Coordination Chemistry Reviews, 124 (1993) 63–105

4. Copper

Brian P. Murphy

CONTENTS

INTRODUCTION

It is inevitable in a review of such a prolific area as copper co-ordination chemistry that something has either been missed or, for reasons of conciseness, omitted. To those authors who fall into these categories, I extend my apologies. In an attempt to contain the review to a manageable size, the material covered has been restricted largely to English language publications which appear in the popular academic chemistry journals of 1990. Without such restrictions the task would have been unduly cumbersome: the first computer search of Chemical Abstracts yielded 37,478 references with *copper* in the title or abstract; the field was subsequently restricted by intersecting

0010-8545/93/$24.00

this field with other keyword fields such as *complex, ligand, crystal* etc. The space limitation permits only the most cursory treatment of any one publication, and so the review is intended for the reader's perusal rather than the in-depth interest of a particular specialism. By and large, the review pays particular attention to structural information, with the intention that the reader will be able to use such information to identify material worthy of deeper investigation with respect to his/her interest. Throughout, commonly accepted ligand abbreviations are used without decoding; for example, bpy for bipyridine.

Copper co-ordination chemistry has become a diverse field of interest which intersects with many other research domains. A dominant part of much of the current research is the study of the chemistry of complexes containing two or more coppers. In deference to this trend, this review deals first with the polynuclear complexes, then moves to mononuclear, followed by other key fields of general interest. In this connection, inclusion of organometallic references in this review has been kept to a bare minimum; references relating to copper-containing superconductors, a rapidly expanding and highly specialised area, have also been largely excluded.

4.1 HOMOBINUCLEAR COMPLEXES

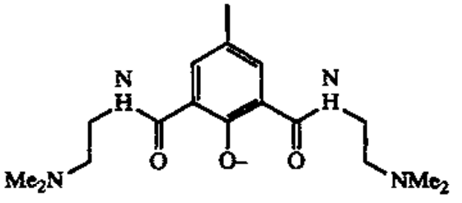
The study of both homo- and hetero-binuclear copper-containing complexes continues to be an area of intense activity in 1990. These studies largely centre on magneto-structural correlations between the metal centres, catalysis, and biomimicry; the latter are reserved for the section on *Biological Copper.*

4.1.1 Binuclear copper(II)

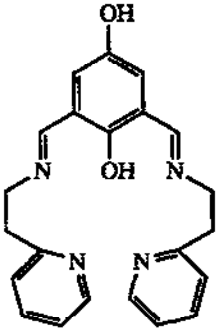
A wide range of binuclear complexes containing acyclic ligands is reported, the metal centres being held together by usually with the aid of one or more bridging ligands, the nature of which plays a role in the degree of communication between the copper atoms.

Large antiferromagnetic coupling occurs in the complex μ-hydroxo-μ-perchlorato-bis[(diethylenetriamine)perchloratocopper(II)] [1]. The X-ray crystallographic study confirms the copper(II) centres as being tetragonally elongated octahedra comprising an N_3O_3 donor set with one single-atom bridging perchlorate and one bridging hydroxide. The Cu----Cu separation is 3.435(1) Å and a large antiferromagnetic coupling ($J = -374$ cm^{-1}) is observed, the Cu(1)-O(H)-Cu(2) angle being 128.1(4)°.

In another structurally characterised single hydroxo-bridged complex $[Cu_2L(\mu\text{-}OH)(MeCN)]_2[Cu_6I_{10}]$, where $L^- =$ 2,6-bis(N,N-dimethylaminoethylformimidoyl)-4-methyl-phenolato (**1**) [2], antiferromagnetic coupling is also present ($2J = -478$ cm^{-1}); the influence of hydroxo group on the metal-metal interaction being emphasized by the drop in coupling observed when bromide is used as the bridging ligand ($2J = -157$ cm^{-1}). One exogenous hydroxide and one endogenous alkoxide bridge have been reported for the complex of the *p*-hydroquinone derivative of (**2**) to give $[Cu_2L(OH)][ClO_4]_2$ [3]. While no magnetic data are reported, it is interesting to note that the ligand has been oxidised.

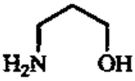


(1)



(2)

Both intramolecular antiferromagnetic and ferromagnetic coupling have been reported in doubly [4] and triply [5] bridged complexes respectively. The ferromagnetic behaviour in the latter is retained even when the nature of the bridging oxygen is changed from $[Cu_2(OAc)_3(bpy)][ClO_4]$ to $[Cu_2(OH)(OH_2)(OAc)(bpy)_2][ClO_4]_2$. The anionic hydrotris(pyrazolyl)borate(1–) ligand induces dimer formation by virtue of the three-dimensional disposition of the pyrazolyl nitrogens, [6], which leaves vacant co-ordination sites on the metal; the dihydroxo-bridged complex $[CuL]_2(OH)_2$ exhibits strong anti-ferromagnetic coupling [6a], while the peroxo-bridged analogue has been examined as an oxygenation catalyst [6b].

