotonation giving the aggregate $[Cu_{10}(L)_9][ClO_4]$ [368].

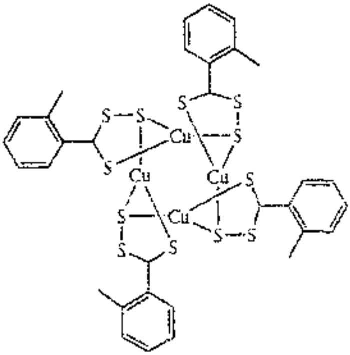
N,*N*-dimethylthioacetamide adsorbed on Cu surface was studied by surface-enhanced Raman spectroscopy and the findings correlated to those of previously reported for Cu(I)-acetamide complexes [378]. Mixed valence $[Cu^{I}Cu^{II}_3(L)_3][ClO_4]_2$ with triangular Cu(I) is formed by the reduction of $[Cu(en)_2][ClO_4]_2$ in $MeOH/H_2O$ with *N*,*N*′-1,2-ethanediylbis(L-cysteine)dimethylester [379].

Several thiolates were studied by FT ion cyclotron resonance MS following gas phase laser ablation formation. The studies reveal that CuL^+ and CuL_2^+ species are present With protonated thiols coordinated to copper [380]. Several Cu_nS_m clusters have been isolated from the reaction of cuprous salts with thiolates in the presence of appropriate bases. $[Cu_4(SPh)_6]^{2-}$ appears with trigonal planar copper environments' mean distances being 2.281 and 2.744 Å for Cu–S and Cu–Cu, respectively. For $[Cu_4(SPh)_6]^{2-}$, one digonal and four trigonal copper atoms are present With $Cu–S_{trig}$ and $Cu–S_{dig}$ mean distances of 2.269 and 2.173 Å, respectively, while a product with the stoicheiometry $[Cu_5(SPh)_7]^{2-}$ Was also isolated from the in-situ reduction of $Cu(NO_3)_2$ [381]. Electrochemical oxidation of metallic copper in dithiole solutions (1,2-dimercaptoehtane, 1,2-dimercaptopropane, 1,4-dimercaptobutane) in acetonitrile forms $[Cu_2(S_2R)]_n$ [382]. In methanol, dimercaptoethane and dimercaptopropane, bis anions give adamantane-like Cu_4S_6 clusters $[Cu_4(L)_3]^{2-}$ as well as solvated ones [383]. Clusters are interconnected by hydrogen bonding to solvent molecules. $[Cu_8(S_2C=CR_2)_6]^{4-}$ clusters are reversibly protonated in acetonitrile to form $[Cu_8(L)_{6-n}(LH)_n]^{(4-n)-}$ (R = $COOEt_2$, $n = 1, 2, 3$, $COOBu^t_2$, $n = 1, 2$) Stoicheiometric reaction with H^+ leads to formation of $[Cu_{10}(LH)_6(L)_2]$ with almost trigonal planar copper centers [384]. A tetrahedral Cu_4 core was observed in $[Cu\{\mu_3\text{-}SC(=NMe)(OEt)\}]_4$ and octahedral Cu_6 in $[Cu\{\mu_3\text{-}SC(=NC_3H_5)(OMe)\}]_6$ the rigididy of which is confirmed by ^1H NMR in solution [385]. Crystallization of the interesting $[Cu(SCF_3)]_n$ from acetonitrile produced $[Cu(SCF_3)]_{10}\cdot 8MeCN$ where both digonal and trigonal copper centers are present [386].

Bulky 2-alkyl(dimethylamino)-3-alkyl arenethiols react with CuO in ethanol to produce trimeric arenethiolates [387]. The triboluminescent crystals of $[CuS(2\text{-}CHMeNMe_2)_2]_3$. THF reveal the presence of a Cu_3S_3 ring with short Cu···Cu distance of 2.828(1) Å. Substitutents R in the arene affect the conformer present in solution as studied by ^1H and ^{13}C NMR. Analogous products were derived from 5-trimethylsilylarenethioles and CuCl where Cu_nS_n cores are present [388]. Luminescence of some such arethiolates is reported and a literature survey of absorption and emission maxima is also included [389]. The observed lowering of the MLCT excitation energy is attributed to the three electron two center S–S interaction. Reflux of Cu_2O in ethanol with two equivalents of 2-[(R)-1-(dimethylamino) ethyl]thiophenolate leads to formation of trimeric $[Cu(L^-)]_3$ studied by various spectroscopic techniques. Low-temperature NMR studies reveal the existence of two species in equilibrium while a C_3 symmetric unit is observed by X-ray diffraction [390]. Several Cu(I)-thiolate model compounds containing different proportions of digonal and trigonal copper sites were studied, using Cu K-edge X-ray absorption spectroscopy. The edge spectra show little variation between the models, although systematic trends in the average Cu–S bond length derived from EXAFS can be used to estimate the fraction of digonal versus trigonal copper sites [391]. Photoelectron spectroscopy of SMe_2, and MeS^- bound to Cu(I) sites at single crystal surfaces has been used as models of the blue copper protein bonding and correlated to SCF–Xa calculations [71].

Reaction of *fac*(S)-[M(2-aminoethane thiolate)$_3$] with $Cu(NO_3)_2$ in water (M = Rh, Ir) afforded clusters with a $Cu_4M_4^{III}$ core where CuS_3 coordination is observed [392]. Sulfur addition to the coordinated dithiolene ligands in the $[Cu_8(L)_6]^{4-}$ cluster (L = 1,1-dicarbo-*tert*-butoxyethylene-2,2-thioperthiolate) results in the formation of the $[\{Cu_4(SL)_3\}_n]^{m-}$ clusters whose molecularity depends on the nature of the counterions (Bu_4N, $n=2$, $m=4$; K, $n=1$, $m=2$). The crystal structure of $K(Ph_4P)[Cu_4(SL)_3]\cdot 3Me_2CO$ has been determined revealing a copper tetrahedron with a single copper coordinated to the thio groups and the other three bridged by the perthio groups of the ligands [393]. $[Cu(MeCN)_4][BF_4]$ reacted with $Pt(dtc)_2$ in CH_2Cl_2 to give $[Pt_3(dtc)_6Cu_2][BF_4]_2$. The crystal structure of the diisopropyldithiocarbamate has been determined [394]. Hexameric cluster compounds have been obtained with di-*n*-propyldithiocarbamate and all the metal ions of group 11 [395]. Dithiocarbamate and dithiophosphate complexes of divalent copper are reduced photochemically by irradiation at their MLCT bands. Only partial reconversion is accomplished by keeping the monovalent copper complexes in the dark [396]. 2-Mercapto-2-methylbutane produces the corresponding copper thiolate which reacts with CS_2 and gives the mixed ligand cluster Cu_8(thiolate)$_4$(trithiocarbonate)$_4$ which further reacts with PPh_3 and $PPhCy_2$ to give the 1:2 adducts [397]. Reaction of 2,4,6-trimethyltrithioperoxybenzoate or *o*-methyltrithioperoxybenzoate with $Cu(NO_3)_2$ in DMF results in the formation of Cu_4L_4 clusters, the structures of which have been determined [398]. An interesting insertion reaction occurs when elemental sulfur is added to Cu(*o*-tolyldithiocarboxylate) in toluene resulting in formation of the tetrameric Cu(*o*-tolyperthiocarboxylate), **XVIII** , where each Cu is bonded to four S_3 ligands [399]. CuS_3 chromophores are observed in the products of [Cu(perthiocarboxylate)]$_4$ with triphenylphosphine in a 1:2 or 1:4 ratio in pyridine and toluene, respectively, which are formulated as {{Cu(perthiocarboxylate)}$_2$-{Cu(thiocarboxylate}$_2$}.py and [Cu(thiocarboxylate)]$_4$, **XIX** [400].

Several $R_2S(CH_2)_nSR_2$ ligands (R = Me, Ph; $n=1$, 2, 3) have formed complexes of the formula $[Cu(L)_2][PF_6]$ which have been studied by IR, ^1H and ^{63}Cu NMR [401]. MoS_4^- reacts with three equivalents of CuCl and dithiocarbamate in DMF to give $[Mo_2Cu_5S_8(dtc)_3]^{2-}$ with trigonal and both slightly and highly distorted tetrahedral copper environments [402]. ^{51}V NMR studies determine the ligand exchange reactions occurring in $[(VS_4)Cu_4(\text{dithiocarbamate})_n(\text{thiophenolate})_{4-n}]^{3-}$ in DMF. The structures of the products with $n=0$, 1 and 2 are also reported [403]. CuS_4 tetrahedra were observed by X-ray powder diffraction in the polymeric product of the reaction of $(NH_4)_2WS_4$ with $[Cu(MeCN)_4](BF_4)$ [404]. $[MoO_2S_2]^{2-}$ reacts with CuCl in the presence of sodium dimethyldithiocarbamate in DMF to form $[Mo_2Cu_5S_6O_2(dtc)_3]^{2-}$ which is composed of two units, $MoOS_3Cu_2$ and $MoOS_3Cu_3$, linked by two Cu–S bonds and a bridging dithiocarbamate anion. Analogous clusters are obtained with tungsten and diethyldithiocarbamate [405].



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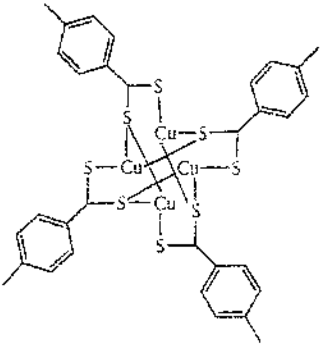


XIX

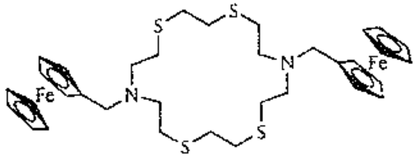
Reaction of CuCl with MS_4^{2-} in the presence of dithiocarbamates in DMF resulted in the formation of polynuclear species of the formula $[Cu_3(dtc)_3\{MS_4\}]$ where M = Mo, W. The local copper environment is a CuS_4 one with two sulfur atoms originating from the dithiocarbamate ion [406]. Defective cubanes of the formula WCu_2S_4 and WCu_3S_4 bridged by dithiocarbamate ions and joined by two weak Cu–S bonds are observed in $[Et_4N][W_2Cu_5S_8(dMe_2tc)_3]$ [407]. The structure elucidation of several $[MoS_4M(L)]^{2-}$ complexes (M = Cu, Ag) has been assisted by ^{33}S NMR studies [408].

Copper(I) is extracted into $CHCl_3$ by *ortho-*, *meta-* and *para-* cyclophane thiacrown ethers bearing 4-(4-nitrophenylazo)phenol as chromogenic, especially by the *ortho-*

analog [409]. Reduction of $CuCl_2$ was achieved by 2,5,8-trithia[9]-*o*-benzenophane in THF to give $CuCl_2L$, which in refluxing MeOH gives the corresponding Cu(I) compound [410].

[Cu([9]aneS_3)$_2$][PF_6] reveals distorted tetrahedral CuS_4 coordination sphere with the participation of a monodentate and a tridentate ligand. Its electron transfer kinetic parameters were studied in aqueous media on glassy carbon electrode and proved to follow an electrochemical-chemical-electrochemical square mechanism [411]. The kinetics of electron transfer reactions involving [Cu([14]aneS_4)]$^+$ reacting with a series of selected counter reagents have been measured in aqueous solution at 25 °C. Several oxidants and reductants were employed to provide a variety of rate constants and reaction potentials [412]. Macrocyclic polythia-ligands such as [24]aneS_8 and [28]aneS_8 form mononuclear cationic complexes [Cu_2(L)]Y (Y = ClO_4, PF_6, BF_4) with CuS_4 chromophores while [18]aneS_6 forms the mixed ligand [Cu_2(L)(MeCN)$_2$]$^+$ with an CuS_3N environment [413,414] while 1,3,6,9,11,14-hexathiacyclohexadecane forms [Cu(L)][ClO_4] [415]. For several polythiacrown ethers the $Cu^{+/2+}$ electrocouple in MeOH/H_2O is used for stability constant measurements [416]. The structure of bis(2,5,8-trithia[9]-(2,5)thiophenophane-S^2,S^3)copper(I) cation has been reported and cyclic voltametric studies conducted [417].

The structure of the monomeric copper hexafluorophosphate complex of the new macrocycle 7,16-bis(ferrocenylmethyl)-1,4,10,13-tetrathia-7,16-diazadicycloo ctadecaene, **XX**, has been studied [418], while tetrakis(ethylthio)tetrathiafulvalene forms polymeric chains of [Cu(L)][ClO_4] [419].



XX

(Cp)$_2$Ti{(SCH_2CH_2SCH_2)$_2$CH_2} reacts with [Cu(MeCN)$_4$][PF_6] in THF to afford the heterobimetallic compound [(Cp)$_2$Ti(μ-{SCH_2CH_2SCH_2}$_2$CH_2)Cu][PF_6] which undergoes an irreversible reduction at −0.90 V in contrast to what has been observed for related macrocyclic Ti–Cu species [420]. The d→s and d→p emissive metal centerd exited states of group 11 metal metallothioneins have been prosposed as the responsible for the emissions obaserved in the region 530-600 nm at 77 K [421]. The copper metallothionein excibited luminescence at 600 nm at r.t., which was ascribed to cluster formation and the consequent presence of Cu–S chromophore in the compound [422].

2.2.2.2. Silver complexes. X-ray scattering revealed the formation of Ag(SCN)$_4$ units in AgSCN/KSCN melts [423]. The formation of Ag(THT)$_2^+$ upon dissolution of Ag^+ in THT is confirmed by large angle X-ray scattering [424]. Reaction of

$AgNO_3$ with $(NBu_4)_2S_6$ in acetonitrile in the presence of NEt_4Cl yields $[(NMe_4)\{Ag(S_5)\}]_\infty$ with parallel anionic chains separated by the cations [425].

Bisethyl, (2-chloroethyl)ethyl and bis(2-chloroethyl) sulfide follow this order of decreasing stability constant in their Ag(I) complexes as studies in aceton, methanol, DMF and DMSO reveal. A probable explanation is the formation of sulfonium compounds by the chlorinated sulfides [426]. Reduction of bis[di(2-ethyl)hexyloxy)thiophosphoryl)disulfide occurs during its application for silver cation extraction in hexane since after re-extraction, SH signals appear in the ^1H NMR of the ligand [427].

The *S*-coordination of thiurea is confirmed by ^1H NMR and solution and solid-state IR and Raman studies of $Ag(tu)_2(NO_3)$ and comparison with $Ag(SMe_2)(N0_3)$ and $[Ag(SMe_2)_2](NO_3)$ [428]. The reaction of $AgClO_4$ with disulfides in pyridine or DMSO depends on many factors, as butanedisulfide does not form complexes in either solvent, phenyldisulfide only reacts in pyridine and both $Ag(THT)^+$ and $Ag(THT)_2^+$ are shown to exist in DMSO [429]. Potentiometric studies of the silver complexes formed with thiurea, thiohydantoin, cystein, thiobarbituric acid in perchloric acid have been carried out [430]. *N,N*-dimethylthioacetamide adsorbed on Ag surface was studied by surface-enhanced Raman spectroscopy, the shifts observed being comparable with those of previously described complexes [378].

The silver thiolates $AgSC_nH_{2n+1}$ ($n=4$, 6, 8, 10, 12, 16 and 18), consisting of $[Ag(SR)]_\infty$ layers with the R groups lying on both sides of a "central slab of Ag and S atoms", are found to behave as thermotropic liquid crystals. X-ray diffraction studies for the compound with $n=6$ reveal a packing similar to that found in the solid while for $n=18$, the micellar phase consists of $[(Ag(SR)]_8$ cyclic substructures [431]. Several $AgS(CH_2)_nCH_3$ thiolates synthesized are extremely insoluble but give powder X-ray spectra which indicate presence of layers of AgSR along a line of Ag atoms [432]. Complex formation between protonated 4-mercapto-1-methylpiperidine and silver has been studied by titration in aqueous methanol in a variety of pH environments [433]. The complexation of 3-(dimethylamino)propane-1-thiol and 3-aminopropane-1-thiol to silver has been studied in a wide range of pH values in aqueous methanol and the presence of species $[Ag_n(L)_m]^{n+}$ with varying n/m ratios reported. It was shown that in weakly acidic media the nuclearity of the species depends on the thiol used [434]. The reaction of 3-dimethylphenylsilyl-pyridine-2-thiol with $AgNO_3$ affords $[Ag_6(L^-)_6]$ and $[Ag_8(L^-)_6][Ag(NO_3)_2]_2$ when the thiol or the $AgNO_3$ is in excess, respectively. Both structures are reported [435]. The anion of 1-methyl-piperidine-4-thiol is obtained at $pH \approx 8.5$ and upon coordination $\{[Ag_{13}(L^-)_{16}]^{3-}\}_n$ is obtained where $Ag_{10}S_{16}$ units are linked by silver atoms giving rise to a lot of digonal, trigonal and tetrahedral silver sites [436]. Sterically hindered thioles $HSCH_{3-n}(SiRR'R'')_n$ react with $AgNO_3$ in the presence of triethylamine in C_6H_6/MeCN to produce polymeric thiolates. For $SiMe_2Ph$, trimeric discrete units, for $SiMe_3$ tetrameric rings, for $CH(SiMe_3)_2$ tetramers weakly interacting through Ag…S, forming T-shaped silver environments were observed, while a three-dimensional polymer was obtained for $\{Ag_4(SCH_2(SiMe_3)\}_3(OMe)\}$ [437].

The disodium salt of *o*-xylylene-α,α′-dithiolate with $AgNO_3$ in MeOH afforded $[Ag_4(L^{2-})_3]^{2-}$ the structure of which reveals trigonal silver coordination [438]. The zinc derivative of 5,10,15,20-tetrakis[*o*-(tetrahydro-2-thienoylamino)phenyl] porphyrin was found to bind two silver(I) ions. Fluorescence measurements reveal the presence of intramolecular photoexcited electron transfer in this donor–acceptor system [439].

Metal-free phthalocyanines and metal phthalocyaninates (M = Ni, Cu, Co, Zn) carrying eight alkylthio-groups on peripheral positions reacted with silver(I) salts to form complexes with a phthalocyanine:metal ratio of 1:4. Spectrophotochemical investigation of these reactions revealed that complexation with Ag(I) results in aggregation [440].

In $(NMe_4)_2[Ag(diethyldithiophosphate)_2]_2$ produced in $MeOH/CH_2Cl_2$, two ligands are monodentate and two bridging with one sulfur atom being doubly bridging [441]. Zwitterionic $Ph_3P^+C(CH_3)_2CS_2^-$ forms both $[Ag(L)_2][ClO_4]$ and $[\{Ag(L)\}(ClO_4)]_n$ in CH_2Cl_2, the latter reacting with PPh_3 to yield $[Ag(L)(PPh_3)][ClO_4]$ [442].

The Schiff base derived from 2-amino-4,6-di-*tert*-butyl-phenol and 2-mercapto-5-methylisophthalaldehyde forms $(L^{2-})Pd(PPh_3)$ to which $AgClO_4$ adds forming $[(L)PdAg(PPh_3)]_2(ClO_4)_2$ with a Ag_2S_2 core with an acute Ag–S–Ag angle of 61.9(1)°, silver chelated by one and S-bonded to another ligand and being 2.779(3) Å away from the adjacent silver atom [443].

Cationic AgL^+ and Ag_2^+ triflates and neutral complexes of the formula Ag(L)X (X = Cl, Br, I) are reported for cyclopolythiaethers $[9]aneS_3$, $[12]aneS_3$ and $[18]aneS_6$. Crystal structure determinations reveal trigonal elongation for $Ag([9]aneS_3)_2^+$ and tetrahedral AgS_3O environment in $Ag([12]aneS_3)^+$ [444]. A diversity of activity is obsereved with tetrathia-cyclo-12, -13, -15 and -16anes and the corresponding -14ane with respect to the extraction of Ag^+ in $CHCl_3$ and CH_2ClCH_2Cl in the presence of picrate ions as the isolated compounds are [Ag(L)](picrate) and $[Ag(L)_2]$(picrate), respectively [445]. Several macrocyclic thioether esters and thioesters form $[Ag(L)_2][CF_3SO_3]$ in $MeOH/Me_2CO$ [446]. $AgClO_4$ reacts with 2,5,8,10- tetrathia[12](2,5)-thiophenophane in $MeCN/CH_2Cl_2$ to yield $[Ag_2(L)_2][ClO_4]_2$, a local AgS_5 environment to which the thiopheno-sulfur atom is not participating [447]. Axially distorted octahedral silver is present in $[Ag([18]aneS_6)][PF_6]$ produced in $H_2O/MeOH$ 1:1 as deduced by its crystal structure determination [448]. Nitrate and acetate polymeric silver(I) complexes with 1,5,9,13-tetrathiacyclohexadecane-3,11-diol have been prepared in which the silver atoms are tetrahedrally bound to four thioether groups from four ligand units [449]. Reaction of $AgNO_3$ with one molar equivalent of 1,4,10,13-tetrathia-7,16-diazacyclooctadecane or its 7,16-dimethyl analog in refluxing aqueous methanol affords complex cations $[Ag(L)]^+$. The metal ions are bound to highly distorted octahedral environments [450]. Interconversion between the four coordinated and the two remote sulfur atoms of 1,3,6,9,11,14-hexathiacyclohexadecane silver perchlorate occurs in solution as ^1H NMR studies reveal [451]. Reaction of $AgNO_3$ with 1,4,7,10,13-pentathiacyclopentadecane in refluxing aqueous methanol afforded complexes $[Ag_n(L)_n][PF_6]_n$, $[Ag_2(L)_2][BPh_4]_2$, and $[Ag(L)][BPh_4]$. The two independent infinite chains of cations in the former are antiparallel with distorted octahedral Ag(I) with one thioether donor from an adgacent cationic fragment asymmetrically bridging two metal centers. The structure of the $[Ag_2(L)_2]^{2+}$ shows [4+1] and [3+1] thioether donation, respectively, while the monomer contains discrete cations and anions [452]. 2,3,8-Trithia[9]-*o*-benzenophane forms $[Ag(L)_2][Y]$ with distinctively different structures as anion Y varies. Octahedral silver with two facially coordinated ligands is observed for $Y = ClO_4$ and BF_4, while tetrahedral silver coordinated to two sulfur atoms of each ligand is the case for $Y = BPh_4$ and three facially coordinated and one exodentate S from a second ligand form the tetrahedral metal environment in the case of $Y = CF_3SO_3$. However, in solution, ^1H NMR studies reveal fast interconversion of the possible configurations [453].

Silver is extracted in $CHCl_3$ by *ortho*-, *meta*- and *para*-cyclophane thiacrown ethers bearing 4-(4-nitrophenylazo)phenol as chromogenic, especially the *meta*-isomer [409]. Silver selective complexing agents in acidic media have been found among the series of cyclic dithiamonoaza, tetrathiamonoaza and tetrathiadiaza rings with hydrazone moieties attached to the nitrogen heteroatom of the ring [454]. The corresponding *N*-phenyl substituted analogs react similarly forming [Ag(L)(laurate)] complexes in 1,2-dichloroethane [455].

Nine sulfur-containing dipeptides have been shown to react with Ag(I) and Cu(II) forming linear AgS_2 environments in the process. Their formation constants have been determined at 298 K [456]. The elucidation of the solution structure of the silver-substituted yeast copper-metalthionein from *Saccharomyces cerevisiae* was carried out by ^1H ^{109}Ag heteronuclear multiple quantum coherence transfer and the specific connectivities between 10 of the 12 cysteine residues and seven bound Ag ions have been established. Both digonal and trigonal AgS_n environments are verified [457]. $[CpMo(\mu\text{-}S)(NBu^t)\cdot I_2]_2$ reacted with excess $AgCF_3SO_3$ to yield $[CpMo(NBu^t)_S]_5[Ag(MeCN)(CF_3SO_3)]_3[Ag(CF_3SO_3)]_2$ where silver coordinates to two sulfido bridges [458].

2.2.2.3. Gold complexes. $Au(SCN)_2^-$ is the common product of $Au(NH_3)_4^{3+}$ or *trans*-$Au(NH_3)_2X_2^-$ in aqueous acidic media with SCN^- in the halogeno complexes the initial step being SCN^- substitution of the halides. Mixed halogeno-thiocyanato complexes are reduced more rapidly [459].

FT ion cyclotron resonance MS detects the presence of AuL^+ and AuL_2^+ as reaction products of Au^+ with H_2S, RSH and PhSH in the gas phase; the corresponding products of Au^- are mainly RS^- [460]. Extended hydrogen bonding is present in $[Au(L)_2]Cl$ produced by in situ reduction of $HAuCl_4$ with 4-amino-3-methyl-1,2,4-Δ2-triazoline-5-thione [461]. Homoleptic Au(I) complexes with several heterocyclic thioamides are reported with the general formula $[Au(L)_2][ClO_4]$ the structure of the one with pyridine-2-thione been reported [462]. The existence of Au(L)(SCN) and $Au(L)_2(SCN)$ with L = imidazoline-2-thione and 1,3-diazinane-2-thione has been verified by IR and ^{13}C NMR measurements. Recorded are also the latter's complexes of the formula $Au(L)_2X$ with X = Cl, Br [463]. Glutathione, cysteine and several other thiones react with $Au(CN)_2^-$ and ^{13}C NMR and Raman studies confirm that $Au(SR)(CN)^-$ is formed and further disproportionates to $[Au(SR)_2]$ $[Au(CN)_2]$ [464].

The reaction of $[N(PPh_3)_2][Au(acac)_2]$ with HSR gave the complexes

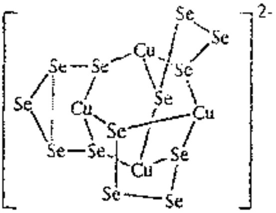
$[N(PPh_3)_2][Au(SR)_2]$ (HSR = benzoxazoline-2-thione, pymtH, pytH, 2,3,4,6-tetra-*O*-acetyl-1-thio-*β*-D-glucopyranose 4,2-thiouracil, 2,3-4,2-thiouracil, 2,3- dihydro-*1H*-benzimidazole-2-thione, 2-thiomalic acid, 2-sulfanylethanol, D-penicillamine); the crystal structure of the benzoxazole-2-thione complex has been solved revealing the usual linear gold coordination [465]. 4,5-dimercapto-1,3-dithiole-2-thionate affords di-, tri- or tetranuclear gold(I) complexes containing μ- or μ_3-bridging ligands [466].

Captopril forms with Au(I) a 1:1 crystalline complex [Au(L)]. The exchange reactions of thiomalate and cyanide with the complex have been studied using ^{13}C NMR spectroscopy and the formation of a very high-molecular-weight polymer was observed [467]. The chloro-ylide gold complex $[AuCl(CH_2PPh_3)]$ reacted in acetone with bis(diphenylthiophosphoryl amine to afford $[Au_2(\mu\text{-}L)_2]$ which cannot be obtained by replacement of dppm from its corresponding complex by addition of excess ligand [267]. Gold thiomalate is the starting point for many reactions and studies. Reaction at pH = 7.2 with imidazoline-2-thione and 1,3,-diazinane-2-thione affords complexes of the formula Au(thiomalate)(L) [468]. The compound is also in exchange with thiuracil in water, a phenomenon enhanced by the increase of the thiuracil molar ratio and the observation is made that in a $Au(thiuracil)_3^+$ environment cysteine is not able to coordinate to gold [469]. Direct reactions of L-methionine and DL-selenothionine to gold thiomalate are reported in D_2O in a range of pH values and discussed in view of the ^{13}C NMR spectra obtained [470]. $[Au(PPh_3)]_2(i\text{-}MNT)$, $K_2(i\text{-}MNT)$ and $(NBu_4^n)Br$ or $(AsPh_4)Cl$ in dichloromethane yield $[Au(^*i\text{-}MNT)]_2^{2-}$ with Au···Au of 2.796(1) Å. The (initial) compound showed two luminescence bands, the final one at somewhat shorter wavelength and readily oxidizes with X_2 in THF to give A(II) adducts [471]. Solid-state phosphorescence, but not in solution, is observed for $[Au(dtc)]_2^{2-}$, $[Au(i\text{-}MNT)]_2^{2-}$ and $[Au(PPh_3)]_2(i\text{-}MNT)$ [252]. Planar anion with Au...Au 2.283(2) Å is present in $[N(n\text{-}Bu)_4]_2[Au_2(i\text{-}MNT)_2]$ which undergoes a readily oxidative addition with $PhICl_2$ or Br_2 in acetonitrile and CH_2CL_2/THF respectively [472].

Reactions of $[Au_2(\mu\text{-}dppm)_2][ClO_4]_2$ with $[AuX_2]^-$ (X = Cl or Br) afforded dinuclear $[Au_2(\mu\text{-}L\text{-}L)_2]$ [L-L = S_2CNR_2, R = Me, CH_2Ph)] or trinuclear $[Au_3(\mu\text{-}L\text{-}L)_3]$ (L-L = S_2COR, R = Me, Et, pytH) complexes [473]. Reduction of $NaAuCl_4$ in water by Na_2SO_3 at 0 C and subsequent addition of dithiocarbamate leads to the formation of Au(Rdtc) where R corresponds to the heterocycles piperidine, 4-phenyl-piperidine, morpholine, thiomorpholine, piperazine, *N*-methyl and *N*-phenyl-piperazine. Reaction of Au(Rdtc) with the corresponding thiuram disulfides leads to their formation of the trivalent gold $Au(Rdtc)_3$ complexes [474]. Four equivalents of $MeCS_2H$ in ether or two equivalents of sodium salt of $PhCS_2^- Ph_2C{=}CS_2^-$ react with $NaAuCl_4$ and $HAuCl_4$, respectively, to give $[Au(S_2CMe)]_4$, $[Au(S_2CPh)]_n$ and in Et_2O/MeOH $Au(S_2CPh)(S_2C{=}CPh_2)$ with stronger bonding towards the ethylenic ligand [475].

2.2.3. Selenium and tellurium donors

Polyselenide copper compounds are rare and the interesting feature in the structure of $[PPh_4]_2[Cu_4(Se_4)_{2.4}(Se_5)_{0.6}]$, **XXI** is the presence of two different polyselenides

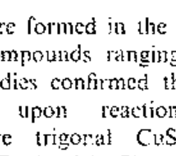


The dashed line represents the alternative bond in the case of $Cu_4(Se_4)_3$ anion

XXI

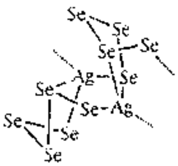
[476]. Several chalcogenides were formed in the gas phase by laser ablation and studied by MS techniques. Compounds ranging from CuE^- to $Cu_{21}E_{11}^-$ were obtained [477]. ^{77}Se NMR studies confirmed the insertion of Se in the Cu–S bond of Cu(CN)(thienyl) upon reaction with WSe_4^{2-} to afford $(WSe_4)(Cu(selenothienl)_2$ where trigonal $CuSe_3$ is present [478]. Several $R_2E(CH_2)_nER_2$ ligands (E = Se, Te, R = Me, Ph, $n = 1, 2, 3$) have formed complexes of the formula $[Cu(L)_2][PF_6]$ which have been studied by IR, ^1H, ^{63}Cu and ^{77}Se NMR [401]. The polytelluride produced by the reaction of Li_2Te with three equivalents of Te in DMF, afforded anionic complexes of the formula $[(Te_4)M(\mu\text{-}Te_4)M(Te_4)]^{4-}$ (M = Cu, Ag) with trigonal metal environments [479]. Reaction of CuCl or $AgNO_3$ with (1,2-dimethoxymethane)$LiSeC(SiMe_3)_3$ in 1,2-dimethoxyethane at -20 °C forms $[M\{SeC(SiMe_3)_3\}]_n$ ($n = 4$, M = Ag) while in benzene, $[Cu\{SeC(SiMe_3)_3\}_2][Li(1,2\text{-dimethoxymethane})_2]$ is obtained. Analogous reactions with $[Cu(PCy_3)_2][BF_4]$ and $AgBr(PCy_3)_2$ afford $[M\{SeC(SiMe_3)_3\}$-(PCy_3), the solid-state structure of the copper compound being dimeric [480].

$NaSe_5$ reaction with $AgNO_3$ in the presence of a suitable anion in DMF afforded

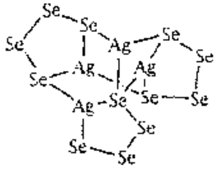


XXII

silver polyselenides in the form of polymeric $[(PPh_4)(AgSe_4)]_n$, **XXII**, with infinite macroanionic chains with $AgSe_4$ rings and trigonal silver or one-dimensional polymeric $AgSe_5$ units with $AgSe_4$ rings and tetrahedral silver atoms $[(NMe_4)(AgSe_5)]_n$ **XXIII** tetrameric $[(NEt_4)(AgSe_4)]_4$, with a planar arrangement of two trigonal and two tetrahedral silver atoms and discrete $(NPr_4)_2[Ag_4(Se_4)_3]$, **XXIV**, with a tetrahedron of trigonal silver atoms [481]. Homoleptic silver(I) complexes $[Ag(RE(CH_2)_nER)_2][BF_4]$ (R = Me, Ph, E = S, Se, $n = 2,3$; E = Te, $n = 3$) have been prepared and characterized by FAB MS, and multinuclear (H, Se, Te and Ag) NMR spectroscopy. The silver atom is tetrahedrally coordinated in either monomeric $[Ag(MeSe(CH_2)_2SeMe)_2]^+$ or polymeric $[Ag_n\{PhSe(CH_2)_3SePh\}_{2n}]^{n+}$ fashion [482].



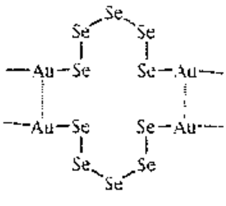
XXIII



XXIV

Telluride $[PPh_4][C_4H_3STe]$ reacts with $AgNO_3$ in DMF to form $[Ag_4(L)_6]^{2-}$ where a Te octahedron is inscribed by an Ag tetrahedron presenting remarkably acute Ag-Te-Ag angles of 69(2) [483]. Telluroether $MeTe(CH_2)_3TeMe$ and $AgBF_4$ react in acetonitrile to yield $[Ag(L)_2]_n[BF_4]_{2n}$ while $[Te(p\text{-}FC_6H_4)]_2$ results in the formation of $[Ag_2(MeCN)_4(\mu\text{-}L)_{2n}[BF_4]_2$ [484].

Extraction with ethylenediamine of an alloy with nominal constitution $KAuBiTe_3$ and treatment with NEt_4Br in MeOH yields $[NEt_4]_4[\{(\eta^3\text{-}Te_3)Au\}_2(\mu\text{-}Te_2)]$ [485]. K_2Te and $AgNO_3$ in the presence of elemental sulfur in DMF afford $Ag_3Te(TeS_3)_2^{3-}$ with a cage structure as does the corresponding selenide [486]. Analogous reaction with AuCN affords an eight-membered ring of $[Au_2(TeS_3)_2]^{2-}$. Li_2Te and three equivalents of Te formed in DMF polytellurides to which $[AgI(PMe_3)]_4$ adds in the presence of NEt_4Cl and PPh_4Cl forming $[PPh_4]_2[NEt_4][AgTe_7]$ which possesses a bicyclic anion with a local $AgTe_3$ environment [487]. Diselenolene $[Au\{Se_2C=C(CF_3)_2\}_2]^-$ reveals in electrochemical studies that substitution of S by Se does not drastically affect the complex electronic structure [488]. Na_2Se_2 and Na_2Se_3 react with AuCN in DMF to afford $[PPh_4][Au_2(\mu\text{-}Se_2)(\mu\text{-}Se_3)]$ while with K_2Se_4 $[PPh_4][Au_2(\mu\text{-}Se_2)(\mu\text{-}Se_4)]$ is obtained [489]. The anionic $[AuSe_5]_n^{n-}$ **XXV** revealed a crystal structure of one-dimensional



XXV

chains with bismonodentate Se_5^{2-} units, dimerized through short interchain Au... Au interactions [490].

2.2.4. *Mixed-group 16 donors*

Absorption and emission spectra of the cluster compound [Cu(di-*n*-propylmonothiocarbamate)]$_6$ are reported and the crystal structure solved [395]. The aquo-cluster $[Mo_3S_4Cu(H_2O)_{10}]^{5+}$ was obtained from the oxidation of $[Mo_3S_4Cu(H_2O)_{10}]^{4+}$ or by the addition of CuCl to $[Mo_3S_4(H_2O)_9]^{4+}$ in aqueous hydrochloric acid [491].

Reaction of (phenylthio)ethanoic acid with $AgClO_4$ in EtOH produced the 1:1 polymer with a AgO_3S chromophore in a distorted trigonal pyramidal fashion [492] where a oxathia five-membered and a dioxa four-membered chelate rings were formed. Complexes of the formula $[\{Ag(hfac)\}_m(SR_2)_n]$ ($R = Me, Et, Pr^n, Bu^n, m = 1, n = 1$) and $[\{Ag(hfac)\}(1,4\text{-oxathiane})_n]$ ($n = 1, 2$), were prepared by the reaction between the Lewis bases and Ag_2O in the appropriate ratios. The oligomeric intermediate $[\{Ag(hfac)\}_2(H_2O)]$, formed by the 1:2 reaction of Ag_2O with Hhfac was also isolated. The complexes were characterized by ^1H and ^{13}C NMR and IR spectroscopy. The oxathiane complex is monomeric in the solid state with the 1,4-oxathiane ligands coordinated to the silver(I) center exclusively via the S atoms [493].

The crown ether derivative of dithiomaleonitrile produced by template Mg^{2+} cyclization gave oxa-crowned tetraaza porphyrins. The nickel porphyrin was found to bind to Ag(I) through the peripheral five atoms. In solution, no nitrogen coordination is verified while both $AgNS_2$ and AgO_2S_2 coordination sites were observed in the solid state [494].

The sandwich-like tetrametallic $[Ag_4(L)_2]^{4+}$ were obtained from 9,19-disubstituted 1,4,7,11,14,17-hexathiacicosanes and silver triflate in MeCN. For the dioxo-compound two AgO_2 and two AOS_3 sites were determined [495]. 1,4,7-Trioxa-10,13-dithiacyclopentadec-11-en-11,12-dicarbonitrile formed [Ag(L)][BF_4] in both polymeric and discrete monomeric, the tetrafluoroborate ion participating in the coordination environment in the latter. Polymeric compound is also formed by 1,4,7,10-tetraoxa-13,16-dithiacycylooctadec-14-en-14,15-dicarbonitrile with AgO_3S coordination in the solid state but fluxional in solution [496].

The AgS_3O environment is observed in the product of the 1,3,5-trithiane reaction with $Ag(CF_3SO_3)$ in MeCN/THF which has the formula $[Ag_2(L)_2(\mu\text{-}L)_2][CF_3SO_3]$ [497]. The stoichiometries of ligand-to-silver 2:1 and 1:1 for phosphoramidothioic and phosphoramidodithioic ion and the complex IR and UV spectra argue in favor of *O* and/or *S* coordination to silver [498]. The excitation and emission specra of hexameric silver clusters with di-*n*-propyl- monothihocarbamate are reported [395]. The structure of $[Ag(L)_3(ClO_4)]_n$ is reported, where L = the macrocycle produced from the 2+2 condensation of 3,7-dithianonane-1,9-diol and 3,6-dichloropyrimidazine in EtOH. The polymeric compound reveals local AgO_2S_2 chromophores [499].

The interactions of thio- and selenocyanate with aurothiomalate in aqueous solution were studied by ^{13}C NMR spectroscopy. The former induces further polymerization while the latter forms initially monomeric $[Au(SeCN)(tm)]^-$ which further disproportionates [500].

The salts $LiEY(SiMe_3)_3$ (E = S, Se, Te, Y = C, Si, Ge) react with AuCl(THT) in benzene or hexane to afford $[Au\{EY(SiMe_3)_3\}]_n$, tetrameric for E = S, Te and Y = C as crystal structure determination reveals. Similar reaction with $AuCl(PPh_3)$ in Et_2O yields $[Au(PPh_3)\{EY(SiMe_3)_3\}]$ as the crystal structure for E = Te, Y = C confirmed [501].

2.3. *Complexes with group 17 donors*

2.3.1. *Copper complexes*

A peguiliar CuI_2H environment was observed in $(Cp)_2TaH[(\mu\text{-}H)Cu(\mu\text{-}I)_2Cu(\mu\text{-}H)]_2TaH(Cp)_2$ produced by the reaction of tantalocene trihydride and CuI; a dangle bridging Cu_2I_2 unit was observed in the case of *tert*-butyl substituted cyclopentadienyl [502]. Raman studies on metal halide–CuCl melts in the presence of $AlCl_3$ and corresponding freezing point measurements indicate the presence of $CuCl_2^-$ units while in $AlCl_3$–CuCl melts $CuAlCl_4$ units are existing [503]. Polymeric $Cu_3I_5^{2-}$ chains are observed in $[Cu_3(3\text{-aminopropanolate})_4][Cu_3I_5]$. The anion is formed by reacting CuI and NBu_4I in acetonitrile [504]. $CuCl_3^{2-}$ is present in solutions of CuCl in the presence of chloride ions.

Increased ionic strength and $[H^+]$ inhibit luminescence of the species which is observed at 470–480 nm. The emitting state is probably a CTTS one, the hydrated electron formation being antagonistic to its decay [505]. The luminescence properties of iodocuprtes is studied in water. Primary oxidation occurs but Cu(II) scavenges the hydrated electrons that are formed as well [506]. Loosely associated $CuCl_2^-$ are present in $[PEt_4]_2[Cu_2Cl_4]$ [507] while an interesting mixed valence $Cu_2CkI_4^-$ species was obtained upon recrystallization of $[NEt_4]_4[Cu_4Cl_{12}]$ from MeCOOEt/$MeNO_2$ [508]. $CuCl_3$ anions are present in ionic compounds with Me_2NH_2 or $(CH_2{=}CHCH_2)_2NH_2$ countercations which result from the reaction of $CuCl_2$ with $S(NR_2)_2$ in ethanol [509].

Orbital overlap and symmetry analysis based on EHT computations attempt to explain the energy changes through a step process leading from $Cu_2Cl_4^{2-}$ to $Cu_2Cl_4^-$ through $Cu_2Cl_6^{3-}$ [510].

The anionic units $[CuBr_3]^{2-}$ and $[CuBr_2]^-$ have been studied in salts with PPh_3Me as the countercation. $CuBr_3$ appears to be symmetric around one of the Cu–Br bonds and the linearity of the $CuBr_2$ ion has also been verified [511]. The above anions in 5 M ionic, neutral or acidic media show CTTS bands and in high concentrations the formation of $Cu_2Br_5^{3-}$ and Cu_5Br^{4-} is proposed [512]. $CuBr_3$ is observed in the mixed valence [6-amino-1,3,-dimethyl-5-((2-carboxyphenyl)azo)uracil]$_4[Cu_2Br_7]$ prepared with $CuBr_2$ in methanol [513]. In the reaction of CuO with 6-methyl-2-hydroxypyridine in DMF followed by interaction with Br_2 the mixed valence polymeric $Cu_3Br_4(DMF)_2(H_2O)$ compound is obtained where the unique $Cu^{II}Cu^{I}_2Br_2$ is present [514] with the monovalent copper situated in a distorted tetrahedral environment of four bromine atoms.

Piperazine and CuI in aqueous HI give $[LH_2]_2[Cu_2I_6]\cdot H_2O$ while with excess CuI $[LH_2][Cu_2I_4]$ is obtained. The compounds were studied with respect to their structure, thermal and electrical properties [515]. Polyhalide anions of Cu(I) studied by Cu NQR revealed resonances (in MHz) $CuCl_2^-$ (30.70 or 31.15 depending on the counterion), $CuBr_2^-$ (28.85), $Cu_2Br_4^{2-}$ (30.647 to 32.217) $Cu_2Br_5^{3-}$ (31.397), CuI_3^{2-} (26.29), $Cu_4I_4^{2-}$ (24.385 to 26.375) and $Cu_4I_6^{2-}$ (26.15, 26.80) [516], [517]. Large angle X-ray scattering in acetonitrile, pyridine and DMSO characterize compounds of the formula CuX_2^-, CuX_3^{2-} and $Cu_2X_4^{2-}$ [518].

2.3.2. *Silver and gold complexes*

4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane reacted with KCl and AgCl in DMF to afford $[KL][AgCl_2]$, which upon replacement of chloride yielded $[KL]_4[Ag_4Br_8]$ and $[KL]_2[Ag_2I_4]$, respectively [519]. Weakly coordinating $M(OTeF_5)_6^-$ (M = Nb, Sb) or $M(OTeF_5)_6^{2-}$ (M = Ti, Zr, Hf) form 1:1 silver complexes which, upon recrystallization from haloalkanes produce $[Ag(haloalkane)_3]_n[Y]$, with $n = 1$ or 2 depending on the charge of Y. The crystal structure of $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$, $[Ag(CH_2Br_2)_3][Nb(OTeF_5)_6]$ and *catena*-poly[$Ag(CH_2BrCH_2Br)_2$-*μ*-(CH_2BrCH_2Br)-Br:Br′][$Sb(OTeF_5)_6$] are discussed, the last two being the first metal bromoalkane complexes reported [520]. Reactions of $AgOTeF_5$ and $PdCl_2$ or AgF and $HOTeF_5$ in dichloromethane or 1,2-dichloroethane, afforded chlorocarbon solvated silver complexes of the formulae $Ag_2(solvent)_4Pd(OTeF_5)_4$ and $[Ag(solvent)(OTeF_5)]_2$ [521]. Reaction of *trans*-$[M(py)_4X_2]Br$ (M = Rh, Ir, X = Cl, Br) with AgBr in a 1:1 ratio in water forms *trans*-$[M(py)_4X_2][AgBr_2]$ as confirmed by IR measurements [522].

Polymeric chains of AgI_3^{2-} ions in the form of corner-sharing tetrahedra were observed in $\{[NH_4][AgI_3]\}_\infty\cdot H_2O$, while one-dimensional infinite polymeric anions in the form of edge-sharing tetrahedra were found in $\{[NMe_4][Ag_2I_3]\}_\infty$ [523]. $TeEt_3I$ and Ag(*O,O*-diethyldithiphosphate) react in water at 70 C to produce $[TeEt_3][Ag_4I_5]$, probably through AgI addition to an intermediate of the formula $TeEt_3I$. The tetrahedral environment around silver has been deduced by ^1H MAS measurements [524]. A 2:1 reaction of NPr_4I and AgI in DMF affords $[NPr_4]_4[Ag_4I_8]$ with tetrahedral silver atoms possessing one terminal Ag–I bond [525]. Discrete anions are present in the ionic compound $[Ag\{P(2,4,6\text{-}(OCH_3)_3C_6H_2)_3\}_2][Ag_5I_7]$ [218]. The stability constants of several Ag-I aggregates, i.e. AgI, $[Ag_nI_{n+2}]^{2-}$ ($n = 1$–6) are reported as a result of potentiometric measurements in DMF [526]. A unique $[Ag\text{-}I_{11}]^{6-}$ anion was obtained by the reaction of AgI and $SnPr(OH)_2Cl\cdot 3\ 4H_2O$ in DMSO in the presence of NaI, in the form of a one-dimensional twisted double chain of face-sharing iodine tetrahedra [527].

Treatment of AgX with $AsMePh_3I$ leads to iodide incorporation in AgX, when carried out in hot CH_2Cl_2. The compounds isolated present infinite polymer Ag_3I_3X anions (X = Cl, Br, I) [528]. XeF_6 reacts with $BrF_3\cdot AuF_3$ to form $[XeF_5][AuF_4]$ which in anhydrous HF at <0 C reacts with KrF_2 to form $[XeF_5][AuF_6]$. The structures of the products are discussed with respect to the silver analogs and the differences presented attributed to the lower ligand charges of the silver complexes [529].