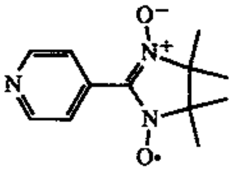


(3)

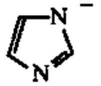
Single [7] and double [8, 9] exogenous alkoxo-bridged complexes have been observed. In $[Cu_2(NO)_2(OEt)_2]$ [8], the copper centres are strongly antiferromagnetically coupled to each other whilst being ferromagnetically coupled to the nitrosyl ligands. Structurally characterised alkoxo bridges, in which the alkoxide is pendant to a chelating ligand such as 3-amino-1-propanol (3), have also been reported [10], again with strong antiferromagnetic coupling. Other endogenous alkoxy bridges, pendant to the backbone of the main ligand, and holding together a dimeric structure are reported [11].

Magnetostructural correlations in complexes containing the $[Cu_2X_6]^{2-}$ moiety, where X = Cl^- and Br^-, have been examined [12, 13]. Antiferromagnetic superexchange is reported for a planar bromo derivative [12], with a much reduced exchange for the chloro analogues [12, 13]. The strength of the exchange in a chloro derivative are reinterpreted on the basis of the tetramer formed by bifolded dimers [13].

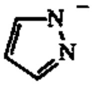
Antiferromagnetic coupling from six $S = {}^1/_2$ spins in the binuclear chloride-bridged complex $[CuL_2Cl_2]_2$, where the ligand L the radical (4), is dominated by the copper-ligand interaction mediated by the nitrogen atom of the pyridine ring [14].



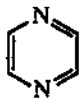
(4)



(5)

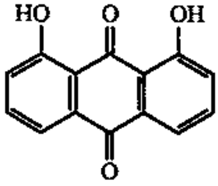


(6)

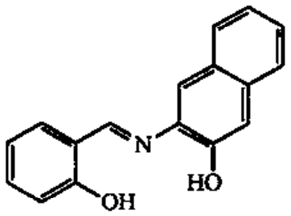


(7)

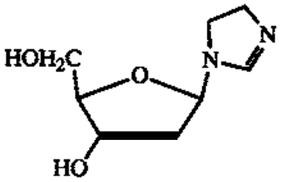
A number of nitrogen-containing heterocycles, such as imidazolate (5) [15,16], pyrazolate (6) [17], and pyrazine (7) [18] have been cited as bridging ligands, as have several mono- [5,19,20] and di-basic [21,22] carboxylic acids. Of the former, type, four methacrylato bridges between the two coppers bring the metals into a 2.655(1) Å contact [20]. Both bridging and terminal azide- [23, 24] and cyanate-containing [25] binuclear centres are also reported. Where the coupling was found to be strong, such as in a room-temperature, esr-silent azide complex [23], the main part of the contribution to exchange was found to be *via* an oxime portion of the ligand rather than the pseudohalide. The oxyanions NO_3^- [26] and CO_3^{2-} [27] have been crystallographically characterised in a bridging role. The μ-carbonato complex has been reported as the product of an interesting reaction between a di-μ-hydroxo copper(II) complex which fixes atmospheric CO_2 as carbonate [27].



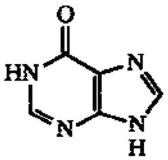
(8)



(9)

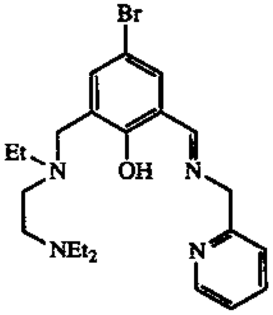


(10)

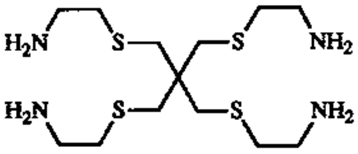


(11)

A number of less common bridging ligands such as the anionic forms of 1,5-dihydroxy-9,10-anthracenedione (8) [28], phenylcyanamides [29], oximides and dithiooximides [30], acetazolamides [31], oximes [32, 33], as well as the Schiff-base product of salicylaldehyde and 2-hydroxynaphthylamine (9) [34] are reported. Of particular structural interest is the formation, in the presence of a polyhydroimidazole ligand, of binuclear metallacyclic structures with large interacting square pyramidal coppers [35]. The neutral bridging ligands 2'-deoxyadenosine (**10**) [36] and hypoxanthine (**11**) [37] have been characterised.