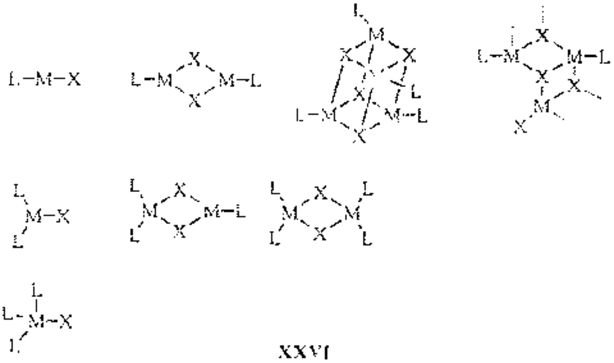
Interestingly, 6-amino-1,3-dimethyl-5-arylazauracils react with in-situ reduced $AuCl_2^-$ to yield $(LH^+)(AuCl_2) \cdot 1.5H_2O$ [530]. The reaction of 2,6-diphenylpyridine and $KAuCl_4$ at pH = 2 gave pyridinium tetrachloroaurate where an interesting three-atom hydrogen bond is present involving two of the chlorine atoms and the pyridinium proton [531].

Reaction of $[NBu^n_4][AuX_4]$ (X = Cl, Br, I) with phenylhydrazine hydrochloride yielded the corresponding Au(I) anions $[NBu^n_4][AuX_2]$ the crystal structures of which were determined [532].

3. Mixed ligand complexes

3.1. Complexes with group 15 and 17 ligands

A wide variety of local and overall structures has been obtained upon reaction of nitrogen or phoshporous bases with group 11 metal halides, depending on the steric demands of the ligands and the reaction conditions. The overall structures range from simple mononuclear to stair-type polymers and the main features of their idealized geometries are summarized in XXVI.



XXVI

3.1.1. Nitrogen and halogen ligands

3.1.1.1. Copper complexes. The mechanism of the transmetallation of Cu_2(*N,N,N',N'*-tetramethylethylenediamine)$_2X_2$ with M(*S*-methylisopropylidene hydrazine carbodithiolate)$_2$ (M = Co, Ni, Cu) has been studied [533]. Several products have been obtained from the reaction of nitrogen donor bases with copper halides. Depending on the concerted effect of the bulk and donor ability of the bases as well as on the halogen involved, a variety of structures has been observed especially in the products with 1:1 stoicheiometry. The structure of the products obtained by dissolution of copper(I) halides in nitriles has been studied and the structure of the complexes [CuX(RCN)] determined for acetonitrile and PHCN. In their vast majority the compounds are stair-type polymers with the exception of $[(CuI)_2(PhCN)]$ [534]. The 1:1 products are all of the stair-type polymer form [535].

The nature of compounds $CuX(MeCN)_n$ and $CuX(py)_n$ formed in acetonitrile and pyridine, respectively, is determined by vibrational spectroscopy utilizing large-angle X-ray scattering and the dimerization reaction constants in DMSO reported to be <0.2, 2 and $>100\ mol^{-1}\ dm^3$ for X = Cl, Br and I, respectively [518]. The enthalpies of salvation of cupras halides in pyridine and acetonitrile were obtained and appeared to be similer with the ones in pyridine being more negative [536]. Cubane-type tetramers obtained with copper iodide and pyridine or morpholine appeared to be photoluminescent in noncoordinating solvents at r.t. The emitting state is suggested to be the $3d^94s^1$ excited state of copper [537]. The quenching of emission from the cluster-centered excited state of these clusters by Tris(β-dionato)Cr(III) complexes and several organic substrates has been investigated in CH_2Cl_2 [538]. The absorption, emission, diffuse reflectance spectra and excited state lifetimes of several $[CuX(L)]_n$ where L = substituted pyridine in CH_2Cl_2 and C_6H_{14} glasses at 77 K as well as in the solid state are reported [539]. Analogous studies were carried out for [CuX{2-(diphenylmethyl)pyridine}] [540]. Luminescence thermochromism was also studied for $[CuX(py)]_4$ [541]. The structures of the dimer $[Cu_2I_2(3\text{-}Mepy)_4]$ and the polymers [CuI(2-Mepy)] and $[CuI(2,4\text{-}Me_2py)]$ have been determined [542]. Mononuclear species have been observed for $CuI(2\text{-methylquinoline})_2$ and $CuBr(3,5\text{-}Me_2py)_2$ [543]. For [Cu(py)Br] a zigzag formation with parallel chains was observed while 2-pyridinecarbaldehyde and 4-benzylpyridine form distorted stair polymers [544] and tetrameric cubane was realized for the more bulky 2(diphenylmethyl)pyridine [545]. Split-stair two-dimensional sheets of [Cu(L)X] (X = Cl, Br) are linked by 4-cyanopyridine [546], while a one-dimensional infinite spine was observed for [Cu(4-vinylpyridine)X and dimeric $[\{Cu(2\text{-vinylpyridine})\}_2(\mu\text{-}X)_2]$ (X = Cl, Br) [547]. The corresponding iodides are one-dimensional stair polymers with noncoordinating vinyl groups. Split-stair polymers were observed for acridine, quinaldine, 2,6-dimethylpyridine, 2,4,6-trimethylpyridine 1:1 adducts with copper halides with the exception of $[\{Cu(2,6\text{-}Me_2py)\}_2(\mu\text{-}I)_2]$ and $[Cu(2,4,6\text{-}Me_3py)_2][CuCl_2]$ [548]. Dimeric compounds were obtained for the more bulky octahydroacridine with almost planar Cu_2I_2, Cu_2Br_2 and butterfly Cu_2Cl_2 cores and monomeric Cu(2,2,6,6-tetramethylpiperazine)X with stabilizing intermolecular hydrogen bonds [549]. The structures of the [CuX(2-aminoquinoline)] complexes are markedly different from each other since the chloride is a stair-polymer, and the bromide dimeric and the iodide are split-stair [550]. The complexes of 4-methylquinoline fall into three categories, $[CuX(L)]_n$ for X = Cl, Br, I, SCN, N_3, CuL_2X (X = NO_3, ClO_4) and $Cu_2X_2L_3$ (X = Cl, Br). The structure of $Cu_2Cl_2L_3$ is of the stair-step type [551]. Distorted tetrahedral environment is reported for $[Cu[di(2\text{-pyridyl})methane]_2][ClO_4]$ prepared in EtOH by the ligand and in-situ reduced $CuSO_4$ [552]. Quinoline itself presents analogous variations having a stair-polymer chloride, a tetrameric "baskets" bromide and iodide and an extended-stair thiocyanate [553]. The emission spectra of [CuI(quinoline)$_2$]$_2$ and [CuI(quinoline)]$_4$ were obtained at ambient and at low temperatures and are quite distinct having maxima at around 620 and 580–590 nm, respectively, owing probably to the different environments of the metal centers and therefore to the different emissive states [554]. It is of interest to note that CuX with bipyridine produces dinuclear halogeno bridged compounds of the formula [(bpy)Cu(μ-X)$_2$Cu(bpy)] for X = Br, I while for X = Cl the ionic compound [Cu(bpy)$_2$][CuCl$_2$] is produced [555]. Three halogeno complexes of the formula Cu(3,5-Me$_2$py)$_3$X have been obtained and their crystal structures investigated [556]. The observed distorted symmetries are accounted for by the intra and intermolecular hydrogen bonds to the halogen atoms. Reaction of CuI with *p*-tolylisonitrile and nitrogen bases in THF led to the formation of mononuclear [CuI(bpy){(*p*-tolyl)CN}] and dimeric [Cu$_2${2-(1-benzyl-2-phenyl)benzimidazole}$_2${NC(*p*-tolyl)}$_2$(μ-I)$_2$] [557]. Oxidation of [CuCl(py)]$_4$ in PhNO$_2$ proceeds with initial insertion of O$_2$ in the Cl- core, which is the rate determining step of the reaction [558] in a manner analogous to the oxidation of [CuBr(*N*,*N'*-diethylethylenediamine)]$_2$, which results in the mixed valence compound [CuBr(L)]$_4$O$_2$ [559].

1,2,4-triazole affords compounds Cu(L)Cl$_2$ and Cu(L)$_2$Cl$_2$, which are reversibly reduced at 0.33 and 0.34 V and show an irreversible peak at −0.65, −0.66 V [560] while 1,8-bis[bis(1-methylbenzimidazol-2'-vinylmethyl)amino]-3,6-dioxaoctane in MeCN–MeOH gives Cu(L)Y (Y = ClO$_4$, BF$_4$, Cl, Br) or Cu$_2$(L)X$_2$ (X = Cl, Br, I) [561]. *N*,*N*-bis(3,5-dimethyl-1-pyrazolyl-methynyl)amnoethane and *N*,*N*-bis(1-pyrazolyl-methyl)aminoethane form mononuclear Cu(L)X complexes with coordinating X (X = Cl, Br, I, SCN) and [Cu(L)$_2$]Y With Y = CF$_3$SO$_3$, BF$_4$, possessing local CuN$_2$X$_2$ and CuN$_4$ environments, respectively, [562]. Benzimidazole reacts with CuI to afford Cu$_2$I$_2$(L)$_4$ in THF, stair-polymer [Cu(μ_3-I)(L)]$_n$ in MEOH and the solvated [Cu$_4$(μ_3-I)$_4$(L)$_4$]$^{2-}$ in diglyme, while 2-phenyl and 1-benzyl-2-phenyl substituted polymers in THF form Cu$_2$I$_2$(L)$_3$·2THF and CuI(L)$_2$·THF [563]. Thiazolyl, imidazolyl, and *N*-methylbenzimidazolyl lithium salts react with CuX in the presence of CF$_3$SO$_3$H at −80 °C (*N*-methylimidazolyl only at −40 °C) to form the dimers of the formula [Cu$_2$(μ-X)$_2$(L)$_4$] which were studied by NMR. The structure of Cu$_2$Cl$_2$(methylimidazole)$_4$ was solved [564]. The interesting feature of these compounds is the presence in the final products of halogen atoms besides the use of lithiated reagents. Products of the stoicheiometry Cu(L)$_2$Br and (CuL)$_2$Br are obtained with 1-phenyl-3,5-dimethylpyrazole [565].

The reaction of cuprus halides with 2,2'-dipridylamine in various molar ratios yields a variety of products, e.g. (CuX)$_2$L (X = Cl, Br), (CuX)$_3$L$_2$ (X = Cl), (CuX)L (X = Cl, Br) and (CuX)L$_2$ (X = Br I) [566]. Pyrazinic acid may act as a monodendate or bidentate ligand and this has been explored in a series of compounds with various anions. Complexes Cu(L)$_2$X·2H$_2$O were obtained for X = Cl, Br (monodentate ligand), Cu(L)X·H$_2$O for X = Br, NO$_3$, ClO$_4$ mixed coordination scheme was observed in Cu(L)$_3$Cl$_2$·3H$_2$O and a stair-ribbon polymer with CuI$_2$N$_2$ environment was the case of Cu$_2$(L)I$_2$·3H$_2$O [567]. Nicotinic acid reacts with divalent copper reduced in situ by ascorbic acid to give zigzag chains of Cu(L)$_2$Cl in which the free carboxylic groups are subject to dimerization [568]. *N*,*N*-diethylnicotinamide forms tetrameric clusters $[Cu(L)X]_4$, which reveal interesting reactivity. Reaction with tetrahalobenzoquinone produces the oxidation product $[Cu(L)X][catecholate]_2$ [569] or mixed valence $Cu_4X_4(L)_4(\mu$-catecholate) [570] with local CuN_3X environment. The clusters are transmetallated by the reaction with *S*-methylisopropylidenehydrazine carbodithiolate metal complexes, $M(NS)_n$ ($n=2$ or 3). $Fe(NS)_3$ initially gives the mixed valence complex $Cu^{I}_2Cu^{II}Fe^{II}L_4(NS)_2X_4$, which further react with $M(NS)_2$ to give complete transmetallation products $Cu(NS)$, $Cu(NS)_2$ and $M_2Fe(OH)(O)L_3X_4$ [571]. Reaction with $Co(NS)_3$ affords $Cu(NS)$ and $[Co_2(L)_4]X_4$ [572] while with $Sn(NS)_2Cl_2$ initially $[Cu_2(L)_2(\mu\text{-}Cl)_3Sn(L)Cl_2]$ is formed, which treated with nitrobenzene afforded $[Cu_2(L)_2(\mu\text{-}Cl)_3(\mu\text{-}O)SnCl_2(L)]$ while with a further equivalent of $Sn(NS)_2Cl_2$ complete transmetallation was achieved [573]. In general, with divalent metal carbodithiolates, clusters $[Cu_3M(L)_3X_4]$ are obtained which are further oxidized to yield $[Cu_3M(H_2O)(L)_3(\mu\text{-}O)_2X_5]$ [574].

Absorption and emission maxima of $[Cu_2I_2(PPh_3)_2$ (di-2-pyridylketone)] in $CHCl_3$ and $[Cu_4I_4$(di-2-pyridyketone)$_2]$ in acetone are reported as well as their catalytic activity in the photochemical transformation of NBD to QDC with quantum yields of 0.25 and 0.36 respectively (irradiation at $\lambda > 320$ nm for 12 h) [292]. Monoaza-alkenes of the formula $RN=CR^aCR^b=CHR^c$ react with CuCl in a wide range of molar ratios giving various products in different solvents of the formula $[\{Cu(L)_2\}_2(\mu\text{-}Cl)][CuCl_2]$, $[\{Cu(L)\}_2(\mu\text{-}Cl)]$ and $[Cu(L)_2Cl]_2$ [575].

3.1.1.2. Silver and gold complexes. Detailed structural studies reveal that for several *N*-heterocycles, the local silver environment in $Ag(L)_nX$ complexes is AgNX regardless of the *n* value predicted by elemental analysis [576]. The enthalpies of salvation of silver halides in pyridine are in general more negative than the corresponding ones in acetonitrile in both solvents the range obtained is less than 10 kJ mol^{-1} [536].

An unusual *trans*-AgN_2F_4 chromophore with Ag–N = 2.163(7) and Ag–F = 3.011(8) Å was observed in $[Ag(2,6\text{-}Me_2py)_2(BF_4)]_\infty$ where BF_4 anions are bridging adjacent Ag atoms [577]. A more limited array of structural types is observed in AgX products with *N*-bases, in relation to their copper analogs. Stair polymers are observed for $[Ag(py)Br]_\infty$, $[Ag(py)I]_\infty$, $[Ag(2,4,6\text{-}Me_3py)X]_\infty$, $[Ag(quinaldine)X]_\infty$ (X = Cl, Br), cube tetramers for $[Ag(piperidine)X]_4$ (X = Br, I), and $[Ag(2,2,6,6\text{-}tetramethylpiperidine)I]_4$, a novel "tube" polymer is realized for $[Ag(NHEt_2)X]_n$ [578] while infinite one-dimensional polymer is obtained for $Ag(piperidine)_2Cl$ [579].

AuX formation in pyridine and acetonitrile was verified by EXAFS studies and appeared to be less favoed in pyridine owing to solvation effects [580]. ^{197}Au Mössbauer results confirmed the existence of both Au(L)Cl and $(LH)(AuCl_2)$ for *N*-alkylimidazoles and benzoxazole ligands, the ratio of the product depending on a balance between electronic and steric factors. Analogous studies were carried out for the $Au(L)_2Cl$ series of compounds [581]. When coordination of inosine, guanosine, imidazole and its derivatives as well as of several substituted pyrazoles is considered, the Au(L)Cl complexes are linear while in the $Au(L)_2Cl$ analogs, the second ligand is just hydrogen bonded to the chlorine ion [582].

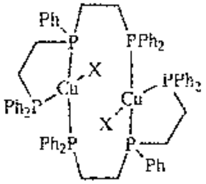
3.1.2. *Phosphorous and halogen ligands*

3.1.2.1. Copper complexes. Several completes of the formula $[Cu(PPh_3)_2X]$ were isolated and their solid state ^{31}P NMR spectra related to their structure [583]. Coordinated X (C, Br, I) reveal ⟨δ⟩ values from −5 to −6 ppm while ionic ones range close to zero. The corresponding $[Cu(Pph_3)_3X]$ were isolated in two phases, a trigonal and a triclinic one, the latter corresponding to solvated compounds [584]. The ^{31}P NMR are quite distinct for the two groups of compounds. The ionic compound $[PPh_3Me]$ $[Cu(PPh_3)Br_2]$ is obtained by refluxing PPh_3MeBr, CuBr and PPh_3 in CH_2Cl_2 and its structure elucidated by ^{31}P NMR and far-IR where the Cu–Br bonds resonate at 195 and 150 cm^{-1} [585]. Cu NQR measurements on $[Cu\{P(OMeC_6H_4)_3\}X]_2$ (X = Cl, Br) confirm the three-coordinate environment for copper. Along this line, several studies on other three-coordinate species, e.g. $[(CuX)_2(dppm)]_2$, $[Cu(PCy_3)_2][ClO_4]$, $[CuX(PCy_3)]_2$ are reported [586]. $Cu(Pcy_3)_2(FBF_3)$ was studied as catalyst in *trans*-stilbene cyclopropanation with $N_2{=}CH(CO_2Et)$ where alkene intermediate presence was proposed to account for its activity [277]. Its reaction with NaX in water gave the metathesis Products $Cu(PCy_3)_2X$ (X = Br, I) probably with trigonal planar geometry around the metal center [294].

Pseudotetrahedral copper is present in $[PPh_3Me]$ $[Cu(PPh_3)_2I_2]$ and $[PPh_3Me][Cu_2(PPh_3)_2(\mu\text{-}I)_3]$ as interpreted by far-IR measurements [587]. Bulky phosphines form monomer or dimer compounds like CuP(2,4,6,-trimethoxyphenyl)$_3$X [588], $CuPPh_2$(*o*-tolyl)X for which two district species were identified by ^{31}P CP/MAS, far-IR and crystal structure determination for X = Cl, Br [589], $[CuX\{P(p\text{-tolyl})_3\}]_2$ (X = Cl, Br) [590], while the less bulky P(*m*-tolyl)$_3$ formed with CuI a dimeric compound with one trigonal and one pseudotetrahedral copper atom [591]. A rare example of a Cu(I)–F bond is the $[CuF(PPh_3)_3]\cdot 2EtOH\cdot 4PPh_3$ complex where Cu–F is qual to 2.115(9) Å. The compound has been studied by ^{31}P CP/MAS [592]. Reaction of $P(p\text{-}OMeC_6H_4)_3$ in acetonitrile with CuI forms the ionic compound $[Cu(phosphine)_2][CuI_2]$ with two equivalents of CuI the monomeric CuI(phosphine) is obtained [593]; both compounds were studied by far-IR and ^{31}P. The structure of $CuBr(PMePh_2)_3$ and the otherwise inaccessible product of its reaction with $BH_3\cdot THF$ in THF, the dimeric $[CuBr(PMePh_2)]_2$ were solved [594]. Several *o*- and *p*-substituted bromobenzenes reacted with copper in THF at −108°C in the presence of trimethylphosphine to give several organic reduction and coupling products as well as the structurally characterized $CuBr(PMe_3)_3$ [595]. Several $[CuX(PR_3)]_n$ clusters have been used as photocatalysts in the isomerization of NBD to QDC and of *trans*- to *cis*-stilbene, their activity being related to the phosphine cone angle. Formation of a Cu–NBD complex is anticipated except for the complex of P(*o*-tolyl)$_3$ [596]. The crystal structures of $CuI(PCy_3)_2$ and $[CuI(PCy_3)]_2$ are reported and discussed with respect to other analogous structures. EHT orbital energy considerations were used to express the effect of the halides on the overall structure [597].

1-phenyldibenzophosphole forms tetrameric $[Cu(L)X]_4$ and monomeric CuL_3X and 1-phenyl-3,4-dimethylphosphole besides these also products of the formula CuL_2X which are dimeric for X = Br and I, while for X = Cl, the ionic $[Cu(L)_4][CuCl_2]$ was obtained. All the compounds were identified by far-IR and ^{31}P CP/MAS measurements [598]. Anionic complexes of the formula $Cu(PPh_3)X_2$ are monomeric for X = Cl, Br and dimeric for X = I as far-IR and ^{31}P CP/MAS measurements show [599].

The dimeric $[(PMe_3)_2Cu(\mu\text{-}I)_2Cu(PMe_3)_2]$ and the one-dimensional cubanoid $\{Cu_4Cl_4(PMe_3)_3\}_\infty$ were prepared in benzene suspension, and characterized by X-ray studies and vibrational (far-IR and Raman) spectroscopy [600]. Bis(diphenylphosphino)ethane forms several complexes with copper halides, which show marked versatility in solution. $(CuCl)_2(dppe)_3$ is shown to dissociate to $[CuCl(dppe)]_2$ while by addition of dppe, the equilibrium involves $[Cu(dppe)_2]Cl$ which has been characterized by NMR spectroscopic techniques [601]. The vibronic structure of the $[CuI(dmpp)]_4$ emission spectrum observed at 15 K has been discussed [541]. The structure of the dimer $[Cu(triphos)X]_2$, XXVII, has been determined and the CuP_3X environment ascertained [602]. Diphenylmesityl and phenyldimesitylphosphine being very bulky form dimeric adducts with copper halides [603] as is the case of tri-*o*-tolylphosphine for which additionally $[CuX(MeCN)\{P(o\text{-tolyl})_3\}]_2$ were obtained and studied by IR, ^{31}P CP/MAS [604]. Reaction of CuX_2 with α,α'-bis(bis(2-(diphenylphosphino)eethyl)amino)ethane and the corresponding *m*-xylene afford complexes $[Cu_2(L)]X_2$ ($X = MeCO_2, ClO_4, SO_4$) or $[Cu_2(L)X_2]$ (X = Cl) [605]. Racemic mixture of N,N′-bis[*o*-(diphenylphosphino)benzylidene-2,2′-diimino-1,1′-binaphthyl] reacted with $[Cu(MeCN)_4][PF_6]$ to give $[Cu(L)][PF_6]$ while with $Cu(PPh_3)_2Br$ monomeric $Cu(L)Br$ was produced where NMR measurements indicate intramolecular exchange of imino groups [606].



XXVII

IR and Raman studies confirmed the bridging role of halogen in Cu(1-dipehnylphosphino-*o*-carborane)$_2$X a product of 1:4 reaction of CuX with the ligand in EtOH. Reaction products for 1:2 and 1:3 ratios are of the formula CuLX and $Cu_2L_3X_2$ respectively [607].

The complex $[ReCl(CO)\{N_2(p\text{-}MeC_6H_4)\}(L\text{-}PP')(L\text{-}P)][PF_6]$ ($LH_2C{=}C(PPh_2)_2$) reacts with CuX in CH_2Cl_2 to give $[Re(\mu\text{-}Cl)(CO)\{N_2(p\text{-}MeC_6H_4)\}(\mu\text{-}L)_2CuX][PF_6]$ which was characterized by ^{31}P

NMR, IR and crystal structure determination [608]. Phosphine functionalized *p-tert*-butyl-calix[4]arene and *p-tert*-butyl-calix[8]arene added to $Cu(CO)Cl$ in THF at r.t. to afford $[L(CuCl)_4]_2$ where aggregation leads to terminal $CuCl_2$ or trigonal $CuCl_2P$, bridged CuP_2Cl and a central $CuP(\mu\text{-}Cl)_2$ metal sites [609].

3.1.2.2. Silver complexes. An interesting route to the known $[AgCl(PPh_3)]_4$ is through the reaction of $[N(PPh_3)_2][Ag(C_2Ph)]$, produced by the reaction of $N(PPh_3)_2Cl$, $(AgC_2Ph)_\infty$ and PPh_3 in a 1:2:3 ratio in acetone with either $AuCl(PPh_3)$ or *cis*-$PtCl_2(PPh_3)_2$ [610]. The chair and cube isomers of $[AgI(PPh_3)]_4$ were identified by their emissions at 12 K both of which are observed to red-shift with temperature raise [611]. $[AgX(L)]_4$ and $[AgX(L)_2]_2$ are obtained with 1-phenyl-3,4,-dimethylphosphole, $[AgX(L)_3]_2$ and $AgX(L)_3$ with 1-phenyldibenzophosphole. These as well as $[Ag(L)_2][BF_4]$ are studied by far-IR and ^{31}P CP/MAS as well as ^{31}P NMR in solution, revealing dissociation to $[Ag(L)_4]X$ and $[AgX(L)]_n$ [612]. Monomeric linear $AgX\{P(2,4,6\text{-}(OMe)_3C_6H_2)_3\}$ exists in the solid state on the basis of ^{31}P CP/MAS, far-IR and crystal structure measurements while AgL_2I is the structure proposed for the corresponding iodide. In solution ^{31}P NMR show that ionization to $[Ag(L)_2]X$ occurs [613]. ^{31}P CP/MAS studies on $AgX(PPh_2Bu)$ are reported and related to the compounds structures. The observed disorder in the iodine compound is reflected to the singlet broadband obtained in the spectrum [614]. The observed J_{AgP} splittings for a series of $Ag(PPh_3)_3X$ complexes ($X = Cl, I, BF_4, NO_3$) are correlated to their structure. The structures of several $Ag(PPh_3)_3X$ complexes prepared in refluxing acetonitrile were determined [615]. In the case of I and BF_4, complexes, crystal structure determinations confirm halogen coordination to the metal [616]. ^{31}P NMR studies on $Ag(L)Y$ complexes ($Y = Cl, I, NO_3, ClO_4, MeCO_2$; L = 1,1,1-Tris-((diphenylphosphino)methyl) ethane) show J_{AgP} splitting at 193 K only for NO_3 and ClO_4 while the rest appear to be still dynamic. An AgP_3I environment is present in the solid state but in solution only two of the available P atoms are coordinated [617].

The tetrameric "cubane" $[Ag_4I_4(PMe_3)_4]$, has been synthesized and its vibrational spectra recorded, assigned, correlated with the proposed structures and compared with analogous compounds [600]. The structures of the silver(I) complexes $[AgBr(PPh_3)_2]$ and $[Ag_2X_2(PPh_3)_4].2CHCl_3$ ($X = Cl, Br$) have been determined by single-crystal X-ray diffraction and correlated to their vibrational spectra. The ^{31}P CP/MAS spectra of the dimers show separate chemical shifts for the crystallography inequivalent phosphorus atoms, and $^2J_{PP'}$ coupling between these atoms [618].

$CoCl_2(Ph_2PCH_2C(O)Ph)_2$ reacted with two equivalents of $AgBF_4$ to afford $Ag(Ph_2PCH_2C(O)Ph)_2Cl$ while $CoX_2(PPh_3)_2$ gave $[Ag(PPh_3)_2][BF_4]$ and in excess of PPh_3, also $Co(\mu\text{-}Cl)_4\{Ag(PPh_3)_2\}_2$ [619]. 1,2- and 1,3-bis((Diphenylphosphino)methyl)benzene formed complexes of the formula $[AgX(L)]_2$ ($X = Cl, I, NO_3$) with bridging anions and the diphosphine ligands being chelating (1,2-) or bridging (1,3-) respectively [620]. *Trans*-$PtCl_2(C_6Cl_5)_2$ and $AgL(OClO_3)$ yielded $PtCl(C_6Cl_5)_2(\mu\text{-}Cl)AgL$ ($L = PEt_3, PPh_3$) or $Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2AgL$ ($L = PPh_2Me$), in the former O–Cl···Ag interaction to the

C_6Cl_5 ring is observed. Both compounds add a further $AgL(OClO_3)$ molecule to form trinuclear complexes [621]. Polymeric $[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]$ is formed by *trans*-$PtCl_2(C_6Cl_5)_2$ and $AgNO_3$ or $AgClO_4$ in $MeOH/Me_2CO$ and further reacts with EPh_3 (E = P, As, Sb) or PEt_3 to form $PtAgCl_2(C_6Cl_5)_2L$. The crystal structures of the products with PPh_3 and $PMePh_2$ as well as of the ionic starting compound are reported [622]. Reaction of $Ag(PPh_3)(ClO_4)$ With *trans*-$PtCl_2(C_6Cl_5)_2$ in CH_2Cl_2 produces $Cl(C_6Cl_5)Pt(\mu\text{-}Cl)Ag(PPh_3)$ which further reacts with $Ag(PPh_3)(ClO_4)$ to afford *trans*-$Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PPh_3)\}_2$ where a Cl-Ag-P angle of 148.5(3)° is observed [623]. In analogous compounds with bromine dimerization takes place the product being $[(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)]_2$ with a central Ag_2Br_2 core intermolecular Ag···Br contacts and, interestingly, a O–Cl···Ag intramolecular interaction of 3.007(3) Å giving rise to an AgPBrBr′Cl environment [624]. Reaction of *cis,cis,trans*-$[RuCl_2(CNPh)_2(dppm\text{-}P)_2]$ having two monohapto dppm ligands with $AgClO_4$ gave the heterometallic complex $[(dppm)(PhNC)_2ClRu(\mu\text{-}dppm)AgCl](ClO_4)$ [625]. Reaction of $Ag(dppm)(NO_3)$ with $SnPh_2Cl_2$ in MeCN–MeOH produced $[Ag_3(\mu\text{-}Cl)_2(\mu\text{-}dPPM)_3]$ $[SnPh_2(NO_3)_2Cl]$ studied by X-ray and NMR measurements [228].

Treatment with $NaBH_4$ of a mixture of $[AgCl(PPh_3)]_4$, $HAuCl_4$ and PPh_3 in a 1:4:8 ratio in ethanol gave a dark red crystalline product with the stoicheiometry $[Au_{13}Ag_{12}(\mu\text{-}Cl)_6(PPh_3)_{10}Cl_2]\cdot n$EtOH, composed of two eicosahedral clusters sharing a vertex [626].

3.1.2.3. Gold complexes. Exclusion of water and air allows $AuCl(PR_3)$ (R = Et, Ph, OEt, OPh) and $AuCl(PR_3)_2$ (R = Ph, OEt) initially electrochemically oxidized to AuX_4^-, to be re-reduced by addition of PR_3 in a variety of solvents, i.e. MeCN, THF, CH_2Cl_2 [627]. Triphenylphosphine and 1-phenyl-3,4-dimethylphosphole form compounds Au(L)X and $[Au(L)_4][PF_6]$ and for the phosphole ligand $Au(L)_3X$ was also obtained (X = Cl, Br, I). In the chlorides the irregular phosphorous environment in the solid state is reflected in the appearance of the ^{31}P CP MAS spectra [628]. ^{31}P CP/MAS and crystal structure determination are reported for a series of $Au(PPh_3)(Y)$ compounds (Y = NO_3, $MeCO_2$, SCN, CH_3, CN, Cl, Br, I) [629]. The synthesis, IR and Raman studies are reported for $AuX(PEt_3)$ (X = Cl, B, CN, SCN) [630]. $AuCl(Me_2S)$ readily displaces Me_2S and coordinates with diphenylphosphino acetic and benzoic amide, Tris(diphenylphosphinoalkylamino)amine, bis(diphenylphosphino alkylamido)methylamine to give compounds Au(L)Cl where *P*-bonding to the metal is observed [631]. Displacement of Me_2S by $P(2,4,6\text{-}(OMe)_3C_6H_2)_3$ occurs yielding complexes of the formula AuX(L)3, which are shown, by ^{31}P NMR to turn, in solution, to the corresponding $[Au(L)_2]^+$ complexes [632]. A series of $Au(PPh_3)_nCl$ (n = 1–4) are obtained in solution as ^{31}P NMR measurements reveal, while 5-phenyl-dibenzophosphole only forms the ones with n = 1 and 4. The compounds undergo fast exchange even at 183 K and when a mixture of ligands is used, ^{31}P NMR identifies mixed-ligand species [633]. A variety of complexes is obtained by the reaction of PMe_2hexyl and PPh_2Bu^n with $(NEt_4)(AuBr_2)$ in $CDCl_3$ depending on the reactant ratio and these are Au(L)Br, $Au(L)_2Br$, $[Au(L)_3]Br$ and $[Au(L)_4]Br$ while with $R_2P(CH_2)_6PR'_2$ (R,R′ = Me, Ph) $(AuBr)_2(\mu\text{-}L)$, Au(L)Br and $[AuBr(\mu\text{-}L)]_2$ are obtained [634]. $P(CH_2OH)_3$ reacts with Au(cyclooctene)Cl to form $Au\{P(CH_2OH)_3\}Cl$ which further reacts with nucleosides (L = guanosine, adenosine, cytidine) in DMSO but only in the presence of $AgNO_3$ forming $[Au(L)\{P(CH_2OH)_3\}][NO_3]$ as IR and ^1H NMR studies confirmed [635]. Both LMCT and MLCT bands were observed in the UV–Vis and MCD spectra of $AuX(PR_3)$ complexes (X = Cl, Br, R = Me, Et) in acetonitrile solution [636]. Analogous study and band assignement was carried out on AuX_2^- and $Au(PEt_3)_2^+$ complexes as well.

Several biphosphines e.g. $Ph_2P(CH_2)_nPPh_2$ (n = 1–4), $Ph_2PCH{=}CHPPh_2$, $Ph_2PCH_2CH_2PEt_2$, $Et_2PCH_2CH_2PEt_2$, form $[(AuX)_2(\mu\text{-}L)]$ which are capable of further reacting with L [637]. It is observed that 5- and 6-membered rings are stable while ligands that would form 4- or 7-membered rings upon chelation yield annular or polymeric species [638]. The crystal structure of *cis*- and *trans*-bis(diphenylphosphino)ethylene were compared with the ones adopted in the corresponding $[(AuCl)_2(\mu\text{-}L)]$ complexes, and discussed in view of the complex ^{197}Au Mössbauer spectra. The *trans*- ligand also produced Au(L)Cl which is presumably polymeric with a AuP_2Cl environment. A close contact of $Au\cdots Au$ 3.05(1) Å has been observed for $[(AuCl)_2(\mu\text{-}cis\text{-}L)]$ [639]. The isomerization of *cis*- to *trans*-bis(diphenylphosphino)ethylenedigold dihalides has been achieved photochemically and followed by ^{31}P NMR measurements [640]. $[Au_2(dppm)_2][BH_3CN]_2$ with NaI formed $[Au_2(dppm)_2(\mu\text{-}I)][BH_3CN]$ which, upon recrystallization decomposes to $[Au_2(dppm)_2][Au(CN)_2]$ and treated with Nadtc yields $[Au_2(dppm)_2(\mu\text{-}dtc)][BH_3CN]$ [641]. Bis-diphenylphosphinomethane and $HAuCl_4$ in EtOH gives an equilibrium mixture of $(AuCl)_2(dppm)$, $[AuCl(dppm)]_2$ and $[Au_3Cl_2(dppm)_2]Cl$ in fast exchange, faster between the two terminal compounds than between the last two ones as ^{31}P NMR studies indicate. The solid state luminescence of the last complex is attributed to the presence of short $Au\cdots Au$ interactions on the basis of its crystal structure determination [642]. The ^{197}Au Mössbauer spectrum of the bis(diphenylphosphino)amine complex $[(AuCl)_2(\mu\text{-}L)]$ has been obtained at liquid helium temperature [265]. The bis(diphenylphosphino)methanido complex of gold is dimeric and upon reaction with MeI in MeOH yields $(AuL)_2(\mu\text{-}I)$ while reaction with $BrCH_2COPh$ leads to the formation of $[Au(dppm)Br]_2$ [643]. Diphenylphosphinodiphenylaminomethane reacts with either $Au(PPh_3)Cl$ or with *in situ* reduced $AuCl_4^-$ to afford $Au(L)_2Cl$, dissociating in acetonitrile as variable temperature ^{31}P NMR reveals. Its solid-state structure reveals a T-shaped AuP_2Cl environment [644]. Successive additions of equivalent moles of $Au(Me_2S)Cl$ to bis(diphenylphosphinomethyl)phenylarsine afforded complexes $Au_2Cl_2(\mu\text{-}L)$, self-associating even in solution at low temperatures and $Au_3Cl_3(\mu\text{-}L)$ with a bent Au_3 chain, while NH_4PF_6 addition to the former afforded the tetramer $[Au_4Cl_2(\mu\text{-}L)_2][PF_6]_2$ [645].

Analysis of the $^{31}P\{^1H\}$ spectra of mixtures $[NEt_4][AuBr_2]$ and $PPhMe_2$ or PB^n_3 in CD_2Cl_2 has been used to verify the presence of species with varying molecularity in solution as well as to determine their exchange kinetic parameters [646].

The complexes $[AuXP\{trimethoxyphenyl\}_3]$ (X = Cl, Br, I) were prepared by reaction of the phosphine with $[AuX(Me_2S)]$ or $[AuX_2]^-$. The complexes were characterized by far-IR and ^{31}P NMR spectroscopy in MeCN. Unlike the corresponding PPh_3 complexes there is no evidence of $^1J_{AuP}$ spin–spin splitting in the ^{31}P CP-MAS spectra. Addition of a further equivalent of phosphine results in the formation of $[Au(L)_2]^+$ [647].

The polymeric complex $[AuCl(dppf)]_n$ is based on trigonal P_2AuCl linkages and has been structurally characterized in both polar and apolar pseudo-polymorphic forms [648]. The ligand 1,1′-bis(diphenylphosphino)octamethylferrocene is found to be chelating in the above complex and bridging in $(AuCl)_2(\mu\text{-}L)$ and $\{Au(C_6F_5)\}_2(\mu\text{-}L)$ to which the corresponding chloro- compound is readily transformed [649].

1,3,5-triaza-7-phosphaadamantane forms both Au(L)Cl in $CHCl_3$ and (L · HCl)AuCl in MeOH/MeCN, which is deprotonated at pH = 4.5. The protonated ligand gives rise to longer Au···Au interactions consequently altering the luminescence properties of the complex [650]. Studies on Au(L)X (X = Br, I) and $[Au(LH)I][AuI_2]$ reveal that the latter compound possesses multiple emitting states [651]. CO interaction with $AuX(PPh_3)$ led to the formation of $Au(PPh_3)CO^+X^-$ ($X = NO_3$, CLO_4, BF_4, OAc), which upon hydrolysis or treatment with proton donors lead to $Au_9(PPh_3)_8X_3$ through "$AuHPPh_3$". The nitrate in CH_2Cl_2 gave $Au(PPh_3)(CNO)$ and the cluster $Au_{11}(PPh_3)_8(CNO)_2^+$ [652].

Phosphonite and phosphinite derivatized calixresorcinarenes $L(O_2PPh)_4$ and $L(OPPh_2)_8$, respectively, readily react with $AuCl(SMe_2)$ in CH_2Cl_2 to form "gold rimmed" calixarenes where the AuCl units are in fast exchange as the single line phosphorous NMR spectra reveal, although in the solid state the phosphonitocalixarene appears with a AuCl unit folded towards its center [653]. The cluster $Au_{55}(PPh_3)_{12}Cl_6$ is soluble in pyridine and dichloromethane but rapidly decomposes in solution. It was found that $Ph_2PC_6H_4SO_3Na$ exchanges with PPh_3 to afford $Au_{55}(L)_{12}Cl_6$, completely dissociating in water to afford $Na_{12}[Au_{55}(L)_{12}]$ [654].

3.1.3. Miscellaneous

The complexes $[Cu_3(L)_2(MeCN)_2(\mu\text{-}X)_2][ClO_4]$ were prepared by the reaction of CuX (X = Cl, I) with bis(diphenylphosphinomethyl)phenylphosphine in MeOH followed by recrystallization from MeCN. The chlorine-containing cation consists of three non-interacting copper(I) ions bridged by two chloride ions on the same side and by two triphosphine ligands. Both complexes display room-temperature photoluminescence [655].

Reaction of CuX and pyridine with two equivalents of PPh_3 in acetonitrile produced $CuX(py)(PPh_3)_2$ where rather short Cu–X and rather long Cu–N distances were observed [656]. With stoichiometric quantities $[Cu(\mu\text{-}X)(py)(PPh_3)]_2$ were obtained. Analogous compounds were obtained with 4-cyanopyridine and as crystal structure determinations show only pyridine nitrogen is involved in the coordination [657]. The corresponding bipyridine complexes were studied by crystal structure determination and ^{31}P CP–MAS measurements revealing, in the case of the chloride, inequivalent phosphorous atoms [658]. The NMR measurements discriminated between the yellow and the orange form of $CuCl(PPh_3)(bpy)$, the yellow one being conclusively attributed to the eclipsed conformation around the Cu–P bond [659].

In the same manner, the two pseudosymmetrically related molecules of $\{Cu(4\text{-Mepy})(PPh_3)Cl\}_2$ were identified [660]. The reaction of CuX With PPh_2(*o*-tolyl) or PPh_3 in the presence of either 4-cyanopyridine or piperidine in refluxing acetonitrile produced compounds of the stoicheiometry $[Cu(\mu\text{-}X)(\text{Phosphine})(L)]_2$ [661]. Analogous reaction produced $[Cu_2(MeCN)_2\{PPh_2(O\text{-tolyl})\}_2(\mu\text{-}Br)_2]$.2MeCN the structure of which has been determined [662].

Several ionic species exchange their anions with $[Cu_2(\alpha,\alpha'$-bis{bis[2-(diphenylarsino)ethyl]amino}ethane)][ClO_4] to form $Cu_2(L)X_2$ (X = Cl, BH_4), $[Cu_2(L)X][ClO_4]$ (X = N_3, NCS), while adducts of the formula $[Cu_2(L)(Y)_2][ClO_4]_2$ are obtained with Y = carbon disulfide, thiurea, triphenylphosphine, triphenylarsine and imidazole [663]. The crystal structure of $AgX(py)(PPh_3)$ is finally determined as dimeric [664] with bridging halogen atoms although in pyridine solution the existence of monomeric $AgX(Py)_2(PPh_3)$ is postulated [665].

The complex $Rh_2(CO)_2Cl_2(\mu\text{-}L)_2$ (L = bis((diphenylphosphino)methyl)phenylarsine) reacts with AgCl in CH_2Cl_2 to give $Rh_2Ag(CO)_2Cl_3(\mu\text{-}L)_2$ with silver bonded to the two arsenic atoms of the metallmacrocycle [666]. Depending on the crystallization conditions two crystal forms of $AuCl(AsPPh_3)$ are obtained which differ in the phenyl group torsion angles and the corresponding region of the Raman spectra [667].

3.2. Complexes with group 16 and 17 ligands

3.2.1. Oxygen and halogen ligands

Cuprous halides in the presence of ascorbic acid appear to catalyze effectively epoxidation of *trans*-stilbene without concomitant formation of benzaldehyde [668]. $AgB(OTeF_5)_4$ produced by addition of $B(OTeF_5)_3$ to $AgOTeF_5$ in 1,1,2-trichlorotrifluoroethane, reveals bonding of silver to three anions involving three Ag–O in the range 2.500(5)–2.756(5) Å and six Ag–F between 2.644(5) and 3.017(5) Å. Mesitylene, CH_2Cl_2 and CH_2ClCH_2Cl form the $[Ag(\text{solvent})_3][B(OTeF_5)_4]$ [669]. Dissolving $AgOTeF_5$ in 1,2,3-trichloropropane yields infinite chains of $[Ag(L)(OTeF_5)]_2$ with silver mono-coordinated to a chlorine of one and bidentate to the other ligand with a central Ag_2O_2 core [670].

3.2.2. Sulfur and halogen ligands

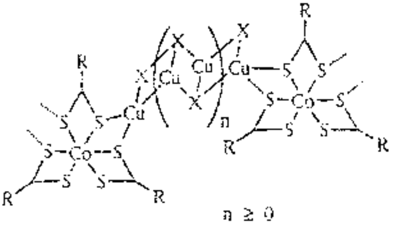
3.2.2.1. Copper complexes. The calculated heats of solution of cuprus halides in tetrathiophene are found to decrease from chlorine to iodine and are consistently higher than the corresponding silver ones, ranging between −279.1, −266.2, −233.7 and −217.4 kJ mol^{-1}, respectively [671]. Cuprus halides react with tetrakis(ethylthio)tetrathiafulvalene to form one- and two-dimensional polymeric complexes of the formula $[(CuBr)_2(L)]$ and $[(CuCl)_2(L)]$ respectively [419].

N-methylimidazoline-2-thione reduces Cu(II) salts in ethanol to produce both mixed valence compounds, i.e. $[Cu^{I}_{10}Cu^{II}_{2}(L)_{12}(H_2O)_4][Y]_2$ with Y = $MeCO_2$, OH,

ClO_4, PF_6, $[Cu_2(L)_2Cl_3]$ and $[Cu_2(L)_4Cl_2]$ [672]. The bulky 3-(triorganosilyl) and 3,6-bis(triorganosilyl)pyridine-2-thione form monomeric CuL_2Cl products [375] as does the saturated seven-membered thiocaprolactam with CuI [673]. The reaction of CuX_2 with 1,3-dithiacyclohexane-2-thione yielded the mixed-valence $Cu_3Cl_4(L)_2(\mu\text{-}L)_2$ where the two bridging ligands connect monovalent and divalent copper atoms, while $Cu_2(L)_2Br_2$ and $[Cu_2(L)Br_2]_n$ were also obtained [674]. In 20% aqueous HCl, 6-mercaptopurine is protonated and the reaction product with CuCl is $Cu_2(\mu\text{-}Cl)Cl(LH)_2$ [675] with protonation occurring at N(1) and N(9). 4,5,6,7-tetrathiocino[1,2-b:3,4-b']diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione forms in THF or acetone complexes of the formula Cu(L)X upon reaction with CuX_2; the same products are obtained by reduction of the Cu(II) analogs and are shown to possess a CuS_2X environment [676]. 1,3-dithiolane-2-thione in refluxing THF reduces CuX_2 to either $[CuX(L)]_n$ or $[Cu_2(L)Cl_2]_n$ where polymeric chains with $CuCl_2S$ or $CuCl_3S$ local environments are present bridged by thione sulfur atoms [677]. Ethyl, phenyl and benzyl substituted 2-propenoylthioureas form complexes of the type $Cu(L)_2Cl$ for which the phenyl substituted compound is structurally characterized [678]. CuL_2Cl is also formed by methylpyruvate thiosemicarbazone and further reacts with PPh_3 to form $CuL_2(PPh_3)Cl$ [679]. *N*-benzoyl-*N'*-propylthiurea is used as a model for the surface binding function of xerogel and in this respect the structure of its copper complexes is interesting. The structure of $Cu(L)_2Cl$ is composed of monomeric units with trigonal copper environment [680].

Relatively stable mixed valence clusters were obtained upon reaction of D-penicillamine with Cu(2+) salts in the presence of chlorides. The solid product of stoichiometry $Na_5[Cu^I_8Cu^{II}_6(L)_{12}Cl]\cdot 56H_2O$ was studied by TG and DSC. The monovalent copper atoms are supposed to exist in a CuS_2Cl environment [681].

A series of Co dithiocarbamates reacted with CuI in acetonitrile to produce polymeric species where $Cu_2(\mu\text{-}I)_2$ bridges are formed between adjacent $Co(dtc)_3$ units. The copper environment consists of two S and two I atoms [682]. Similar reactions in $MeCN\text{-}CH_2Cl_2$ give rise to $2[Co(dtc)_3]\cdot 5CuI$ with Cu_2I_2 bridging units and $[Co(dtc)_3]\cdot 3CuBr.MeCN$ with Cu_3Br_3 oligomers, **XXVIII** [683]. Reactions of diphenyl-, dibenzyl-, diethoxy- and methylphenyl cobalt dithiocarbamates are unsuccessful with either CuBr or CuI and polymeric products with the stoicheiometry $Co(dEt_2tc)_3[CuBr]_2\cdot 2MeCN$ and $Co(dBu_2tC)_3[CuI]_3$ are obtained [684].



XXVIII

Depending on the nature of the dithiocarbamate substituent, analogous reactions with $Cr(dtc)_3$ produce either 1:2 or 1:3 Cr:Cu compounds or no reaction product at all [685]. The structures of *N,N'*-diphenyldithiomalonamide complexes of the formula $[Cu(L)_2]X$ (X = Cl, Br, I) were determined and correlated with their ^1H NMR spectra obtained in DMSO [686].