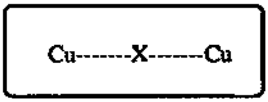
(12)



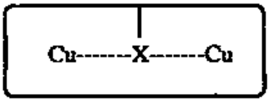
(13)

When the ligands become larger and incorporate two distinct metal binding 'ends', it becomes more practicable to classify the ligands as binucleating, despite the fact that they are still strictly bridging the metal centres. Non-cyclic ligands within this category often share the structural features of: *a*) tripodal amine 'ends' linked by *b*) an organic backbone [38], which can contain additional heteroatoms [39] which, in turn, may act as endogenous bridges [40]. Manipulation of these structural features has been effected to furnish complexes with a range of metal-metal distances, magnetic, and redox properties. Other examples include the ligand (**12**) which contains two chemically distinct metal-binding sites, and forms binuclear copper(II) complexes with a variety of exogenous bridges [41]; in contrast, the ligand (**13**) can hold weakly interacting copper atoms at a separation of 7.127 Å [42].

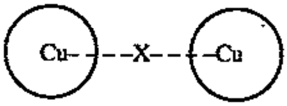
Homobinuclear macrocyclic complexes of copper(II) can be divided into structural types, depending on whether the macrocycle is either binucleating and encapsulates the copper atoms together with exogenous (**14**) and/or endogenous (**15**) bridges; or, is essentially mononucleating but capable of producing bridges to a second copper atom, (**16**) and (**17**). These types are represented diagrammatically with 'X' representing the bridging functionality.



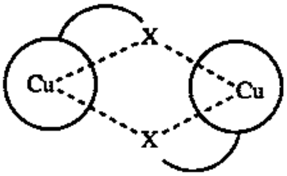
(14)



(15)



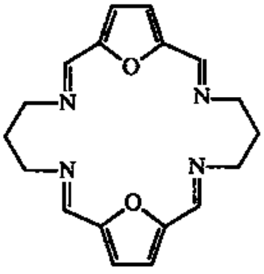
(16)



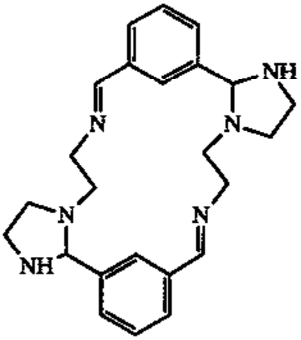
(17)

The small ring size of tridentate macrocycles precludes binucleation within a common macrocyclic cavity [43,44]. The structurally characterised complexes $[Cu_2L_2(\mu\text{-}OH)(\mu\text{-}Cl)][ClO_4]_2$ [44], where L = 1,5,9-triazacyclononane, illustrates this point. Variation of the exogenous bridge in related complexes of the *N*-methylated derivative of this macrocycle allows tuning of the magnetic properties to furnish a range of homobinuclear complexes with no coupling, antiferromagnetic coupling ($2J = -460$ cm-1), and ferromagnetic coupling ($J = +22$ cm^{-1}), as well as Cu-----Cu separations in the range 3.6 to 7.6 Å [45].

In general, expansion of the macrocyclic cavity allows the incorporation of two or more metals [46]. Further, the steric constraints imposed by the macrocycle (**18**) around the bimetallic site has been shown to give rise to the first observation of a truly symmetrical, single-atom, nitrogen-only, bridging isothiocyanate between the copper atoms [47].



(18)

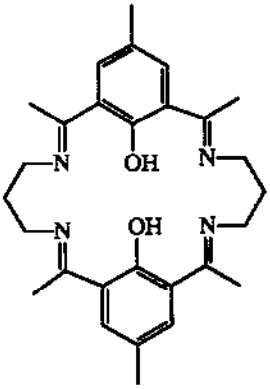


(19)

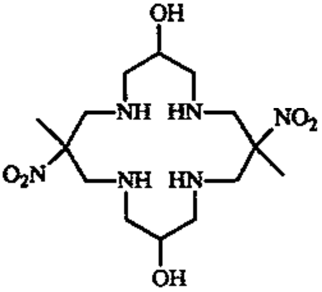
The macrocycle (**19**) has been obtained and structurally characterised in its metal-free form; however, exposure of its dicopper(I) complex to dioxygen, results in the recovery a dicopper(II) derivative in which an exogenous OH$^-$, and an endogenous phenolate bridge (from O_2 insertion), link the two copper centres [48]. An example of a macrocyclic binuclear copper(II) complex containing two endogenous bridges is provided by the ligand (**20**) which forms complexes of the form $[Cu_2LX_2].nH_2O$, where X = axially bound halide and azide [49]. The strong antiferromagnetic coupling ($2J = -750$ to -855 cm^{-1}) observed in these complexes is ascribed to the essentially flat binuclear structure with close metal-metal approach which is facilitated by the macrocyclic ligand constraint; this is illustrated by the crystal structure of the bromide derivative.

Similarly, extremely strong coupling ($2J = -860$ cm^{-1}) is exhibited by another co-planar binuclear copper centre imposed by the macrocycle (21) which contains two endogenous alkoxo bridges [50]; the bridging groups play an important synthetic role in maintaining the integrity of a binuclear transition-state complex in which the Cu_2O_2 moiety templates the macrocyclisation reaction.