A review of the reaction of tetrathiomolubdate and tetrathiowolframate with cuprus halides in ratios varying between 1:1 and 1:6 as well as the corresponding reactions with $MoOS_3^{2-}$ and $MoO_2S_2^{2-}$ are described and several new structures sovled [687]. The solid-state reaction of $MoO_2S_2^{2-}$ with CuI and NEt_4Br followed by successive extractions of the product with CH_2Cl_2 and Pr^iOH yielded $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_4I_2]$ in the form of two nest-shaped fragments connected through a CuI_2Cu bridge [688].

Reaction of CuCl with tetrathiowolframate produce various products of the general formula $[Cu_nCl_nWS_4]$ ($n = 2, 2.5, 3$) depending upon the reaction time and evaporation procedure applied. Cyclic voltametric studies in DMF reveal that the coordination of CuCl protects the WS_4 core from reduction [689]. Upon standing in acetonitrile $[(CuCl)_5WS_4]^{4-}$ was isolated and structurally characterized [690]. Addition of NH_4SCN to $[WS_4(CuCl)_5Cl_2]^{4-}$ yielded $[WS_4(CuNCS)_4]^{2-}$ while with three equivalents of triphenylphosphine $[WS_4\{Cu(PPh_3)\}_3Cl(MeCN)]$ was obtained [691]. Analogous reactions with MoS_4 lead to the isolation of $(CuL)_nMoS_4$ ($n = 1$, 2 or 3) where L = Cl, Br and SPh or CN. The Raman bands attributed to the Mo–S and Cu–S bonds are reported at 80 K and provide indications about the stoichiometry and structure of the product studied [692]. Reaction in a 1:3 ratio afforded $[MoS_4(CuCl)_6Cl_3]^{5-}$ with MoS_4 encapsulated within a distorted octahedron of copper atoms, of which half are trigonal and hald in a tetrahedral environment [693]. Reaction with five-fold excess of CuCl in refluxing CH_2Cl_2 leads to formation of $[MS_4Cu_4Cl_4]^{2-}$ (M = Mo, W). There are differences in the structure of the obtained complexes, which are related to the various counterions used [694]. The reaction of $[NH_4]WS_4$ with CuX (X = Br, I) and a corresponding tetraalkyl halide in the solid state yielded $[NR_4]_4[WS_4Cu_5X_7]$ the structure of which was observed to be an open cubane-like one, while treatment with pyridine in acetonitrile yielded polymeric $[WS_4Cu_6I_4(py)_4]_n$ [695]. Addition of CuCl to $(CuCl)\{Rh(Cp)P(OEt)_3\}(\mu\text{-}WS_4)$ produced $(CuCl)_2\{(\mu\text{-}WS_4)(CuCl)\{Rh(Cp)P(OEt_3)\}$, where two trigonal and two tetrahedral copper centers are encountered. Treatment of the product with moist CH_2Cl_2 yielded a product with the stoicheiometry $[\{RhCpP(OEt_3)\}(\mu\text{-}WOS_3)(CuCl)Cu]_2(\mu\text{-}Cl)_2$ and a dramatically different structure, which treated with H_2S aforded the initial compound [696].

The macrocycle produced from the 2 + 2 condensation of 3,7-dithianonane-1,9-diol and 3,6-dichloropyrimidazine in EtOH forms $[Cu(L)Cl]_n$ which is shown to possess Cu_2Cl_2 cores and tetrahedrally coordinated copper atoms [499].

3.2.2.2. Silver and gold complexes. Polythiaether [9]aneS_3 forms Ag(L)X complexes in which silver is in a tetrahedral AgS_3X environment and the ligands are bridging [444]. Silver halides dissolved in THT form $[AgX(THT)]_4$ as inferred by large-angle X-ray scattering measurements [424]. The crystal structure of

$[AuI(THT)]_\infty$ is reported at 200 K. Infinite Au chains are observed with alternate AuS_2 and AuI_2 environments [697].

Reaction of AuCl(CO) with thiols RSH ($R = Bu^t$, $2,6\text{-}Me_2C_6H_3$, C_6F_5) produced thiolates Au(SR) while reaction with [Na(1,4,7,10,13-pentaoxacyclopentadecane)][SBu^t] yielded among others $[(AuCl)_3SBu^t]^-$: its crystal structure revealed three AuCl groups coordinated to the Bu^tS^- giving rise to a tetrahedral sulfur [698]. Several heterocyclic thioamides form complexes [AuX(L)] ($X = C_6F_5$, Cl) while, upon deprotonation neutral $[Au_2(\mu\text{-}L)_2]$ with both S and N donation to the metal are obtained [462]. Electrogenerated $AuCl_2^-$ at pH = 1.67 (in HNO_3) reacts with cysteinato and penicilaminato ions forming complexes easier to oxidize than $Au(PR_3)Cl$ but more difficult than $Au(PR_3)_2^+$ [699]. Linear AuSCl environment is present in the reduction product of $[AuCl_4]^-$ by dicyclohexylphosphanyl-*N*-methylthioformamide in thiodiglycol [700]. Monomeric compounds of the formula Au(L)Cl are derived from the reaction of $S{=}C(H)NMe_2$, $S{=}C(Cl)NMe_2$, $S{=}C(Ph)SMe$ and dithiazolidine-2-thione with AuCl in THF at r.t. The latter reveals a crystal structure with antiparallel pairs and Au···Au 3.366 Å [701]. The thioether is readily displaced from $AuCl(SMe_2)$ by pyridine-2- or 4-thione in THF resulting in the formation of AuCl(thione) complexes. The corresponding thionato complexes are presumably dimeric for pyridine-2-thione and polymeric for its 4-counterpart [702].

Dimethyldithiocarbamate *S*-methylester is found to form Au(L)X (X = Cl, Br) and $[Au(L)(PPh_3)](NO_3)$ in ethanol while the corresponding *O*-ethyl monothiocarbamate forms $[Au(L)_2]_2Cl$ [703]. Ligand exchange is confirmed in solution for AuCl(1,4,7-trithiacyclononane) while its structure reveals Au···Au contacts of 3.3095(4) Å forming an infinite array of Au atoms [704].

3.2.3. Miscellaneous

Reaction of $[18]aneS_6$ and $AgBF_4$ in $MeNO_2\text{-}CHCl_3$ in the presence of three-fold excess of iodine produced $[\{Ag(L)\}I_3]_n$ while from EtOH $[Ag(L)]I_3$ was obtained [705]. Silver has been found to coordinate to the O and the Br atom of α-bromo ketones in a chelate-like manner and to the pi-systems of phenyl rings. ^1H and ^{13}C NMR measurements of the complexes and of the pure ligands in solution support the results of the X-ray structure determinations [706].

3.3. Complexes with group 15 and 16 ligands

3.3.1. Nitrogen and oxygen donors

3.3.1.1. Copper complexes. Reaction of several substituted pyrazines with $Cu(CF_3SO_3)_2$ in MeOH afforded $Cu(L)_2(CF_3SO_3)_2$ where distorted tetrahedral CuN_3O environment is present [707] while with 2,5-dimethylpyrazine, poly-$[Cu(\mu\text{-}L)(L)(CF_3SO_3)]$ was obtained [708].

Reaction of several 1,2-diones with metallic copper in the presence of nitrogen bases yielded semidione complexes which, upon reaction with copper lead to the formation of binuclear μ-enediolato complexes with three-coordinate metal centers in CuN_2O environments [709]. Reversible oxidation and reduction of complex occurs in well-defined steps. Substitution of O by S leads to more negative first reduction potential and occurrence of the second step quite close to the first one [710].

IR studies revealed that the perchlorate ion is present in various coordination modes in polypyridine complexes, namely noncoordinating in $[Cu_2\{$1.2-bis[6-[2-(6-methyl-2-pyridyl)ethyl]2-pyridyl]ethane$\}][ClO_4]$, monodentate in $[Cu\{$2.6-bis[2-(6-methyl-2pyridyl)ethyl]pyridine$\}(OClO_3)$ and bidentate in $[Cu\{$1.2-bis(6-methyl-2pyridyl)ethane$\}(O_2ClO_2)$ [711].

2.1.3-benzothiadiazole forms two-dimensional $[Cu_6(L)_6]^{6+}$ clusters in $\{[Cu_2(L)_3(ClO_4)][ClO_4].2THF\}$, three-dimensional ones in $[Cu(L)(HPO_3F)]$ with interconnecting anions, $[Cu(L)(NO_3)]$ where a Cu_6 chair is formed and layered overall structure is present, while 5.6-benzo[illegible] gives $[Cu_2L_4(C_2H_4)(Me_2CO)][ClO_4]$ in the presence of ethylene [712].

Phenazine added to $[Cu(MeCN)_4][PF_6]$ in methanol to give $[Cu_2(L)_3(MeOH)_2]\cdot L\cdot[PF_6]_2$ in the form of infinite stacks of alternate ligand and cationic unit, which form a donor-acceptor complex as judged by the observed CT band. In-situ reduction of $Cu(ClO_4)_2$ in MeOH Me_2CO gives infinite chains of $[Cu(L)_2(H_2O)][ClO_4]$ while with $Cu(NO_3)_2$ the compound $Cu(L)_2(O_2NO)$ is obtained [713]. Polymeric nitrate is obtained by the in situ reduction of $Cu(NO_3)_2$ with copper in acetone and in Me_2CO/C_6H_6, $[Cu(MeCN)_4][PF_6]$ yielded $[Cu(L)(PF_2O_2)]_n$ with bridging anions [714].

Cyclohexylcyanamide reacted with $[Cu(3.5\text{-}Me_2pz)]_n$ in acetone to afford $[Cu(3.5\text{-}Me_2pz)(L)]_2$ which further reacted with OCS, SCNPh, OCNCy to give insertion products [715]. The complex of 3.5-dimethylpyrazolate in pyridine appears to be in equilibrium between the forms $[Cu(L)_2py_2]$ and $[Cu_3(L)_6]\cdot py$ which is shifted by temperature [716]. Thiochrome forms a polymeric compound with copper perchlorate with a stair-type chain with Cu···Cu 2.476(3) Å while in solution the prevailing species is a low weight dimer complex [717].

The complex $[Cu(2\text{-thienoyltrifluoroacetone})(\mu\text{-}4.4'\text{-bpy})]$ presents a chain formation confirmed by IR and FAB MS measurements [718]. Condensation of 2.5-diformylfuran and 3-oxapentatne-1.8-diamine produce a Schiff base which in MeCN MeOH gives $[Cu_2(L)][ClO_4]_2$ and $[Cu_2(L)(MeCN)_2][BPh_4]_2$ with local CuN_2O_2 environments [125].

Macrocyclic ligands such as 1.7.11.17-tetraazacycloeicosane-4.14-diol coordinate to monovalent copper and the $[Cu_2(L)]\text{-}[ClO_4]_2$ complex revealed a considerable stability with respect to its oxidation, especially in acetonitrile which was achieved in two steps, the intermediate product being identified and a mixed-valence complex [719]. Asymmetric macrocycles produced by condensation of 2.6-diformyl-4-methylphenolate with mixtures of diamines $NH_2(CH_2)_nNH_2$ (n ranging from 2 to 5) formed in methanol $[Cu_2(L)][ClO_4]_2$ [720].

3.3.1.2. Silver complexes. The crystal structure determination of α-trisilver amidoselenate Ag_3NSeO_3 reveals helical packing due to a Ag···O coordination between adjacent units [721] while in $[Ag(NH_3)_2][Ag_2NSeO_3]\cdot 3NH_3\cdot 2H_2O$ only AgN_2 environments are encountered [722]. Bridging urea and NO_3 are found in

$[\{Ag(NO_3)\}_2(urea)_3]_n$ produced by boiling $AgNO_3$ and urea in a 1:2 ratio in water, the local silver environments being AgO_3 and AgO_3N [723].

1,4,7-Tri-isopropyl-1,4,7-triazacyclononane formed $[Cu(MeCN)(L)][PF_6]$ in THF which upon reaction with $NaNO_2$ in MEOH yielded a nitrito bridged dimer of the formula $[\{Cu(L)\}_2(\mu$-$ONO)][PF_6]$ which was studied spectroscopically and electrochemically in order to model analogous nitrite to NO conversions in copper-containing enzymes [724]. Analogous reactions were carried out using hydridotris((3-*tert*-butyl)pyrazolate)borate which formed with CuCl in THF a dimeric complex with digonal copper centers which readily uptakes NO to yield monomeric $[Cu(L)(NO)]$ [725]. The four-electron donor nature of 5-aza-2,8-dioxa-1-phosphabicyclo-[3.3.0]octa-2,4,6-triene is verified in $[\{Ag(MeCN)_3\}_2(\mu$-$L)][SbF_6]$ from which it is displaced by MECN and THF [726].

Recrystallization of $AgNO_3$ from 4-benzoylpyridine or pyridine-4-carbonitrile produces products $[Ag(L)_2(NO_3)]$ which are polymeric in nature and present structures with monodentate nitrates and monodentate and chelating nitrates respectively [727]. Chelating nitrate and bridging 1,8-naphthyridine are present in $[Ag_2(O_2NO)_2(\mu$-$L)_2]$ giving rise to a local AgO_2N_2 environment [728]. The complex of silver perchlorate with diacetylpyridine was structurally determined to be of the formula $[Ag(L)_2][ClO_4]$ with a AgN_2O_2 environment [729].

Polymeric 1:1 compounds were formed by the reaction of 4-nitro-imidazole with either $AgNO_3$ or $AgBF_4$ in aqueous media as ^{13}C NMR and IR studies reveal; in acidic media neutral imidazole forms $[Ag(L)_2][Y]$ ($Y = NO_3$, BF_4), dissociating in DMSO [730]. Silver amine complexes with phthalic $Ag(L)(NH_3)_2$ and trimesic acid $(NH_4)[Ag_3(L)_2(NH_3)_2(H_2O)_2]\cdot H_2O$ have been prepared. The former is a hydrogen-bonded chain polymer with linear AgNO environment and each phthalate oxygen bonded to separate silver atoms while the latter is a two-dimensional sheet polymer [731]. Ammonium silver bis(nicotinate) hydrate possesses a N_2O chromophore with bridging nicotinate and ammonium silverdipicrate dihydrate presents a NO_3 local environment with one ligand *O*-monocoordinated and another contributing a bridging oxygen atom. All the above complexes are prepared by reacting the neutral ligands with $AgNO_3$ in aqueous ammonia [359]. Under similar conditions, *catena*-(pyridine-3-carboxylato-*(O,O')*silver) is produced which possesses a trigonal NO_2 chromophere with each atom originating from a different ligand.

Polydentate *N*-[*N*-(5-methylthienylidene)-L-methionyl]histamine with activated acid function forms $\{[Ag(L)][CF_3SO_3]\}_n$ in MeOH as a chiral polymer where two nitrogen and two sulfur atoms from three ligands are close to one silver and a weak Ag···O interaction at 2.568(4) Å is also detected [732].

A sandwich-like conformation and a AgN_2O_2 environment is observed in bis(1,9,12,15-tetraoxa-5,7-nitrilo-10,13,16-tribenzo-heptadeca-3,5-diene) silver nitrate prepared in MeOH [733]. Condensation of 2,6-diacetylpyridine with 3,6,9-trithiaundecane-1,11-diamine forms a cyclic Schiff base which coordinates to $AgClO_4$ to form a cationic complex unit where mer-triaza and fac-triangular sulfur moieties bind to silver [734].

Condensation of Tris(propylamino)amine and 1,4-dibenzaldehyde in a 2:3 ratio in the presence of $AgNO_3$ in MeOH, treated with $NaClO_4$ resulted in the formation of a mixed valence cryptate of the formula $[Ag^{I}Ag^{II}(O)L][ClO_4]$ with Ag^{I} in a N_4 and Ag^{II} in a N_2O environment respectively [735]. The Schiff base produced by the condensation of 2,5-diformylfuran and 3-azapentane-1,5-diamine reacted in MeCN/MeOH to give $[Ag_2(H_2O)_2(L)](ClO_4)_2$ with a local AgN_2O_2 environment [126]. The formation of AgL^+ with cryptand 4,7,13,26-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane is reported on a variety of solvents including acetonitrile, methanol, water and pyridine [736].

3.3.2. *Phosphorus and oxygen donors*

3.3.2.1. Copper complexes. The 2-methylquinolin-8-olate reaction with CuCl in THF disproportionates to metallic copper and CuL_2 but the presence of *p*-tolylisonitrile stabilizes the polymeric $[Cu(L)\{CN(p\text{-tolyl})\}]_n$ and CO the tetrameric $[Cu(L)(CO)]_4$ which easily substitutes CO with phosphorous bases forming $Cu(L)(PPh_3)_2$ and Cu(L)(dppe) [737].

$Cu(\eta^5\text{-}Cp)(PMe_3)_2$ reacts with substituted acetylacetones to give $[Cu(acac)(PMe_3)_2]_n$ the crystal structure of the tfa compound is reported [738]. Several $Cu(diketonate)(PR_3)_n$ with PMe_3, PEt_3, acac, tfac, hfac have been studied. An interesting reaction is the one of $Cu(hfac)(PMe_3)_2$ with excess PMe_3, which leads to formation of $[Cu(PMe_3)_4][hfac]$ [739]. Vapor pressure measurements are reported for $[Cu(PMe_3)_n](\beta\text{-diketonate})$ ($n = 1, 2$ for acac, tfac, hfac; $n = 1$ for dpm) [740]. Analogous compounds are realized for $P(Bu^n)_3$, PPh_3 and PCy_3; the structures for some of the tricyclohexylphosphine complexes are reported [741] along with an ^{31}P NMR study.

Reaction of $Cu(NO_3)_2$ with PPh_3 in refluxing ethanol produced $Cu(PPh_3)_2(ONO_2)$ [Cu–O = 2.274(4) Å] while $Cu(PPh_3)_2(BH_4)$ in the presence of $HClO_4$ reacts with PPh_3 to give $Cu(PPh_3)_2(O_2ClO_2)$ [Cu–O = 2.26(5) Å] [742]. Anion coordination was also observed for the perchlorate complexes of $[M(PR_2R')_3]X$, where M = Cu, Ag or Au and R,R′ = phenyl, cyclohexyl, cyclopentyl and cycloheptyl and for the corresponding tetrafluoroborates of PPh_2Cy and $PPh_2C_7H_{13}$ [743].

The complexes $[(R_3P)_2Cu(\mu\text{-}L)]_n$ (R = Ph, Cy; L = cyanoacetate), have been synthesized. The first complex is a dimer, both in solution and in the solid state, with bonding through both the carboxylate functionality and the N, while the second is monomeric with monodentate carboxylate. Both complexes readily undergo reversible decarboxylation-carboxylation [744]. Depending on the concentration and temperature of the solution, and the reactant molar ratio the reaction of copper(II) acetate with triphenylphosphine in ethanol produced $[Cu^{I}(PPh_3)_2(MeCO_2)]$, $[Cu^{II}(PPh_3)_2(MeCO_2)_2]$ and the mixed valence $[Cu_2(PPh_3)_4(MeCO_2)_3]$ which were shown to co-exist in solution [745]. $[Cu(PPh_3)_2]^+$ formed on Cu anode in the presence of PPh_3 in acetonitrile solution reacts with several carboxylic acid anions to form $Cu(PPh_3)_2(O_2CR)$ where chelating or monodentate carboxylates are present depending on their steric interactions and their donor ability [746]. Reaction of copper with di-*tert*-butyl-azodiformate in the presence of phosphines affords $[Cu_2(L)(PPh_3)_4]^+$, or $[Cu_2(L)(P\text{–}P)_2]^+$ where P–P is α,ω-diphenylphosphinopentane or hexane [747]. Diphenylphosphinomethane acts as a bridge between copper atoms in $[Cu(O_2CPh)(dppm)]_2$ and $[Cu(\mu\text{-}PhCO_2)(dppm)]\cdot H_2O$; in both cases benzoate is exchanged with noncoordinating PF_6 and BPh_4 ions and completely replaced by N_3 or SCN [748]. Reaction of Cu(9,10-phenanthrene semiquinonate)$(PPh_3)_2$ with dibenzolyperoxide in CH_2Cl_2 leads to formation of phenanthrenequinone and $Cu(PPh_3)_2(O_2CPh)$ where the benzoate ion is bidentate. It is interesting to note that several other organic peroxides do not react [749]. Cu(benzene-1,2-dioxyacetate)(H_2O) reacts with four equivalents of triphenylphosphine to give Cu(acetate)$(PPh_3)_2$ which ionizes in MeCN but not in CH_2Cl_2, is irreversibly oxidized and reduced and in the solid state is polymeric owing to hydrogen bonding between the carboxylate ions [750]. Copper butyrate reacts with dicarboxylic acids in the presence of triphenylphosphine to give $Cu(PPh_3)_2$(dicarboxylate monoanion) where the free carboxylic groups form an extended hydrogen bond network. Malonate and succinate undergo facile CO_2 extrusion [751]. The products with $Cu(acac)_2$ give $Cu^{II}\{Cu(PR_3)_2$(dicarboxylate monoanion)$\}_2$ where for PPh_3 the acid is bidentate and for the bulkier Pcy_3 it is monodentate [752]. $Cu(PPh_3)_2(BH_4)$ reacts with 3,5-dinitrobezoic acid in THF to afford $Cu(PPh_3)_2$(benzoate) where monodentate anion is present [753]. $Cu(PPh_3)_2$(cyanoacetate) in THF at 40°C gives $[Cu(PPh_3)_2]_2[CO_3]$. Under the same conditions $Cu(PPh_3)_2$(phenylmalonate benzylester) gives $[Cu(PPh_3)_2(OCO_2H)]_2$ with bridging carboxylate [754].

1,1′-bis(diphenylphosphino)ferrocene in the presence of its oxo-analog (OL) form $[Cu(L)(OL)][BF_4]$ [755]. $[Cu(\mu\text{-}ONO_2)(L)]_2$ reacts with carboxylates to form $Cu(L)(\mu\text{-}O_2CR)$(R = i-Pr) or $[Cu(L)(\mu\text{-}O_2CR)]_2$ while treatment with one equivalent of dppf forms $\{Cu(L)(ONO_2)\}_2(\mu\text{-}L)$ and with iodides readily displaces NO_3 resulting in the formation of $\{Cu(L)\}_2(\mu\text{-}I)_2$ [756].

3,5-di-*tert*-butyl-1,2-benzoquinone reacts with copper in the presence of triphenylphosphine to give $Cu(PPh_3)_2$(quinone) while with two equivalents of copper $[Cu^I(MeCN)(PPh_3)_2][Cu^{II}(catecholate)_2]$ results with catecholate bridging thus giving rise to CuNPO environment [757]. 1,6-bis(diphenylphosphino)hexane forms $Cu_2(\mu\text{-}L)_2(\mu\text{-}X)_2$ ($X = ClO_4$, both mono-and bidentate, NO_3 bidentate, PF_2O_2 bidentate, $MeCO_2$, $EtCO_2$), while the corresponding pentane gives $[Cu(L)_2][ClO_4]$ [758].

Silyloxides $[CuOSiR_3]_4$ react with phosphines to give dimers $[Cu(OSiR_3)(L)]_2$ ($L = PPh_3$, PMe_2Ph; R = Ph) or monomer $Cu(OSiMe_2Bu^t)(PPh_3)_2$. A planar Cu_4O_4 core is present in triphenylsilyloxide and a $Cu_2O_2P_2$ one in $[Cu(OSiMe_2Bu^t)(phosphine)]_2$ [759]. Ab initio studies on the insertion reaction of CO_2 to Cu–X bonds were performed on the model compounds $Cu(PH_3)_2H$ and $Cu(PPh_3)_2H$. The insertion is computed to be facile in the case of electron-rich X and the stable products are predicted to be of the formula $Cu(PH_3)_2(\eta^2\text{-}O_2CH)$ [760] and $Cu(PH_3)_3(\eta^1\text{-}OCOH)$ [761] respectively.