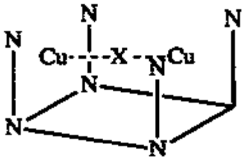
A number of binuclear copper(II) complexes of tetraaza-macrocycles containing the chelating substituents 2-aminoethyl [51], 2-pyridylmethyl [52], and 2-benzimidazoylmethyl [53], which are pendant to the macrocyclic nitrogen atoms, have been reported. In these cases the binuclear structure has been achieved by the exocyclic co-ordination of the copper atoms to the ligands as represented by (22).



(20)



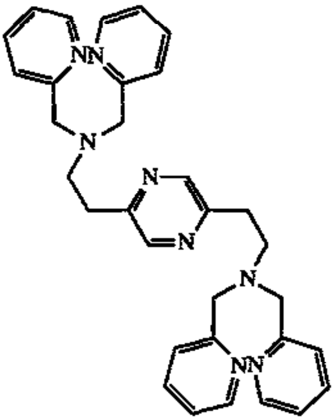
(21)



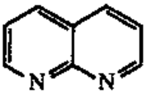
(22)

4.1.2 *Binuclear copper(I)*

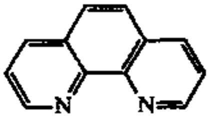
The large binucleating ligand, 2,5-bis[*N*,*N*-bis(2'-pyridylethyl)aminomethyl]pyrazine (23), has been used to synthesise binuclear complexes of copper(I) [40] in addition to the copper(II) complexes already reported. The crystal structure of $[Cu_2L_2][ClO_4]_2$, where L = 1,8-naphthyridine (24) reveals a short Cu----Cu separation of 2.506(2) Å; the complex reversibly binds π-acids such as CO, C_2H_2, and C_2H_4 [54]. Although metal-metal bonding is not claimed in this complex, it is interesting to note that the disilver(I) analogue exhibits a metal-metal distance which is significantly shorter than that found in the metallic form of the element. A number of other structurally characterised examples of binuclear copper(I) complexes of non-macrocyclic ligands containing nitrogen heterocycles appear [55-58]. In view of the close metal contacts mentioned above, the insertion of a 'copper nitrene' into a carbon-hydrogen bond of $CuLCl_2$, where L = 1,10-phenanthroline (**25**), is reported to give a complex in which a 2.600(2) Å gap separates the copper atoms, a distance approaching the 2.55 Å measured for metallic copper [57]. Synthetic and structural studies of mixed-ligand systems involving nitrogen heterocycles along with 'soft' phosphorus- [58, 59] and sulfur-containing [59, 60] ligands are reported. The high stability of a dicopper(I) complex, containing two thiophenolato bridging ligands and a terminal η^2-thiacycloheptyne ligand, is associated with a large reduction in the internal strain of the terminal ligand as a result of complexation [61].



(23)

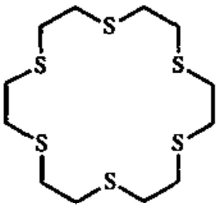


(24)

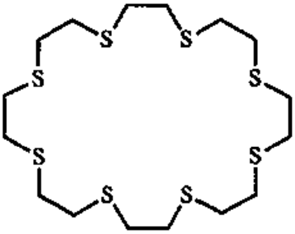


(25)

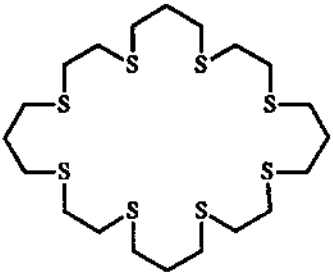
Macrocyclic ligand control of the Cu----Cu separations has been demonstrated in the synthetic and structural studies of binuclear tetrahedral copper(I) complexes of a range of thioether crowns of the type [18]-ane-S_6 (**26**) [62], [24]-ane-S_8 (**27**) and [28]-ane-S_8 (**28**) [63]. The intermetallic distances of 4.428(2), 5.172, and 6.454(3) Å respectively, are in accord with the increasing size of the macrocyclic cavity. Electrochemical and ESR spectroscopic studies of the oxidation products of the S_8 series are also reported.



(26)

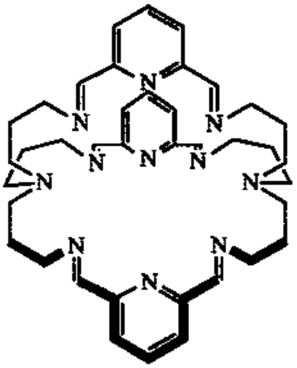


(27)

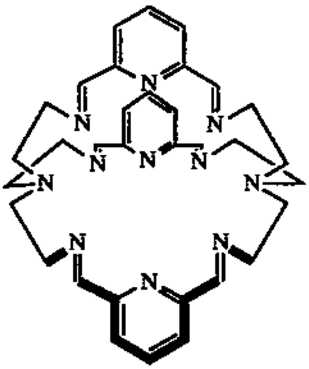


(28)

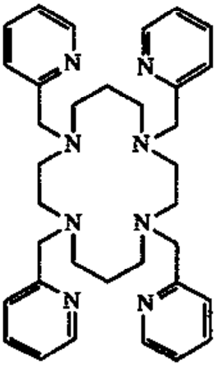
When three moles each of tris(3-aminopropyl)amine and 1,3-benzenedicarboxaldehyde are condensed in the presence of silver(I), and the product transmetallated with copper(I), a binuclear complex of a (3+3) hexa-imine cryptand **(29)** is produced [64]. The structure of the complex is reported, while the template route to this macrocycle complements the metal-free route reported for the closely-related system based on tris(2-aminoethyl)amine by Nelson *et al* in 1988 **(30)** [65].



(29)



(30)



(31)

The exocyclic di-copper(I) complex of the macrocycle (**31**) has been structurally characterised and the quasireversible binding of dioxygen reported [66]. The low co-ordination number requirement of the copper(I) ion is expressed in the use of only six of the potential eight nitrogen donors of the ligand, each copper adopting a trigonal geometry. Evidence for copper-mediated O_2 incorporation is by way of isolation of the copper(II), CuL_2, where HL is pyridine-2-carboxylic acid derived from the 2-pyridylmethyl pendant substituent of the macrocycle.

4.1.3 Heterobinuclear complexes

Heterobinuclear complexes containing copper(II) together with the ions titanium(III) [67], chromium(III) [68], manganese(II) [69], iron(II) [70], cobalt(II) [70-73], cobalt(III) [74], nickel(II) [16, 33, 70-73, 75, 76], zinc(II) [16, 71-73], platinum(IV) [77] and gadolinium(III) [78]. Studies involve X-ray crystallographic [67, 74, 76, 77], magnetic [68-71, 73, 76-78], electrochemical [73], thermodynamic [75], and kinetic [72] examination.

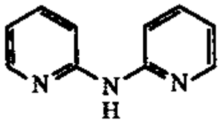
Examples of heterobinuclear copper(I) together with iron (as a ferrocenophane tetrathia-macrocycle) [79], zinc(II) (in *scaffolding-like* materials) [80], ruthenium(II) (as an exodentate chelate to an endodentate copper(I)-macrocycle complex [81], and platinum(II) (in $[CuPt(CN)_4]^-$) [82]. Physicochemical measurements of the copper-iron complexes [79], show that, although the complexes are formed by reaction of the appropriate ligand with $Cu(BF_4)_2$, the copper is present as copper(I) while the iron is present in the ligand backbone as ferrocenium.

4.2 POLYNUCLEAR COMPLEXES

4.2.1 Trinuclear Complexes

4.2.1.1 Homotrinuclear Complexes

Homotrinuclear complexes can be either *linear* or *cyclic* with respect to the metal core. The complexes $[Cu_3L_4X_2].H_2O$, where X = Cl^- or Br^- and HL = bis(2-pyridyl)amine (**32**), is an example of the first of these structural types [83]. Each of the four ligands co-ordinates in a unindentate manner to each copper atom, forming a four-column cylinder within which the Cu_3-chromophore is situated. The central copper(II) atom thus involves a co-planar CuN_4 chromophore, while the terminal copper(II) atoms co-ordinate an additional halide to adopt a square pyramidal geometry. Little mention is made in the abstract of the very close metal-metal distances of 2.471(1) and 2.468(1) Å in these strongly antiferromagnetically coupled, ESR-silent, complexes. Semiconductor activity has been found in stacked copper(II)-porphyrinato trimers, with large exchange interactions existing within the trimer [84].



(32)

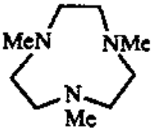
Several other linear Cu_3-cores have been either structurally characterised or proposed on the basis of magnetic and spectroscopic information. Thus, bridging bis(oximato) ligands give rise to a planar terminal CuN_4-chromophore with a central, flattened tetrahedral CuO_4 chromophore [85]. Triply bridged coppers, from six μ_2-triazole ligands, again produces the linear Cu_3 core, this time with an octahedral CuN_6-unit as the central chromophore, while tetragonal pyramidal CuN_3O_3 (oxygen is from water) chromophores terminate the trinuclear chain [86]. An almost linear trimer (Cu-Cu-Cu = 175.04(2)°) with copper-copper distances of 2.9515(5) Å and 3.0106(5) Å, and with two of the copper atoms having a distorted square pyramidal geometry while the central copper is found in an octahedral environment, was realised with 3-aminopropanol, $H_2NCH_2CH_2CH_2OH$ [87]. The crystal structure of $[Cu_3L_2(FH_2CCO_2)_4(EtOH)_2]$, where HL = $Et_2NCH_2CO_2H$, shows terminal square-planar $CuNO_3$ and central CuO_4 chromophores [88]. Bridging glyoximate ligands have also afforded complexes in this category [89]. The magnetic non-equivalence of two types of copper atom in this structural category permits straightforward structural inferences to be made on the basis of spectroscopic and magnetic data [90, 91]. A trinuclear copper(I) complex of formula $Cu_3Cl_3(R_2Te)_2(H_2O)$ has been reported [92], but structural detail is limited. Detailed magneto-structural correlations within copper trimer stacks of type $[Cu_3X_8]^{2-}$, where X = Cl or Br, have been published [93].