5.3.2.2. Silver and gold complexes. ^{31}P CP MAS studies of the compounds $Ag(NO_3)(PPh_3)_n$ ($n = 1$–4) have been carried out, compared with the corresponding solution studies and correlated to the crystal structure data for the complexes with

$n = 2$–4 [762]. A series of [Ag(phosphine)$_n$][ClO$_4$] and the corresponding tetrafluoroborates have been reported with phosphines of the formula PR$_3$, PR$_2$Ph, PRPh$_2$ (R = p-F, p-Cl, p-Me, p-MeOC$_6$H$_4$). IR studies revealed partial anion coordination, especially for [Ag{P(p-MeOC$_6$H$_4$)$_3$}$_2$(OClO$_3$)] [771]. Tricyclohexylphosphine reacts in acetonitrile affording [Ag(L)$_2$(O$_2$NO)] and [Ag(L)$_2$(OClO$_3$)] respectively with J_{AgP} of 457 and 447 Hz, an observation accounted for by dimerization of the perchlorate in solution [763]. The crystal structure determination of [Ag{As(C$_6$H$_5$)$_3$}$_3$][ClO$_4$] and [Ag{PPh$_2$(C$_6$H$_{11}$)}$_2$][ClO$_4$] revealed weak metal-perchlorate ion interactions [743].

Ag(hfac) produced by reacting Hhfac and Ag$_2$O in THF, is reactive towards dmpm forming Ag$_2$(μ-dmpm)$_2$(hfac)$_2$ where the diketonate anions may be regarded as ionic due to their loose contact with silver [764]. An unusual coordination environment which is typically described as AgP$_3$O$_2$ was observed in Ag(ONO$_2$)(PPh$_3$)$_3$, a by-product of the reaction of AgNO$_3$ and PPh$_3$ with phenylacetylene in aqueous ethanol [765]. Ag(O$_2$CNR$_2$) formed by the reaction of Ag$_2$O with secondary amines in the presence of CO$_2$, reacted with two equivalents of PPh$_3$ to afford Ag(PPh$_3$)$_2$(O$_2$CNR$_2$) [766]. Reaction of bis(diphenylphosphino)methane with two equivalents of AgOAc to form [Ag$_2$(μ-OAc-O,O')(μ-OAc-O)(μ-dppm)$_2$]·2H$_2$O, reacting rapidly with two more equivalents of dppm to yield [Ag(η^2-OAc)(μ-dppm)]$_2$·2CHCl$_3$. ^{31}P NMR studies reveal that Ag$_2$(μ-OAc)(μ-dppm) is the sole dissociation product in solution [767]. An AgO$_3$N environment was the result of the reaction of AgNO$_3$ and Picloram in aqueous ammonia, the product being [(picloram)Ag(H$_2$O)]$_2$·2H$_2$O [768].

Semichelate semibridging nitrate and bridging 1,1'-bis(diphenylphosphino)ferrocene (dppf) are present in [Ag(NO$_3$)(dppf)]$_2$. The corresponding perchlorate [Ag(OClO$_3$)(dppf)] replaces the perchlorate ion by PPh$_3$ or SPPh$_3$ affording [Ag(dppf)(L)](ClO$_4$) while with PPh$_2$Me [Ag(dppf)(L)$_2$][ClO$_4$] is obtained and with bidentate ligands such as phenanthroline, bipyridine, bis(diphenylphosphino)methane disulfide or with Na(S$_2$CNR$_2$) (R = Me, Et) four-coordinate complexes [Ag(dppf)(L-L)][ClO$_4$] and [Ag(S$_2$CNR$_2$)(dppf)] are realized [769]. Reaction with sodium carboxylates produces Ag$_2$(HCO$_2$)(μ-L)$_2$ with syn-μ-L, two chelate bridging and two triply bridging and chelating L, [Ag$_2$(MeCO$_2$)$_2$(μ-L)]$_2$ with a chair conformation of four tetrahedral silver with syn-μ-L, two chelate bridging and two triply bridging carboxylates, [Ag$_2$(PhCO$_2$)(μ-L)] with μ-benzoates giving rise to trigonal silver environment [770].

Planar *mer*-triaza and *fac*-triangular trithia moieties are observed in the coordination sphere of silver with the macrocyclic ligand derived from the condensation of 2,6-diacetylpyridine and 3,6,9-trithiaundecane-1,11-diamine in the presence of AgClO$_4$ [734]. The stability constants of silver 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane complexes have been calculated in a range of solvents [771].

The IR and Raman studies of Au(acac)(PPh$_3$) are reported along with several bis(isonitrile)gold(I) complexes [772]. Reaction of silver N-benzoyl-2-alaninate with Au(PPh$_3$)Cl in CH$_2$Cl$_2$–C$_6$H$_6$ produces Au(PPh$_3$)(L) where the acid ion is monodentate to the gold [773].

Potassium phenolate reacts with $(AuPR_3)(BF_4)$ in THF affording $[(AuPR_3)_2OPh][BF_4]$ (R = Et, Ph, *o*-tolyl) characterized by NMR measurements. The more sterically demanding quinolin-8-olate reacts with two equivalents of $(AuPR_3)(BF_4)$ yielding the dimer $[(AuPPh_3)_2(L^-)][BF_4]$ with an AuOP and an AuNOP environment owing to intramolecular Au···O interaction [774].

Relativistic electronic structure calculations have been carried out for the main-group element-centered octahedral gold cluster cations $[(LAu)_6X_m]^{m+}$ (with central atoms X = B, C, N and L = PH_3, PMe_3) as well as for the corresponding four-and fivecoordinate element-centered cations $[(LAu)_4X_m]^{(m-2)+}$ and $[(LAu)_5X_m]^{(m-1)+}$ [775].

3.3.3. *Nitrogen and sulfur donors*

Several heterocyclic compounds, especially thioamides, have been shown to coordinate to group 11 metal ions in a bridging fashion. A recent review [776] appeared discussing in detail the structural features of the complexes of bridging thionates, in which, several points concerning group 11 thionates are presented.

3.3.3.1. Copper complexes. Reaction of metallic copper with sulfur in refluxing pyridine afforded the cluster $Cu_4(S_5)_2py_4$ investigated by TGA and X-ray diffraction [777]. The tetramer [Cu(tri-*tert*-butoxylsilanethiolate)]$_4$ readily reacts with Lewis bases to form compounds fo the formulae $[Cu(L)]_2(bpy)_2$ or $[Cu(L)(phen)]$ [778].

Reduction of $CuCl_2$ with five equivalents of pyridine-2-thione in ethanol and subsequent reaction of the product $Cu(pytH)_3Cl$ with $[Cu(MeCN)_4]^+$ resulted in the formation of an insoluble product of the stoicheiometry $[Cu(pyt)]_n$ in which the thionate ligand is probably bridging through S and N [779]. Reaction of $[Cu(MeCN)_4][PF_6]$ with pyridine-2-thione in acetone revealed the successive formation of several species in solution, while over a period of one month crystals of the corresponding hexameric thiolate emerged [780]. Similar reactivity was observed for quinoline-2-thione in THF [781]. Partial deprotonation of dioxa- and oxathiazoline-2,4-diones and dithiones occurs upon reaction with copper salts to produce N,S or N,O bridging ligands. XPES core line binding energy shifts for a series of these complexes was correlated to CNDO derived atomic charges [782]. Electrochemical deposition of 4,6-dimethylpyrimidine-2-thione (LH), on copper anode in acetonitrile affords the hexamer $[Cu_6(L)_6]\cdot H_2O$ which upon reaction with 1.5 equivalent of diphosphines forms $[Cu(L)(dppm)]$ and $Cu_2(L)_2(dppe)_3$, respectively. The ^1H, ^{13}C and ^{31}P NMR data are reported and the structure of the initial cluster presented [783]. The compound $[cyclo\text{-}\{bis\text{-}\mu_2(\eta^2\text{-}S,\eta^1\text{-}N\text{-}L)\text{-}bis\text{-}\mu_3(\eta^2\text{-}S,\eta^1\text{-}N\text{-}L)Cu^I_4\}\cdot toluene]$ was obtained electrochemically using a copper anode and thiazolidine-2-thione solution in toluene [784]. Imidazoline-2-thione reacts with CuSCN in MeCN/EtOH to give $Cu(L)_2(NCS)$ [785]. *N*-methyl-imidazoline-2-thione solutions form electrochemically, on a copper anode, $[Cu(L)]_4$ with a slightly flattened Cu_4 tetrahedral core [786]. The reduction of $CuCl_2$ with 4-amino-3-methyl-1,2,4-Δ^2-triazoline-5-thione in water at different pH values produced several mixed valence copper complexes where both amino and azo- nitrogen atoms coordinate to copper [461]. In an analogous reaction, its 1,4-dihydro- counterpart formed initially $\{Cu_2Cl_4(L)\}_n \cdot nH_2O$ which was readily reduced by copper to yield the mixed valence $\{Cu_2^{II}Cu^{I}Cl_5(OH_2)(L)_2\}_n \cdot 2nH_2O$ [787].

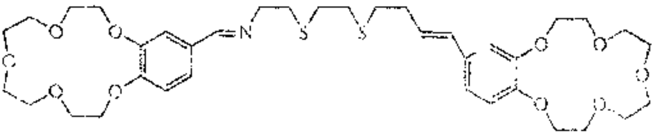
Copper arenes react with CS_2 in the presence of diimines to afford Cu(dithioarene)(diimine) compounds, the corresponding perthioarene ones as well as {Cu(perthioarene)}$_2$(diimine) and Cu$_2$(μ-perthioarene)(μ-dithioarene)-(diimine)$_2$ [788]. 1,1'(2,2'-bis(1,2,3-trithio-1,3-propanediyl))ferrocene in CH_2Cl_2 reacted with $[Cu(MeCN)_4](BF_4)$ to afford either $[Cu(L)(MeCN)_2][BF_4]$ or $[Cu(L)_2][BF_4]$ the latter giving NMR similar to that for the free ligand [789].

The mixed valence *catena*-{[1,6-bis(5'-methylimidazol-4'-yl)-2,5-dithiahexane]-Cu$_2$(μ-SCN)$_3$Cu} possesses a distorted tetrahedral $CuNS_3$ chromophore and reveals a three-dimensional network through thiocyanato bridging of neighboring units [790]. Derivatives of the Cu(I) form of Dopamine-β-hyroxylase have been made in which the Cu_B center was studied by EXAFS and IR. It has been found to be coordinated to two histidines, a sulfur and a fourth, as yet unidentified ligand. The site appears not to be perturbed by Cu_A removal. EXAFS results indicate that CO does not displace the S ligand but the weakly bound ligand X [791].

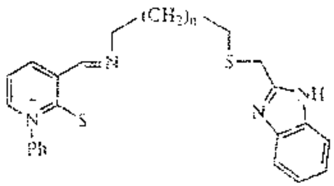
CuSCN adds to MS_4^{2-} in acetone to give $[MS_4(CuNCS)_2]^{2-}$ and polymeric $[MS_4(CuNCS)_4]$ with Cu atoms bonding to MS_4 edges [792]. Addition of 1.5 equivalent of CuCl and phenanthroline to WS_4^{-2} in acetonitrile leads to formation of $[WS_4\{Cu(phen)\}_2]^{2-}$ [793]. Treatment of MS_4^{2-} and CuCl with KSCN in acetone acetonitrile at various ratios, poduced compounds with the stoicheiometries $[MS_4Cu_4(NCS)_5]^{3-}$ $[MS_4\{Cu(NCS)\}_4]^{2-}$ (M = Mo,W) and $[WS_4\{Cu(NCS)\}_2]^{2-}$ [794].

The Schiff bases derived from 3-formyl-1-phenyl-2(*1H*)-pyridinethione and a variety of amines form 1:1 complexes with divalent copper which are reduced in acetonitrile and DMF in the region −0.17 to +0.24 V [795]. Thirty two- and thirty four-membered macrocyclic Schiff bases with two N_2S_2 donor sets form $[Cu_2(L)]^{2+}$ in a mixture of MeCN CH_2Cl_2. Tetrahedral copper environments are observed with an overall helical structure [796]. The Schiff base derived from 1,2-diaminoethane and 2-(phenylethylthio)benzaldehyde forms $[Cu(L)][ClO_4]$ with CuN_2S_2 environment [797].

Polythiaether compounds react with copper salts to form ionic or molecular complexes depending on the coordinating ability of the anions. For example, 2,5,8-trithia[9]-*o*-benzenophane forms with $[Cu(MeCN)_4][ClO_4]$ the $[Cu(L)(MeCN)][ClO_4]$, but readily transforms to [Cu(NCS)(L)] upon reaction with thiocyanate [798]. Macrocyclic quadridentate and quinquedentate polyaminopolythiaethers [14]aneN_nS_{4-n} (n = 0-4) and [15]aneN_nS_{5-n} (n = 0–2) use all their heteroatoms for coordination to copper. The stability constants appear to be independent of the anions X within each family of compounds [799]. $Cu(ClO_4)_2$ reacts with 6,7,15,16-tetrahydrodibenzo-[f,m][1,8,4,11]dithiadiazacyclo-tetra decane in refluxing EtOH to give $[Cu(L)][ClO_4]$ which possesses a butterfly CuS_2N_2 chromophore. Reaction with triphenylphosphine in acetone leads to PPh_3 with subsequent macrocycle reorientation to give a trigonal CuNSP coordination environment [800]. The reaction of 1,4,10,13-tetrathia-7,16-diazacyclobutadecane with copper carried out in alcohols produced complexes of the formula $[Cu(L)]^+$ while its di-*N*-methyl substituted analog formed $[Cu_2(Me_2L)(MeCN)_2]^{2+}$ in acetonitrile [801]. Polydentate 2,2'-bis(4-methylthio-imidazol-2-yl)biphenyl [802], *trans*-quadridentate 6,7,15,16-tetrahydrodibenzo[f,m][1,8,4,11]dithiadiazacyclotetradecine and 7,8,16,17,18-pentahydro-*1H,6H*-dibenzo[*g,O*][1,9,5,13]-dithiadiazacyclohexadecine



XXIX



n = 2 - 4

XXX

triflates [803] and Schiff bases **XXIX** and **XXX** give compounds with local CuN_2S_2 environments. ^1H NMR studies of the latter show that longer aliphatic chain gives rise to stronger Cu–N and weaker Cu–S bonding. Redox properties of these compounds are correlated to their structure [804]. For the former, ^1H and ^{13}C NMR studies confirm the coordination environment of the copper center as well as the sodium ion inclusion in the polyether sites [136]. New Schiff-base bis(crown ether) ligands containing recognition sites for transition-metal guest cations have been prepared by the condensation of two equivalents of 15-formyl-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine with diamines H_2NXNH_2 ($X = (CH_2)_2S(CH_2)_2S(CH_2)_2S(CH_2)_3S(CH_2)_2, (CH_2)_2S(CH_2)_6S(CH_2)_2, (CH_2)_3S(CH_2)_2S(CH_2)_3$ or $(CH_2)_2NH(CH_2)_2$). Homometallic copper(I) complexes and heteropolymetallic copper(I)-sodium and potassium complexes have been isolated [805].

Peptide-like *N*-*N*{(5-methyl-2-thienyl)methylidene)-L-methionyl]histamine forms $[Cu(L)][CF_3SO_3]$ which is oligomeric in solution [806]. Phosphohydrazide $SPPh(NMeNH_2)_2$ reacts with $Cu(ClO_4)_2$ to yield a spirocyclic cyclometallophosphohydrazide with CuN_2S_2 local environment [807]. The reaction of Cu^{II}(1,2-(ethylthio)amino-cyclohexane) with Cu^{I}bis(pyrazolyl) dihydroborate proceeds with the formation of a trimetallic mixed valence system where each of the sulfur atoms bridges the divalent and a monovalent copper leading to trigonal coordination around each cuprous ion [808].

1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithia-5-nonanol reacts with two equivalents of $Cu(ClO_4)_2$ in acetonitrile in the presence of SCN^- and ascorbic acid to give $[Cu_2(L)(NCS)_2]$ with bridging thiocyanates [809]. 2-methyl. 2.3-dimethyl and 2.5-dimethylpyrazine undergo analogous reactions in water to afford compounds with the same stoicheiometry [59].

3.3.3.2. Silver and gold complexes. 1-diphenylphosphino-2-thioethyl-ethane reacts with $AgClO_4$ in a 2:1 ratio in Et_2O/propylene carbonate to yield $[Ag(L)_2][ClO_4]$ with chelating N.S ligand [810]. 2-Methylphenyl and 2.6-dimethylphenyl dithiocarbonates react with $AgNO_3$ in DMF and are recrystallized from pyridine to produce $[Ag_4(L)_4py_3]\cdot 1/2py$ and $[Ag_4(L)_4py_4]$, respectively, with the common characteristics that central AgS_3N atoms are observed and of the sulfur atoms half are acting as monodentate and the other half as bridging. For the latter ligand, a 2:1 reaction affords $[Ag_4(L)_6](NO_3)\cdot 1/2DMF\cdot H_2O$ where each silver atom besides being coordinated to four sulfur atoms bears close contacts to two neighboring silver atoms [811].

4,6-diamino-2-methylthio-5-nitrosopyrimidine anion forms $AgL\cdot H_2O$ in water with $AgNO_3$. The presence of water is confirmed by TG measurements while spectroscopic data collected argue for a polymeric structure with N.S coordination to the silver atom [812].

NMR studies verify the pseudotetrahedral environment around silver in the AgL_2 complexes formed in MeOH by thiophene-2-carbaldehyde imines and 5-methyl and 5-(dimethyl-*tert*-butyl)silyl- substituted ones [20]. The photo- and thermal isomerization of silver dithizonate was studied spectrophotometrically in various solvents. The photoisomerization is reversed in the dark [813].

[*N*-*N*((5-methyl-2-thienyl)methylidene)-L-methionyl]histamine forms a cationic 1:1 complex with $AgCF_3SO_3$ which is oligomeric in solution and possesses a AgN_2S chromophore [806]. In $[Ag(L)(NO_3)]$ (L = 1,5-bis(3.5-dimethylpyrazol-1-yl)-3-thiapentane) the metal atom is coordinated, in a distorted-tetrahedral fashion, by two nitrogens, one thioether and a monodentate nitrate anion [814]. N.N′-ethyl-linked [9]-NS_2 coronand reacts with $AgNO_3$ in MeOH to yield $[Ag(L)]^+$ with a very distorted AgN_2S_4 environment [815]. Thia-alkane-bridged bis(benzimidazoles) with various pendant groups were used to assess metal selectivity monitored by ^1H NMR, FAB MS and molecular modeling. Selectivity for silver ion was studied by all of these techniques. Some useful separations were effected, the most striking being that for silver ions over lead. The lack of comparison amongst the results from the methods chosen indicates that a full understanding of the complex kinetics of three-phase transport is still to be attained [816].

2,5,8-trithia[9]-*m*-cyclophane forms in acetonitrile $[Ag(L)][CF_3SO_3]$ with various conformations and degrees of oligomerization in mutual fast exchange. The solid-state structure obtained incorporates a acetonitrile molecule and reveals exodentate sulfur coordination to three different silver atoms, quite similarly to the 5-oxa-derivative [817].

New Schiff-base ligands containing recognition sites for transition-metal guest cations have been prepared by the condensation of two equivalents of 15-formyl-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine with diamines H_2NXNH_2 ($X=(CH_2)_2S(CH_2)_2$, $(CH_2)_2S(CH_2)_2S(CH_2)_2$, $(CH_2)_2$

$S(CH_2)_3S(CH_2)_2$, $(CH_2)_3S(CH_2)_2S(CH_2)_3$ or $(CH_2)_2NH(CH_2)_2$). ^{13}C NMR titration studies suggest that the stoicheiometry of the heteropolymetallic silver(I)–sodium and potassium ligand complexes is dependent upon the stereochemical requirements of the silver(I) guest cation [805]. The macrocycles 1,4,11-trithia-8,14-diaza[5,6]:[16,17]dibenzocycloheptadecane, the 1,4-dioxa-11-aza- analog, 1,12-diaza-3,4:9,10-dibenzo-5,8,15-trithiacycloheptadecan and its 5,8-dithia-15-aza- and 5,8-dioxa-15-thia- analogs react with silver perchlorate in boiling ethanol. In most cases all the heteroatoms bind to the metal [818].

Treatment of $(NH_4)_2MS_4$ (M = Mo, W) with AgI and excess of α- or γ-methylpyridine affords polymeric $[(AgL)MS_4]_n$ with four-coordinate silver atoms [819]. $[Au(THT)_2][ClO_4]$ is a suitable starting material for the synthesis of several products upon THT displacement. In this way $Au(py)_2^+$, $[Au(THT)(L)]^+$ (L = bpy, phen) are obtained, which can further react to give $[Au(PPh_3)(L)]^+$ for which ^{197}Au Mössbauer spectroscopy establishes three-coordination. With $Ph_2PNHPPh_2$ $[\{Au(THT)\}_2(\mu\text{-}L)]^+$ is also obtained [820].

EXAFS studies verify the formation of AuSCN in acetonitrile and pyridine, less stable in pyridine owing probably to solvation [580].

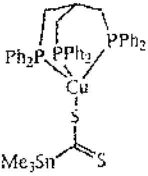
3.3.4. *Phosphorus and sulfur donors*

3.3.4.1. Copper complexes. Benzo-1,3-thiazoline-2-thione reacted in aqueous ethanol with CuX_2 to give a polymeric compound in its deprotonated form, a compound which reacts further with diphosphines to give Cu(L)(dppm) and $Cu_3(L)_3(dppe)_3$, both of which have been structurally characterized [821], mean bond distances being 2.306 and 2.318 Å for Cu–P and Cu–S, respectively. $Cu(PPh_3)_2(NO_3)$ reacts with heterocyclic thiones in EtOH/acetone to give ionic or $[Cu(PPh_3)_2(L)_2][NO_3]$ [822] while the potassium salt of tetraphenyldithioimidodiphosphin reacts with $Cu(PPh_3)_2(NO_3)$ in MeOH/$CHCl_3$ to give $Cu(PPh_3)(SPPh_2)_2N$ where trigonal CuS_2P environment is realized [823]. In analogous reactions several $Cu(thione)_2(PPh_3)_2][ClO_4]$ were isolated and the structure of $[Cu(pytH)_2(PPh_3)_2][ClO_4]\cdot 2CHCl_3$ was solved [824].

Several polypyrazole thiophenolates form readily complexes reducing Cu(II) [825] while 2,5,8-trithia[9]-*o*-benzenophane gives $[Cu(L)(MeCN)][ClO_4]$, which easily substitutes MeCN by pyridine, PhCN and Phosphines as ^1H and ^{13}C NMR measurements reveal [826]. Copper thiolates react with PPh_3 in $CHCl_3$/PrOH. The structure of $(CuSBu^t)_4(PPh_3)_2$ was solved and shows alternating segments of CuS_2, CuS_2P [827]. Bulky thiolates like $SSi(OBu^t)_3$ form tetramers $[Cu(L)]_4$ which react in benzene with PPh_3 to give $Cu(L)(PPh_3)_2$ [828]. Electrochemical synthesis of copper thiolates in the presence of π-acceptors produces mixed ligand complexes of the formulas $(CuSph)_2(PPh_3)$, $(CuSR)_2(PPh_3)$ (R = *p*-tolyl, naphthyl), $(CuSR)(PPh_3)_2$ (*o*-MeC_6H_4, *m*-MeC_6H_4) [829]. Analogous reactions carried out chemically give $Cu(1,2\text{-dimercaptopropane})(PPh_3)_2$, $Cu(1,2\text{-dimercaptoethane})(dppm)_2$ and Cu(1,3-dimercaptopropane)(dppm) [382]. Reaction of diphenylphosphinomethane with several thiolates afforded (CuSR)(dppm) (R = Bu^n, pentyl, Ph), $(CuSR)_2\cdot(dppm)_3$ (R = *o*-tolyl). X-ray structure determination revealed a novel Cu_4S_4 ring [830]. The tetramer [Cu(tri-*tert*-butoxylsilanethiolate)]$_4$ readily reacts with triphenylphosphine to form compounds of the formulae $[Cu(L)(PPh_3)_2]_n$ [778]. Interaction of $[MoOS_3Cu(PPh_3)_2]$ and $Cu(SCH_2CH_2OH)$ in dichloromethane yielded [$MoOS_3Cu_3$(μ_3-SCH_2CH_2OH)(PPh_3)$_2$]$_2$ in the form of two cubane fragments connected by Cu-S bonds [831]. A CuS_2P_2 chromophore is postulated in $[Cu(PPh_3)_2(L)]_2$ produced by thereaction of $Cu(PPh_3)_3Cl$ and $HSCH_2CH(OH)CH_2OR$ (R = H, Me, Et) in THF [832].

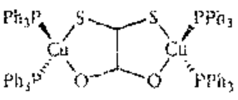
Treatment of $Cu(PPh_3)_2(S_2CSPh)$ with MeOH in CH_2Cl_2 gave the cluster Cu_{14}(μ-S)$(SPh)_{12}(PPh_3)_6$ with a Cu_8 cube inside a S_{12} eicosahedron as determined by X-ray structure determination [833].

Two and a half equivalents of 1-thiophenyl or 1-thioethyl-2-diphenylphosphinoethane react with CuY_2 in $EtOH/CH_2Cl_2$ yielding $[Cu(L)_2][Y]$ ($Y = ClO_4$, BF_4) [834]. ^{13}C NMR studies on several perthio- and dithioarene copper complexes $[Cu(L)]_4(PPh_3)_3$ or $CuL(PPh_3)_2$ indicate that delocalization in the S_2C π-system accounts for the increase in the C shielding observed [835]. A mixture of CuCl(triphos) and SnCl treated with methylithium produced



XXXI

Cu(triphos)$SnMe_3$ on which CS_2 adds to form Cu(triphos)(S_2CSnMe_3), **XXXI** [836]. $Cu(PPh_3)_2I$ and dithioxamide were treated with $Ni(phen)_2Cl_2$ in the presence of NEt_3 to give $\{Cu(PPh_3)_2\}_2$Ni(dithioxamidate) [837]. Reaction of $[Cu(PPh_3)_2]$s with thio-, dithio- and trithiooxalate forms side-on



XXXII

$Cu(PPh_3)_2$(μ-O,S-dithioxalate), **XXXII**, $\{Cu(PPh_3)_2\}_2$(μ-S,S′-S,S′-trithioxalate) [838]. Dithiophosphates react with 2 equivalents of PPh_3 to $Cu(L)(PPh_3)_2$ the crystal structure of which was solved [839].

$[Mo_2S_2(1,2\text{-ethanedithiole})]^{2-}$ reacts with $Cu(PPh_3)_2(S_2P(OEt)_2)$ to give $[\{Mo_2CuS_4(1,2\text{-ethanedithiol})(PPh_3)\}]^-$ [840]. Reaction of UCl_4 with sodium thiophenolate in the presence of cuprous thiophenolate and triphenylphosphine yielded $[(CuPPh_3)(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3(CuPPh_3)]$ where all the thiophenolates are bridging the copper atoms with the central U atom [841]. Reversible one-electron reactions at the central metal atom were observed for the trinuclear clusters $(CuPPh_3)(\mu\text{-}SR)_3Mo(\mu\text{-}SR)_3(CuPPh_3)$ where R = *p*-methyl, *p*-fluoro, *p*-chloro or *p*-

bromophenyl group [842]. Heterometallic clusters were formed by the metallation of $[Pt(PPh_3)_2(\mu\text{-}S)]_2$ with $[MY(\mu\text{-dppf})]_2$ (M = group 11 metal, Y = noncoordinating anion) in methanol, which yielded $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2M\}_2(\mu\text{-dppf})][Y]_2$, several of which were characterized by XPES studies [843]. The solid-state CT emission of $[WS_4Cu_3(dppm)_3]^{-}$ produced by the reaction of WS_4^{2-} and $[Cu_2(dppm)_2(MeCN)_4]^{2+}$ has been attributed to an excitation from an orbital with Cu–P character to a WS_4 centered one [844].

2,5,8,17,20,23-hexathia[9](1,2)[9](4,5)cyclophane reacts with phosphines (PPh_3, PPh_2Me, dppe) in MeCN CH_2Cl_2 to $[Cu_2(L)(phosphine)_2][ClO_4]_2$ studied by ^1H, ^{31}P NMR [845]. Reaction of $[Co_2(\mu\text{-}L)(CO)_6]$ (L = 1,4,7-trithiacycloundec-9-yne) with $[Cu(MeCN)_4][PF_6]$, $[Co_2(\mu\text{-}L)(CO)_6\{Cu(MeCN)\}][PF_6]$ from which MeCN is affords easily displaced by phosphines [846].

3.3.4.2. Silver complexes. Tris(diphenylthiophosphoryl)methanido silver complex with $P(Bu^n)_3$ prepared in $CHCl_3$ and precipitated from EtOH shows in the solid state AgS_3P coordination and $^3J_{PP}$ and $^2J_{AgP}$ of 7.3 and 4 Hz respectively in solution [847]. An AgS_2P_2 chromophore is postulated in $[Ag(PPh_3)_2(L)]_2$ produced by thereaction of $Ag(PPh_3)_3(NO_3)$ and $HSCH_2CH(OH)CH_2OR$ (R = H, Me, Et) in THF [832].

Maleonitrilethiolate readily forms mixed ligand complexes with phoshines, e.g. $Ag_2(L)(PPh_3)_4$ where the existence of both trigonal $AgSP_2$ and tetrahedral AgS_2P_2 is verified [848]. Aryldithiocarboxylates of the formula $[Ag(S_2CAr)(PPh_3)]_2$ and $Ag(S_2CAr)(PPh_3)_2$ are formed with Ar = phenyl *o*- and *p*-tolyl. The latter complexes undergo dissociation in solution with fast phosphine exchanges while in the solid state the dithio ligand is proved to be chelating with one sulfur atom bonded two both silver atoms [849]. Cationic $[Ag(PR_3)_2]^{+}$ react with $[M(MNT)_2]^{2-}$ in CH_2Cl_2/H_2O to give $[M(MNT)_2\{Ag(PR_3)_2\}_2]$ (M = Ni, Pd, Pt, R = Ph, *n*-Bu) which reveal $E_{1/2}$ positive by approximately 150 mV relative to $[M(MNT)_2]^{2-}$. Ag to M contacts shorter than the van der Waals radii are present [850].

The thermodynamic parameters for complexation of silver(I) with Ph_2PCH_2SPh and $Ph_2P(CH_2)_2SR$ (R = Me, Et or Ph) have been determined by potentiometric and calorimetric techniques in propylene carbonate and DMSO at 298 K. The different behavior of the ligands in the two media is discussed in terms of the different physicochemical properties of the two solvents [851].

Four tetrahedral AgS_3P and two trigonal AgS_3 are observed in $[\{Mo_2Ag_6S_6(SBu^t)_2\}_2](O)_2(PPh_3)_4$ obtained from the treatment of $\{MoAg_2S_3\}(O)(PPh_3)_3$ with $AgSBu^t$ in CH_2Cl_2 and crystallization from PrOH/Et_2O [852]. $MoS_4\{Cu(CN)\}$ and $MoOS_3\{Cu(CN)\}$ react with $Ag(PPh_3)_2(NO_3)$ in MeCN/CH_2Cl_2 to give linear $(PPh_3)_2AgS_2MoS_2Cu(CN)$ and bent $(PPh_3)_2AgS_2MoOSCu(CN)$ trimetallic species respectively [853]. Reaction of $[WS_4Cu(CN)]^{2-}$ and $AgNO_3(PPh_3)_2$ yielded the cluster $[\{AgS_2WS_2Cu\}(CN)(PPh_3)_2]^{-}$ with a linear Ag W Cu arrangement and local AgS_2P_2 and CuS_2C environments [854].

7,8-dithia-7,8-dicarba-*nido*-undecaborate and 7-thio-8-methyl-7,8-dicarba-nido-undecaborate react with $AgNO_3$ in MeOH in the presence of triphenylphosphine to give $Ag(L)(PPh_3)$. Similar reaction with bipyridine is reported instead of PPh_3 but when (1′,13′-dithia-4′,7′,10′-trioxatridecane-1′,13′-diyl)-7,8-dicarba-*nido*-undecaborate are used the macrocylce's oxygen and sulfur heteroatoms bind to silver making unnecessary the presence of Lewis bases for stabilization of the complexes [855].

Reaction of $[Co_2(\mu\text{-}L)(CO)_6]$ (L = 1,4,7-trithiacycloundec-9-yne) with $AgBF_4$ and PPh_3 yields $[Co_2(\mu\text{-}L)(CO)_6\{Ag(PPh_3)\}][BF_4]$ where the $Ag(PPh_3)^+$ fragment is coordinated by all three sulfur atoms of the polythiaether [846].

3.3.4.3. *Gold complexes.* Thiuracilate reaction with $AuCl(PPh_3)$ in MeOH affords $Au(PPh_3)(L)$ studied by IR and X-ray diffraction [856]. Identical reaction with $AuCl(PEt_3)$, $[Ag(PPh_3)_n](NO_3)$ and $[Au(dppe)_2]Cl$ is reported where the product of the latter has the formula $[Au(dppe)_2](L^-)\cdot LH$ [857]. The anion of 6-mercaptopurine coordinates to Au in the presence of phosphines and IR, ^1H and ^{31}PNMR spectra confirm the existence of $Au(L)(PR_3)$ (R = Et, Ph, *p*-tolyl, Cy), $(AuL)_2(\mu\text{-}P\text{–}P)$ and $(AuCl)(\mu\text{-}P\text{–}P)(AuL)$ where P–P = dppm, dppe, dppp [858]. Reaction of $AuCl(PPh_3)$ with $Pb(SR)_2$ in dry acetone resulted in formation of $Au(PPh_3)(SR)$ (R = Et, Pr, Bu, Ph, Bz, Mes, C_6F_5) which were studied by IR, ^1H, ^{13}C and ^{31}PNMR spectroscopic techniques [859]. Mercaptooxopurines 8-mercaptotheophylline, 8-mercapto-2-thiotheophylline and 8-methylthiotheophylline react in alkaline media with $AuCl(PPh_3)$ or $(AuBr)_2(dppe)$ to afford $[Au(PPh_3)(L^-)]$, $[\{Au(PPh_3)\}_2(\mu\text{-}L^-)]$ and $AuCl(\mu\text{-}L^-)(\mu\text{-}dppe)Au$, $[(AuL)_2(\mu\text{-}dppe)]$, respectively. ^1H, ^{13}C and ^{31}PNMR data are reported and the crystal structure of $Au(PPh_3)$(8-mercaptotheophyllinato-S)]determined [860]. The purines are bonded through the S8- and in the case of bridging conformation N7- is also involved.

Deprotonation of benzenehexathiol in the presence of $[Au(PPh_3)Cl]$ gave an hexanuclear gold(I) compound where the hexagon of the benzene carbon atoms is surrounded by a hexagon of sulfur atoms, followed by a hexagon of gold atoms and the wheel-like structure is completed by six peripheral phosphine ligands [861]. Reaction of $[AuCl_4]^-$ with 2,2′-thiodiethanol in MeOH followed by addition of bis(diphenylphosphinomethyl)phenylphosphine and NaSCN gave $[Au_4(L)_2(SCN)_2]^{2+}$ and $[Au_3(L)_2]^{3+}$ consisting of nearly linear Au chains with weak Au-Au intramolecular bonding interactions. Both complexes show RT photoluminescence. The photophysical properties of $[Au_3(L)_2]^{3+}$ are discussed [862].

The reaction of $[\{P(Pr^i)_3\}$(2,3,4,6-tetra-*O*-acetyl-1-thio-*β*-D-glucopyranosato-S)]gold(I) with serum albumin has been studied in buffered aqueous solution using ^{31}P NMR spectroscopy. The reaction occurs at cysteine-34 via displacement of the anions to form $\{(AlbS)Au\{P(Pr^i)_3\}\}$ from which the phosphine is displaced by cyanide. $\{P(Pr^i)_3\}AuCl$ behaves analogously but further reacts at weak binding sites analogous to the histidine binding sites of auranofin. In order to interpret the protein studies, a variety of potential reaction products ($\{P(Pr^i)_3\}AuX$, X = CN, AtgS, Cl; $YP(Pr^i)_3$, Y = O, S) were prepared and characterized by ^{31}P NMR spectroscopy [863].

Mixed ligand dithiolate phosphine complexes of gold show linear AuSP environment $[Au_2(\mu\text{-}S(CH_2)_3S)(\mu\text{-}dppm)]$, linear and irregular trigonal gold in

$Au_2(\mu\text{-MNT})(PPh_3)_2$ and $Au_2(\mu\text{-}S_2C_6H_4)(PPh_3)_2$ due to intramolecular Au···S interaction. In addition, $AuPEt_3^+$ and $Au_2(\mu\text{-}S_2C_6H_3Me)^{2-}$ form $[Au_2(\mu\text{-}S_2C_6H_3Me)(PEt_3)_2]$ with two AuS_2 and two AuS_2P local chromophores [864]. Reactions of $[Au_2(\mu\text{-dppm})_2][ClO_4]_2$ with $[AuX_2]^-$ (X = Cl or Br) afforded dinuclear $[Au_2(\mu\text{-L-L})_2]$[L-L = S_2CNR_2, R = Me, CH_2Ph] which further reacted with $[Au_2(\mu\text{-P-P})_2][ClO_4]_2$ (P-P = dppm, dppe) leading to the heterobridged dinuclear complexes $[Au_2(\mu\text{-}S_2CNR_2)(\mu\text{-P-P})](ClO_4)$ [473].

Complexes $Au(L)_2(S_2COR)$ (R = Me, Et, Bu, L = PPh_3, $P(CH_2CN)_3$) luminesce in solution and in the solid state probably through a $n \rightarrow \pi^*$ transition [865]. Substituted benzenethiolates and PPh_3 or 1,3,5-triaza-7-phosphoadamantanetriyl phosphine afford Au(SR)(L), luminescent in the solid state at 77 K. The crystal structures for the triphenylphosphino compound of *o*-chloro-benzenethiolate, and the adamantane phosphine of benzenthiolate, *o*-methoxy-benzenethiolate and 3,5-dichlorobenzenethiolate are reported [866]. ^1H and ^{31}P NMR as well as UV–Vis studies of open-end [Au(*p*-thiocresol)]2(μ-P-P) or cycle dinuclear $Au_2(\mu\text{-}S\text{-}S)(\mu\text{-P-P})$ are reported, *S-S* standing for 1,3-propanedithiol or 3,4-toluenedithiol, P-P = dppm, dppe, dppp, dppb, 1,5-bis(diphenylphosphino)pentane [867]. Aryldithiocarboxylates form $Au(S_2CAr)(PPh_3)$ and $Au(S_2CAr)(PPh_3)_2$, the latter being stable only below 243 K (Ar = Ph, *p*-tolyl, *o*-tolyl). A remarkably long Au–S bond of 2.860(4) Å is observed in $Au(S_2CPh)(PPh_3)_2$ giving rise to a practically AuP_2SS' environment [868]. The diphosphino complexes $[(AuCl)_2(\mu\text{-P-P})]$ where P-P = *cis*-1,2-diphenylphosphinoethylene, dppe, dppb and 1-diphenylphosphino-2-diphenylarsino-ethane react with K(i-MNT) in MeOH to form heterobridged dimers $[Au(\mu\text{-i-MNT})(\mu\text{-P-P})]$ [869]. Both N,S coordination occurs in 6-thiopurinate and 2,6-dithioxanthate in $Au(PR_3)(L^-)$ and $(Au(PR_3))_2(\mu\text{-L})$ complexes while only S coordination is involved in the case of the 2,4-dithiuracilate analogues on the basis of ^1H, ^{13}C and ^{31}P NMR studies (R = Et, Ph) [870].

Characterization by ^{31}P NMR of $[Pt_2(PPh_3)_4(\mu\text{-SAuPPh}_3)_2]^{2+}$ and $[Pt_2(PPh_3)_4(\mu\text{-S})(\mu\text{-SAuPPh}_3)]^+$ confirms the existence of AuSP environment in both cases [871]. Dibenzyldisulfide or sodium benzylthiolate react with $Au(PPh_3)(NO_3)$ in CH_2Cl_2 to produce $[Au_2(PPh_3)_2(\mu\text{-}SCH_2Ph)](NO_3)$, which is shown to dimerize to a rhombic cluster in the solid state [872].

$AuCl(PEt_3)$ ionizes in water and in contact with albumin is shown by ^{31}P NMR measurements to S-bond to it while eliminating a PEt_3 molecule that reduces disulfide bonds [873]. The synthesis, IR and Raman studies of [Au(PEt₃)(L)] (L = SMe_2, tu, H_2O) and $\{Au(PEt_3)\}_2(\mu\text{-S})$ is reported [629].

3.3.5. *Miscellaneous*

Several copper aryloxides react with phosphines and PhNCS to give mixed ligand compounds $[Cu(\mu\text{-SCNPh})(phosphine)_2(OAr)]$ (PPh_3, Ar = 2,6-dimethyl-C_6H_3, 4-methyl-C_6H_4), $[Cu(\mu\text{-SCNPh})(OAr)(phosphine)]_2$ ($P(OMe)_3$, Ar = 2,6-di-*tert*-butyl-C_6H_3 and PPh_3, Ar = 4-methoxy-C_6H_4), $[Cu(\mu\text{-SCNPh})(OAr)]_n$ ($P(OMe)_3$, Ar = 2,6-dimetyl-C_6H_3) [874].

The cyanoacetate complex $[\{(PPh_3)_2Cu\}_2(\mu\text{-L})_2]$ was studied by X-ray diffraction and revealed monodentate carboxylate and cyano moieties bound to the copper centers. Its facile reversible carboxylation-decarboxylation was monitored with IR and ^{13}C NMR measurements [875]. Addition of phenol to $[Cu(phen)(PPh_3)(HCO_3)]$ yielded $[Cu(phen)(PPh_3)(OPh)]$ which treated with CO_2 in water reverted to the initial complex [876].

Both $[Cu(SePh)]_n$ and $[Ag(SePh)]_n$ which were obtained electrochemically and are reactive towards phenanthroline and triphenylphosphine leading to the formation of $[Cu(SePh)(L)]$ compounds [877]. Analogous reactions occur between coinage metal thiolates: in the case of 2-methyl-thiophenol, the gold thiolate is realized in poor yields while the silver one does not react with phenanthroline. The structure of $[Cu(L)(phen)]_2 \cdot MeCN$ is reported [878]. Electro-oxidation of Se_2Ph_2 in the presence of PPh_3 on a copper anode gives $Cu(PPh_3)(\mu\text{-}SePh)_2 \cdot MeCN$ with trigonal $CuSe_2P$ and tetrahedral $CuSe_2P_2$ environments [879].

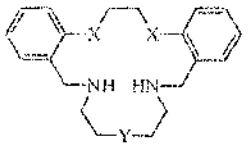
Reaction of CuOAc with $Y(SiMe_3)_2$ and PR_2R' (Y = S, Se, R, R' = Et, Ph) in Et_2O or THF afforded $[Cu_{12}Y_6(PR_2R')_8]$ (Y = S, Se, PPh_2Et; Y = S, PEt_3) and $[Cu_{20}S_{10}(PPh_3)_8]$ [CuSP [880]. The crystal structures of $[Cu_{44}Se_{22}(PEt_2Ph)_{18}]$ and $[Cu_{44}Se_{22}(PBu^nBu^t_2)_{12}]$ were determined [881]. Triethylphosphine and CuCl react in the presence of $Se(SiMe_3)_2$ to produce, except the main product, $Cu_{70}Se_{35}(PEt_3)_{22}$, clusters of smaller nuclearity like $Cu_{20}Se_{13}(PEt_3)_{12}$ [882]. $Cu(PPh_3)_2(BH_4)$ reacts with $AsPh_3$ and $SbPh_3$ under CO_2 to afford $[Cu(PPh_3)_2(O_2CH)]$. The structure of the $AsPh_3$ product has been solved [883].

Mixing CuCl, PR'_3 and $Te(SiMe_3)_2$ in diethylether gave initially $Cu_4Te_4(PPr^i_3)_4$ which was further converted to higher nuclearity Cu–Te clusters. Similar reaction with $PPhEt_2$ afforded clusters of distinctively different nuclearity [884]. Similarly the silylated phosphane PPh_2SiMe_3 gave various phosphido-bridged clusters depending on the bulk of the tertiary phosphine used [885]. A mixed CuPSe environment is observed in $WSe_4(CuPMe_2Ph)_2$ and studies by X-ray, ^{31}P and ^{77}Se NMR reported [886]. The structure of the trimetallic compound $WSe_4[Au(PPh_2Me)]_2$ is also reported and discussed in connection with multinuclear NMR studies [886].

Closo-1,2-dithio-1,2-dicarbadodecaborane reacts with $CuCl(PPh_3)_2$ in EtOH by B^+ elimination becoming better coordinating ligand, therefore resulting in *nido*-7,8-dithio-1,2-dicarbaundecaborate in $Cu(PPh_3)_2(L)$ with both CuS_2O_2P and CuS_2P environments in the same crystal [887]. The reaction of $AgNO_3$ with Na_2Se_x in the presence of R_4NCl in DMF produces $[(R_4N)Ag(Se_x)]_n$, tetrameric for x = 4 with both trigonal and tetrahedral silver environments, polymeric for x = 5 with 1-D macroanions while a $[Ag_4(Se_4)_3]^{2-}$ is also isolated [888].

The solid-state reaction of WS_4^{2-} with two equivalents of AgBr and two of $AsPh_3$ at 100°C extracted with DMF gives $W_2Ag_4S_8(AsPh_3)_4$ with an AgS_3As environment. Studies of the nonlinear optical properties of the product are reported [889]. The systematic variation of the donor atom set in the dibenzo-substituted, 17-membered ring **XXXIII** on the ability of the resultant systems to discriminate between silver(I) and lead(II) has been performed; the compound containing a S_2N_2S donor set yielded discrimination of the order of 10[illegible] in favor of silver(I) in 95% methanol at 298 K [890].

Mixed ligand complexes result from the reaction of Au(L)Cl and L' in the presence



X = O, S
Y = NH, O, S

XXXIII

of $AgSbF_6$ for L = PPh_3, L′ = $SePPh_3$, while other phosphines L′ lead to formation of Au through decomposition and in the case of PMe_2Ph selenium exchange is observed. Crystal structures are reported for $Au(SePPh_3)_2^+$ and $Au(PPh_3)(SePPhMe_2)^+$ [891]. Propylene carbonate was used as the medium for the reactions of $AgClO_4$ with Ph_2PCH_2SPh or $Ph_2P(CH_2)_2SR$ (R = Me, Et, Ph) which result in the formation of several mononuclear and polynuclear species in solution, respectively. Structural determination reveals that the perchlorate ion is also coordinating to the metal [892].

Cationic and neutral oligonuclear organophosphine gold(I) complexes with organic selenolate ligands SeR^- (R = Ph, CH_2Ph, p-$C_6H_4NH_2$, p-C_6H_4Cl or naphthyl) have been prepared. X-ray crystal structure analyses have been performed for $[(AuPPh_3)_2(SeCH_2Ph)][SbF_6]$, the first example of a cationic alkylselenolate-gold complex, $[(AuSePh)_2(\mu\text{-dppe})]$, and $[(AuPPh_3)_2(SeC_{10}H_7)][SbF_6]\cdot[Au(PPh_3)(SeC_{10}H_7)]$ where the cationic and the corresponding neutral selenolate complex are linked by intermolecular Au···Au interactions, forming a trinuclear selenolate [893].

The reaction of $AuCl(AsPh_3)$ with dithiolates produces $[Au_2(L)(AsPh_3)]_n$ (L = 1,2-benzenedithiol, 3,4-toluenedithiol) or $[Au_2L]_n$ (L = 1,2-benzenedithiol) which react with phosphines to afford $[Au_2(L)(phosphine)_2]$ (Phosphines used PPh_3, PPh_2Me). Further reaction with $[Au(PPh_3)(Me_2CO)][ClO_4]$ gives $[Au_3(L)(PPh_3)_3][ClO_4]$ [894].