Examples of cyclic Cu_3 include the metal in both the +1 and +2 oxidation states. The trinuclear iodocuprate complex $[Cu_3(AsPh_3)_3I_4]$ consists of an apical iodide triply bridging to three equivalent pseudotetrahedral coppers, each of which are further doubly bridged by iodide and terminally co-ordinated by a single $AsPh_3$ ligand [94]. Three μ_2-pyrazolate ligands form a large nine-membered cyclic arrangement, incorporating the metals, which is co-planar to within 0.07 Å [95]. Oxidation of $[\{Cu(HL)_2Cl\}_2]$, where HL = pyrazole, yields the trinuclear complex $[Cu_3(OH)(L)_3(HL)_2Cl_2]$ in which the hydroxo group bridges to all three copper(II) ions, while three of the pyrazolato ligands bridge between two metals, closing a circle around the central hydroxide [96].

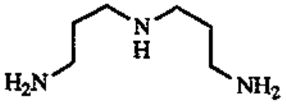
4.2.1.2 Heterotrinuclear Complexes

Linear complexes of the $M_2Cu(II)$ type, with copper at the centre are: $[LFe\{\mu\text{-}(dmg)_3Cu\}FeL]^{2+}$, where L = 1,4,7-trimethyl-1,4,7-triazacyclononane (33), and H_2dmg = dimethylglyoxime [97]; $[(NH_3)_5Co(\mu\text{-}im)CuL(\mu\text{-}im)Co(NH_3)_5]^{4+}$, where H_2L = $HO_2CCH_2NHCH_2CO_2H$ and imH = imidazole, contains such an arrangement [74], and

$[L(H_2O)Ni\{(\mu\text{-pba})_2Cu\}Ni(H_2O)L]^{2+}$, where L = bis(3-aminopropyl)amine (**34**) and H_2pba = 1,3-propylenebis(oxime) (**35**) [98].



(33)



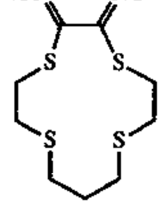
(34)

(35)

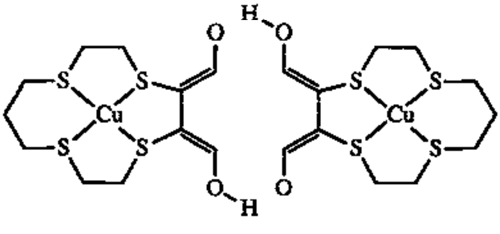
The alternative linear trinuclear unit, $MCu(II)_2$, is found for a series of complexes in which M = Mg, Mn, Co, or Ni, the zinc member of the series serving as structural reference [91]. The macrocyclic ligands (**36**) have two metal binding sites: the S_4-unit of the macrocyclic cavity and the exocyclic glyoxime-fused unit. In accordance with these features, heterotrinuclear complexes of the type (**37**), where M = nickel(II) and cobalt(II) have been proposed [99]. The complex $[\{Cu(bpy)\}_2Cr(ox)_3]^+$ shows distinct ferromagnetism with an increase in magnetic moment to 8.78 μ_B at 5 K from 4.82 μ_B at 300 K [68].

The imidazole-containing ligand, formed by the sequential Schiff-base condensation of 5-chloro-2-hydroxybenzophenone, 1,2-diaminobenzene and imidazole-4-carboxaldehyde (**38**), has been used to form the iron(III)dicopper(II) complex (**39**) in which the central iron is complexed to tetraphenylporphyrin. This compound exhibits a low-temperature ferromagnetic interaction between the heterometals ($J = 22.2$ cm^{-1} in the range 2 – 300 K) [100]. Mention has already been made of the heterobinuclear structure obtained with a tetrathia-macrocyclic ferrecenophane ligand [79]; 2:1 complexation affording the heterotrinuclear complex has also been achieved by using the smaller cavity of the trithia-analogues. Similarly, the use of other ferrocenyl-derived ligands to form 2:1 complexes (**40**), this time with copper(II), have given rise to tetrahedrally distorted copper(II) centre in $FeCu_2$-complexes [101].

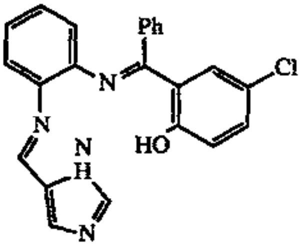
A structurally characterised example of cyclic $M_2Cu(I)$ in an incomplete $\{Mo_2CuS_4\}$ cubane-like core was found [102]. A copper-magnesium complex [103] merits special mention in that the X-ray crystal structure reveals unprecedented magnesium-sulfur(thiophenolato) bonds, two of which bridge to the copper.



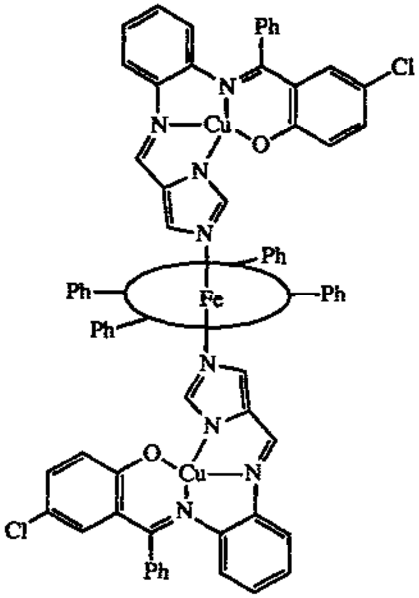
(36)



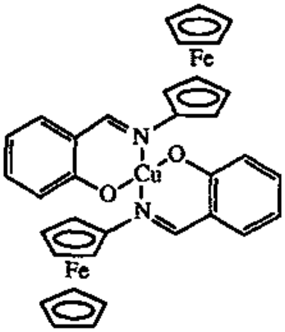
(37)


Ph
N
Cl
N
HO
N
H
N

(38)


Ph
N
Cl
N
Cu
O
N
N
Ph
Ph
Fe
Ph
Ph
N
N
O
Cu
N
N
Cl
Ph

(39)


Fe
N
O
Cu
O
N
Fe

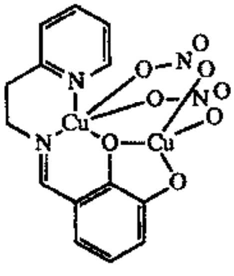
(40)

4.2.2 Tetranuclear Complexes

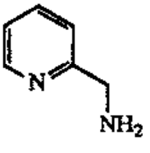
Linear, tetrahedral, ring, and cubane structures have all been realised.

4.2.2.1 Homotetranuclear Complexes

Within this subdivision mixed-valence and copper(I) chemistry is commonplace. A compartmental ligand of the bis(triketonate) type is capable of complexing two binuclear copper(II) units to form a tetranuclear complex [104]. The binuclear units are far apart (6.9 Å) and there is strong interaction within the binuclear units to the extent that the complex is ESR-silent at room temperature. Dimerisation of the binuclear unit **(41)** gives a linear tetracopper(II) compound with intradimer bridging between the external catechols. The related complex derived from 2-aminomethylpyridine **(42)** gives rise to a cubane structure based on a Cu_4O_4 core [105]. Electrochemical studies of these polynuclear complexes are also reported, showing that both the metal and the ligand are electroactive. A coplanar arrangement of four copper(II) atoms occurs the complex anion of some polyoxotungstate salts [106]; each copper forming a CuO_6 octahedron. A planar oxocuprate(II) array of type $Cu_4O_3(OCHMe_2)_2$ has been characterised in a heterometallic alkoxide complex $Cu_4Zr_4O_3(OCHMe_2)_{18}$ [107]; the unit shows antiferromagnetic coupling, with $\mu_{eff} = 1\ \mu_B$ per copper between 100 and 300 K. A tetrahedral cluster of copper(II) ions orientated about a centroidal O atom has been found in a copper-chloride-nicotine complex [108]; each copper atom is trigonal bipyramidal with bridging chlorides to all neighbouring copper atoms, and terminal *N*-bonded nicotine.

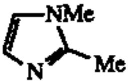


(41)



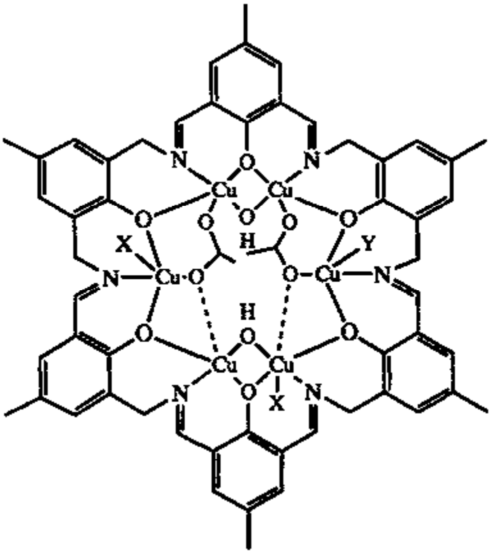
(42)