3.4. Complexes with ligands from all three groups

3.4.1. Copper complexes

The crystal structure of $[Cu_2(MeCN)_2\{PPh_2(o\text{-tol})\}_2(\mu\text{-Br})_2]\cdot 2MeCN$ was determined [895]. Quinaldic acid esters form polymeric $[CuI(L)]_n$ complexes with local CuI_2NO environments and a zigzag chain of CuI (methyl ester) or dimeric ones (isopropyl and *n*-butyl esters) [896]. Reaction of $CuBr_2$ with 1,5-bis(3′,5′-dimethylpyrazolyl)-3-thiapentane in EtOH–Me_2CO reduces the copper and leads to formation of $Cu_4(L)_2Br_4$ with a central Cu_4 core, large Cu–S–Cu angles (160.6°) and sulfur bridged to the next core [897]. Complexes of the formula Cu(L)X (X = Br, Cl, BF_4) have been isolated with 1,5-bis(3,5-dimethylpyrazol-1-yl)-3-thiapentane. The ligand acts as a link between two adjacent copper centers, resulting in a polymeric compound [813].

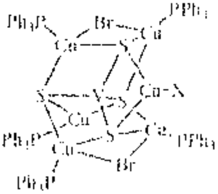
Copper halides react with benzothiazoline-2-thione and PR_3 (R = Ph, *o*-, *m*-, *p*-

tolyl) in a 1:1:2 ratio to afford $CuX(L)(PR_3)_2$ complexes, the crystal structure of the triphenylphosphine chloride being reported [898]. Reaction of CuX(phosphine) clusters with sulfur donor ligands in general produces mixed ligand complexes. $[CuX(PPh_3)]_4$ reaction with pyridine-2-thione, pyridine-4-thione and pyrimidine-2-thione produced several such products the structure of dimeric $[CuBr(PPh_3)(\mu\text{-PytH})]_2$ [899] and monomeric $[Cu(PPh_3)_2(\text{thione})X]$ (thione = benzothiazolidine-2-thione, X = Cl [898]; thione = PymtH, X = Br, [900]; thione = *N*-methylimidazoline-2-thione, X = Br [901]; thione = pymtH, X = I, [902]) were solved. Analogous reactions with tri-*p*-tolylphosphine gave again dimeric complexes the structure of $[CuCl\{P(p\text{-tolyl})_3\}(\text{pymtH})]_2$ [903] and $[CuCl\{P(p\text{-tolyl})_3\}(\text{thione})]_2$ (thione = thiazolidine-2-thione [904], benzimidazoline-2-thione and nitro-benzimidazoline-2-thione [905]) were studied crystallographically. With tri-*m*-tolyl phosphine dimeric compounds $[CuCl\{P(m\text{-tolyl})_3\}(\mu\text{-benzimidazolin-2-thione})]_2$, $[Cu(\mu\text{-Br})\{P(m\text{-tolyl})_3\}(\text{thiazolidine-2-thione})]_2$ [906], $[CuBr\{P(m\text{-tolyl})_3\}(\mu\text{-pymtH})]_2$ [907] and $[Cu(\mu\text{-I})\{P(m\text{-tolyl})_3\}(\text{pytH})]_2$ [908] were structurally characterized. The more bulky tri-*o*-tolyl phosphine gave rise to monomeric products with trigonal copper environment discrete units in the crystallographic unit cell approaching each other in a way that would lead to dimer formation. The structures of $CuBr\{P(o\text{-tolyl})_3\}(\text{thiazolidine-2-thione})$ [909] and $CuI\{P(o\text{-tolyl})_3\}(\text{pymtH})$ [910]. Structure determination revealed that tricyclohexyl phosphine behaves analogously, forming monomeric $CuI(\text{thiocaprolactam})(PCy_3)$ [911]. Electrochemical reduction of a series of iodo- complexes in acetonitrile revealed for the monomeric tri-*o*-tolylphosphine ones three irreversible peaks, and for the dimeric compounds of the other tritolylphosphines four irreversible peaks are observed therefore providing a means to distinguish between the overall structure adopted by the compounds [912]. In the case of tri-*m*-tolylphosphine where both Br and S were observed as the bridging atoms between adjacent coppers analogous measurements showed that the former can be distinguished from the three irreversible reduction peaks they reveal with respect to four of the latter [913]. Monomeric $CuX(PPh_3)_3$ also reacts with sulfur ligands to give monomeric complexes of the formula $CuX(PPh_3)_2L$. Spectroscopic studies were carried out on the complexes of *N*,*N*-dimethyl-*N'*-phenylthiourea, *N*,*N*-dibutyl-*N'*-phenyl-thiourea and thiazolidine-2-thione [914] and the structure of $CuCl(PPh_3)_2$(*N*,*N*-dimethyl-*N'*-phenylthiourea) was reported [915]. Analogous reactions with $CuX(AsPh_3)_3$ produced $CuX(AsPh_3)_2L$ (L = *N*,*N*-dimethyl-*N'*-phenyl-thiourea, *N*,*N*-dibutyl-*N'*-phenyl-thiourea, thiazolidine-2-thione [915], 3-phenyl-2-thioxo-imidazoline-4-one, 5-mercapto-1-phenyl-1,2,3,4-tetrazole [916] or thiocaprolactam [917] for which the bromo compound was structurally characterized). CuCl(dppm) reacts with the disodium salt of 3-methyl-8-ethylxanthine in EtOH–H_2O giving $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-Cl})(\mu_3\text{-L})]\cdot H_2O$ with one copper atom in a P_2ClN and two more in a P_2ClO environment [918]. $[Cu_3Cl_2(dppm)_3]^+$ reacts with sodium alkoxides in THF to give $[Cu_3(\mu_3\text{-Cl})(\mu_3\text{-OR})(\mu\text{-dppm})_3]^+$, while with excess NaOR $[Cu_3(\mu_3\text{-OR})_2(\mu\text{-dppm})_3]^+$ was obtained. Analogous reaction was observed with NaSR [919].

Copper halides react with $P(SR)_3$ in $CHCl_3$ to give compounds of the stoichiometry $CuXP(SR)_3$. Crystal structure determinations revealed the existence of polymeric chains of the type $[CuX(\mu\text{-}P,S\text{-}P(SR)_3)]$ as well as $[CuX\{P(SPr^i)_3\}(MeCN)]_2$ [920]. CuX react with N,N-(dimethylamino)methylferrocene in CH_2Cl_2 to give $[CuX(L)]_2$ which is further oxidized to $[CuX(L)]_2(\mu\text{-}O)_2$ and upon reaction with excess CO_2 gives $[CuX(L)]_4(CO_3)_2$. Attempted crystallization of both these products led to the formation of $[Cu_4(L)_4Cl_6(\mu_4\text{-}O)]$ the crystal structure of which has been determined [921]. The structure of $CuCl(pytH)(PPh_3)_2$ prepared by the successive addition of the ligands to $CuCl_2$ was investigated [922]. The tetrahedral environment around copper is distorted as is evident from the two Cu–P bond lengths realized.

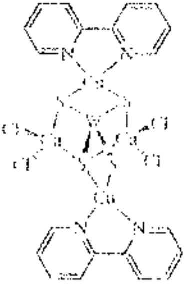
The reation of $AsPh_3$ with $CuBr(thiocaprolactam)_3$ in $CHCl_3$/MeOH yielded a product, the crystal structure of which proved it to be of the formula $CuBr(AsPh_3)(L)_2$ [923]. 2-Benzoylpyridine produces $(CuX)_2L$ (X = Cl, Br, monodentate ligand), CuLX (X = Cl, Br, I, SCN, N_3, bidentate ligand) which are nonconducting compounds and reveal CT bands in the visible and the crystal structure determination for the iodide revealed local $CuNOI_2$ environment [924].

The solid-state reaction of VS_4^{3-} with CuX and PPh_3 in the presence of NEt_4Br



XXXIV

gave $VS_4(CuPPh_3)_4Br_2(CuX)_2$ **XXXIV**, both neat and solvated with CH_2Cl_2 (upon recrystallization) where an octahedral array of copper atoms with both trigonal and tetrahedral copper atoms [925]. Tetrathiowolframate reacts with three equivalents of CuCl in acetonitrile to yield $[WS_4(CuCl)_3Cl]^{3-}$, which readily reacts with bipyridine and triphenylphosphine to give $[WS_4Cu_4Cl_4(bpy)_2]$, **XXXV**, and $[WS_4\{Cu(PPh_3)_2\}_3Cl(MeCN)]$, respectively. In the latter, the copper is situated in a P_2SCl tetrahedron [690].



XXXV

3.4.2. Silver and gold complexes

AgF and triflic acid react in toluene at −196 °C in stainless steel vessels to give $Ag_2(\mu\text{-}O_3SCF_3)_2(CH_3C_6H_5)_2$ with η^2-toluene coordination and an overall AgO_3C_2 environment [926]. Silver halides react with PPh_3 and a series of heterocyclic thiones in a 1:2:1 ratio in acetone to yield $AgX(L)(PPh_3)_2$, the crystal structure of the pyridine-2-thione chloride has been reported [927]. Reaction of AgCl with 1-thia-4,7-diazacyclononane in MeCN forms Ag(L)Cl with the ligand coordinating through all its heteroatoms [928]. When $Ag(CF_3SO_3)$ is used $[Ag_2(L)_2][CF_3SO_3]_2$ is realized where the AgL^+ units are bridged by thioether groups to attain a AgN_2SS' environment [929].

The cubane-like $(MoAg_3S_3Cl(\mu S))(PPh_3)_3$ is obtained by the 1:3:6 reaction of MoS_4^{2-} with AgCl and PPh_3 in CH_2Cl_2 [930]. Treatment of $[Mo_2O_2S_2(S_2)_2]^{2-}$ with AgCl and PPh_3 in a 1:6:12 ratio in MeCN–CH_2Cl_2 produces a cubane-like complex of the form $[MoAg_3S_3Cl_3(O)(PPh_3)_3]$ with silver in a S_2PCl tetrahedron [931]. Reaction of MSe_4^{2-} (M = Mo, W) with three equivalents of $Ag(PPh_3)_3I$ in MeCN–CH_2Cl_2 produces cubane-like $[MAg_3Se_3I(Se)(PPh_3)_3]$ with a Se_3P environment around each silver atom [932]. Chelating 1-thioethyl-2-diphenylphosphinoethane is proposed to exist in Au(L)Cl produced by the ligand's reaction with $HAuCl_4$ in PrOH–Me_2CO [833].

4. Organometallic compounds

There exists a vast amount of clusters and other compounds to which CuMes, $[Cu(PR_3)]^+$, $[Ag(PR_3)]^+$ or even MX (M = Cu, Ag, Au; X = Cl, Br, I) readily add giving rise to new clusters. These types of complexes, besides the superficial similarities reveal a wide variety in nuclearities and conformations which would make any classification extremely difficult and complicated. Therefore, the following section is limited to those complexes which are either simple in structure and in nuclearity or represent examples of new classes of compounds bearing, besides metal–carbon bonds, bonds to atoms originating from groups 15, 16 or 17. Accordingly, an enormous set of clusters with metal–metal bonds were omitted from the present study. It is important though, to note the existence of two reviews concerning the utility of organometallic compounds in the process of thin film formation through metal organic vapor deposition [933,934].

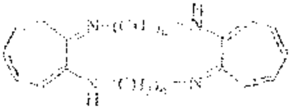
4.1. Copper complexes

A unique CuH_4 environment is observed in $[(L)HRh(\mu\text{-}H)_2Cu(\mu\text{-}H)_2RhH(L)]^+$ produced by the reaction of cuprous triflate and $Rh(L)H_3$ in dichloromethane ($L = CH_3C(CH_2PPh_2)_3$) [935]. Interestingly enough, bis(azol-1-yl)alkanes coordinate to $Cu(NO_3)(EPh_3)_2$ at the expence of a EPh_3 ligand [936]. Analogous reactions occur with the tristolylphosphine complexes. Reactions of CuCl in THF solution with several ligands bearing an ethylenic double bond resulted in the formation of $(CuCl)_x(olefin)_y$ as envisaged by the excitation bands at 238–256 nm. It seems that *trans*-configuration of the ethylene bond is essential in the stabilization of the copper coordination compound [937]. A mononuclear Cu(I) complex is the product of $Cu(ClO_4)_2$ reduction by Cu in the presence of bipyridine and styrene in CH_3OH. The copper environment is a pyramidal one [938] with singly coordinated ClO_4^-. A series of Cu(N–N)(olefin) complexes has been obtained and the influence of the chelate N–N ligand or olefin substituents on the formation constants has been investigated [939,940]. The enhanced basicity of the coordinated diamine results in substantial σ-donation to the metal center which reacts by π-back donation to the ethylene double bond. Reaction of Cu^+ with COD in MeOH produces $[Cu(\eta^4\text{-}COD)_2]^+$ and in the presence of bipyridine, $[Cu(bpy)(\eta^2\text{-}COD)]^+$ according to IR studies of the $\nu_{C=C}$ band [941]. The reaction between dioxygen and mesitylcopper in aprotic solvents leads to the formation of the oxidoromesitylcopper(I) intermediate $[Cu_{10}O_2(Mes)_6]$ and the reductive coupling of mesityl as inferred by ¹H NMR studies [942].

The reaction of $Cu[GaX_4]$ with [2.2]paracyclophane in toluene affords polymeric $[Cu(GaX_4)(L)]_n$ with η^2- coordination of copper to two cyclophane ligands and chelating GaX_4 anion [943]. A helical copper(I) triflate intermediate was isolated as the efficient catalyst for the enantioselective cyclopropanation of styrene [944]. Cuprous triflate reacts with 1,5-hexadiene in toluene at −78°C to afford $[Cu(L)][CF_3SO_3]$ in which rapid diene exchange is observed even at −100°C and from which hexadiene is readily displaced by COD [945]. Trigonal pyramidal environment is present in the compounds $[Cu_2(\mu\text{-}Cl)_2(1,4\text{-pentadiene})]_2$ and $[Cu_2(\mu\text{-}Br)_2(NBD)]_2$ which form regular-to-moderately distorted cages depending the π-acceptor capacity of the diene ligands [946].

The products are identified by ³¹P NMR. Alkynyl complexes are obtained also by the reaction of $[M(\equiv CR)(CO)_2(Cp)]$ (M = Mo, W; R = 2,6-$Me_2C_6H_3$) with $[Cu(THF)(C_5Me_5)]$ in THF at −10°C [947]. Reaction of Li(2-bis(trimethylsilyl)methylpyridine) with CuCl in THF/hexane at −78°C produces the dimer Cu_2L_2, which is further oxidized electrochemically to $[Cu_2L_2]^{2+}$ [948]. Analogous results are obtained with $AgBF_4$ and Au(CO)Cl.

Several diazadienes of the type RN=CR′–CR′=NR react with cuprous triflate in CH_2Cl_2/C_6H_{12} to form 1:1 complexes which further react with alkenes (ethylene, cyclohexene, 3-hexyne, 2-butyne-1,4-diyldiacetate) to form the mixed ligand Cu(diazadiene)(alkene)(CF_3SO_3) complexes. The diazadienes are coordinated through their nitrogen atoms whereas alkenes adopt a η^2-coordination scheme [949]. In the latter triflate is also coordinated through an oxygen atom (Cu–O 2.15 Å) whereas in the former Cu–O distance of 2.64 Å was realized. Tropocoronand ligands (**XXVI**) react in THF under CO with Cu^+ to give $[Cu_2(CO)_2(L)]$ an interesting feature of which is the solubility of the product for $n = 5$ and the insolubility of the one with $n = 6$ [950]. The chromophore is a CuN_2C one, and the compounds readily exchange CO with alkynes. Reaction of Cu^+ with 2,5,8-trimethyl-2,5,8-triazanonane in acetonitrile under CO affords $[Cu(L)(CO)]^+$ where IR studies revealed end-on coordination of CO [951]. CuCl reaction with CO in ethylvinylketone yielded Cu(CO)Cl. IR studies in solution indicate dimerization with bridging CO while in



n = 3–6

XXXVI

the solid state there exist chloro-bridges, the local copper environment consisting of three chlorine and one carbon atom [952].

Tetrameric cuprous carboxylates react with acetylenes to give either [Cu(μ-carboxylate)(PhC≡CPh)]$_2$ or [Cu$_4$(μ-carboxylate)(μ-acetylenedicarboxylate ester)$_4$] in a CuC$_2$O$_2$ environment [953]. The photoreactive species in the photoisomerization of NBD to QDC in THF in the presence of [CuX(ferrocenyldiphenylphosphine)]$_4$ (X = Cl, Br) is an bonded complex of the formula CuX(ferrocenyldiphenylphosphine)(NBD) [954].

Copper cyanide is usually a starting material for Cu(I) synthesis and often CN$^-$ is retained in the complexes. For example, 1-methyl-imidazoline-2-thione gives the polymeric [Cu(L)(CN)]$_n$ where it bridges two adjacent copper atoms and CN$^-$ is also bridging, thus leading to a CuS$_2$NC local environment and a two-dimensional extended array [955]. In [SMe$_2$Ph][Cu$_2$(CN)$_3$], the distorted anionic planes are cross-linked giving rise to both trigonal CuC$_2$N and tetrahedral CuC$_2$N$_2$ environments [78]. The absorption and emission spectra of Cu(CN)$_2^-$ have been determined in water in the presence of 0.2 to 5 M Cl$^-$ and the formation of a luminescent [Cu(CN)$_2$Cl]$^{2-}$ species is confirmed [956]. The reaction product between protoporphyrin and Cu(I) involves Cu coordination to the vinyl positions of the porphyrin as Raman band perturbation studies indicate [957].

1.2. *Silver complexes*

Reaction of Ag[GaX$_4$] with [2.2]paracyclophane in toluene afforded polymeric [Ag(GaX$_4$)(L)]$_\infty$ with mixed η^2,η^1-coordination of silver to two cyclophane ligands and two monodentate GaX$_4$ anions [913]. [N(PPh$_3$)$_2$][Ag(CN)$_2$] reacted with SnPh$_3$Cl, producing anionic complexes characterized by IR and ^{119}Sn NMR spectroscopy, an X-ray structural analysis of the silver complex evidencing an Sn–NC–Ag bridging interaction [958]. Reaction of Li(2,6-bis(trimethylsilyl)methylpyridine) with AgBF$_4$ in THF/hexane at −78°C produces the dimer Ag$_2$L$_2$ [947], while similar reaction with Au(CO)Cl produces the dimer Au$_2$L$_2$ [948].

A sandwich compound was produced by the 2:1 reaction of Ag(CF$_3$SO$_3$) with 1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne in THF. Crystal structure determination of the product revealed silver coordination to the yne sites of two ligands while different initial ratios produced small or no amount of crystals and products with coordinated triflate [959]. Reaction of the sodium salt of hydridotris(3,5-bis(trifluoromethyl)pyrazolyl) borate with AgOTf in THF led to the formation of the silver pyrazolato complex Ag(L) which readily and reversibly coordinated to CO. The structure of this adduct and of that with *tert*-butyl isonitrile were solved [960]. The first isolable silver carbonyl has been obtained by the reaction of $AgOTeF_5$ with $B(OTeF_5)_3$ under CO and its structure determination revealed its stoicheiometry as $Ag(CO)B(OTeF_5)_4$ [961].

4.3. *Gold complexes*

The intermediacy of gold complexes which has been verified in homogeneous catalytic reactions applied in organic synthesis was described in a review [962]. Single crystal luminescence studies of $K[Au(CN)_2]$ are reported for the temperature range 8–300 K. At room temperature, bands are observed at 390 and 630 nm, while the vibronic structure observed at 8 K indicates Au–Au overlap [963]. Carbonyl gold(I) bromide [AuBr(CO)] was obtained in solutions of halogenated hydrocarbons by absorption of CO by $[Au_2Br_6]$ in the presence of cyclohexene or by carbonylation of $[Au_2Br_6]$ [964]. The compound has been studied by spectroscopic methods in solution, including NMR measurements at variable temperature revealing rapid exchange process with dissolved CO [965]. $Au(PPh_3)(C_2Ph)$ was shown to be dimeric in nature with a linear AuCP environment and an Au···Au distance of 3.379(1) Å, the two units being almost orthogonal to each other [966]. The deprotonated dppm readily forms dimeric $[Au(\mu\text{-}L)]_2$ which upon treatment with $[Au(PPh_3)(THT)](ClO_4)$ and $Au(acac)(PPh_3)$ afforded a hexanuclear cluster where four $Au(PPh_3)$ units are coordinated to the central carbon atoms of the dppm ligands while the core of the original complex remains intact [967]. $HAuCl_4$ reacts with 2,5-dimethyl-2,5-isocyanohexane forming $(AuCl)_2(\mu\text{-}L)$ which, in the solid state is shown to form parallel chains of Au atoms [968]. Ortho-cyclometallated gold arylphosphines prepared from the corresponding lithiated phosphines and $AuX(ER_3)$ (E = P, As) in Et_2O prove to be dimeric with linear AuCP or AuCAs environments [969]. Dithiocarbamido methylesters (MeS)SCNHR (R = Ph, *o*-tolyl, *p*-MeOPh, 3,5-dimethylphenyl) displace THT from $Au(C_6F_5)(THT)$ in CH_2Cl_2 as ^1H, ^{19}F NMR and IR studies revealed. Reaction of the products with a small excess of NH_2R' ($R' = Bu^n$, Cy and PhEtNH) leads to amine thioacylation as $Au(C_6F_5)\{S(R'HN)CNHR\}$ are isolated [970]. Reaction of $Au(C_6F_5)(THT)$ with two equivalents of Ph_2CN_2 in Et_2O or one equivalent of $Ph_2C{=}N{-}N{=}CPh_2$ in THF yields $Au(C_6F_5)(Ph_2C{=}N{-}N{=}CPh_2)$ where AuCN environment is observed [971].

The dilithium salt of 1,2-dimethyldicarbadodecaborane reacts in CH_2Cl_2 with AuX(ylide) to form $[Au(ylide)_2][AuL_2]$ (X = Cl, Br, ylide = CH_2PPh_3, CH_2PPh_2Me, CH_2PPhMe_2) [972]. The corresponding $[Au(THT)(ylide)]^+$ CHMePPh3, $CHPhPPh_3$ and CH_2AsPh_3 readily displace THT by phen or $SbPh_3$ to afford $[Au(ylide)(L)]^+$ or by dppm or dpam to give $[\{Au(ylide)\}_2(\mu\text{-}L)]^{2+}$, while $[Au(ylide)\{Co(CO)_4\}]$ and $[Au(ylide)(C_2R)]$ are also obtained, with R = Ph, Bu^t [973]. Ylides CH_2PR_3, $CH(Me)PPh_3$, $CH(Ph)PPh_3$ form $[Au(C_6F_5)(ylide)]$ complexes which react with HCl or HBr in Et_2O to yield

AuX(ylide), while for HClO$_4$, HBF$_4$ the compounds [Au(ylide)$_2$][X] are obtained [974]. Au(C≡CBu^t) reacts with dppm and dmpm in acetone to form the acetylidenes (Bu^{t}C$_2$)Au(L) which show fluxional behavior. In chlorinated solvents [Au$_2$(μ-dmpm)$_2$]Cl$_2$ is isolated [975]. Polymeric (AuC$_2$Ph)$_n$ reacted with dppm in EtOH to afford a photoluminescent compound both in solution and in the solid state, the crystal structure of which revealed a [Au$_3$(μ-dppm)$_2$(C$_2$Ph)][Au(C$_2$Ph)$_2$] with a Au triangle in the cationic unit [976]. A report exists on several multidentate ligands bonding through alkyne and group 15 or 16 donor sites [977]. The reaction of [Au$_2$(μ-(CH$_2$)$_2$PPh$_2$)$_2$] with [Au$_2$(μ-L-L)]$^{n+}$ (n = 0, 1; L-L = S$_2$CNMe$_2$, S$_2$CNEt$_2$, S$_2$CNBz$_2$, dppm, dppe, NH(PPh$_2$)$_2$), afforded the mixed ligand complexes [Au$_2$(μ-(CH$_2$)$_2$PPh$_2$)(μ-L-L)]$^{n+}$ [978].

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