A distorted tetrahedral tetracopper(I) core is present in $[Cu_4(PPh_3)_3Cl(PMe_3)_3]$ and related complexes [109]. The core comprises a six-membered Cu_3P_3 base which is bridged by a CuCl unit *via* two PPh_2 groups. This gives rise to two electron-deficient PCu_3 fragments in the structure which, by way of compensation, possess short Cu----Cu contacts (2.51(2) Å) in the metal-metal bond range. An example of tetrahedral tetracopper(II) is found in $[Cu_4Cl_6(O)L_4].0.25H_2O$ where the structure is maintained by a centrally co-ordinated tetrahedral oxo species, bridging Cl^-, and terminal ligand L = 1,2-dimethylimidazole (43) [110]. The reaction of copper powder with sulfur in pyridine gives rise to $Cu_4S_{10}(py)_4$ amongst other species [111]. This product can exchange the pyridine ligand to give a range of structurally related complexes based on a tetrahedral tetracopper core.



(43)

Ring structures containing four copper atoms bridged by ligands are now well known for copper(I) [112-114], copper(II) [115, 116] and mixed-valence copper [117]. Cubane geometries have also been reported for copper(I) [118], copper(II) [119], and mixed-valence copper [120]. In most cases, structural data are available [112-119]. One structure is the first example of a square planar Cu_4S_4 ring [113]; magnetic data [115, 119], ESR spectral; data [117, 120], electrochemistry [117, 120], and electronic spectra [120] have been studied. An adamantane-type structure is adopted by the $[Cu_4(RS)_6]^{2-}$ species [121].



X = MeOH

Y = H_2O

(44)

4.2.2.2 Heterotetranuclear Complexes

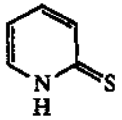
The heterotetranuclear complexes also show a variety of topologies for the metal-copper cluster, from linear Zn-Cu-Cu-Zn (zinc(II)/copper(II)) [122], to planar $MoCu_3$ (molybdenum(IV))

[123]. The cubane $M_2Cu_2^{4+}$ arrangement has been demonstrated for M = Mo and W [124], while a coplanar unit occurs in $(Et_4N)_2[MCu_3S_4L_3]$.DMF, where M = Mo and W, and HL = piperidinocarbodithioic acid [125]. A stepped $M(III)_2Cu(II)_2$ conformation, with exchange coupling between the copper and the lanthanides gadolinium and dysprosium, has been structurally characterised and magnetic studies discussed in relation to their potential as high-T_c superconductors [126]. In all cases the integrity of the metal cluster core is maintained by the ligands. The fitting of magnetic behaviour of $M(II)Cu(II)_3$, where M = Cd, Ni, and Mn, to the cluster topology has also been attempted [127].

4.2.3 Pentanuclear and higher nuclearity complexes

Bow-tie and linear forms of $[L]_4[Cu_5Cl_4]$ (L = 1,4-dimethylpyridinium) are reported [128] along with magnetic behaviour which is difficult to rationalise due the complicated structures involved. Cubane-derived topologies, involving *I*- and *S*-bridging groups, have been characterised in $ReCu_4$ complexes [129]; very short metal Re-Cu contacts (2.638(4) -2.712(4) Å) are remarked upon and formal oxidation states of Re(V) and Cu(I) are assigned.

Six copper(II) centres are bound in a cyclohexane-type boat arrangement within a single macrocyclic ligand cavity **(44)** with two bridging hydroxide groups at the centre of the cavity help maintain the cluster [130].



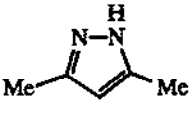
(45)

An octahedral $Cu(I)_6$-core comprising trigonal copper atoms in $[Cu_6L_6]$ has been characterised [131]. The singly deprotonated ligand L = 1-*H*-pyridine-2-thione **(45)**, is bonded to each trigonal face of the octahedron.

Organometallic Pt_2Cu_4 [132], and Ru_4Cu_2 [133] clusters have appeared. The synthesis of M_2Cu_5 clusters involving dithiocarbamate ligands, where M = Mo or W, together with solution characterisation in both cases and X-ray structural characterisation for M = Mo is reported [134].

The electrochemical synthesis of copper derivatives of alkanedithiols [135] has lead to the isolation of octanuclear copper complexes. Reaction of the polymeric copper(I) complex of 3,5-dimethylpyrazolate, **(46)**, with oxygen gives rise to $Cu_8L_8(OH)_8$; this is the first example of a copper complex containing a planar ring of eight metal atoms [136]. It would seem that the planarity of the metal-bridging *N-N*-group of pyrazolate restricts the cluster formation to two dimensions since the same ligand has previously been reported [95] to give rise to planar Cu_3-rings. A complex of formula $[Cu_9Br_2L]^{2-}$ is reported as containing two distinct copper sites, a 5-

coordinate atom and a 6-coordinate atom with the ligand (2-*C*-carboxypentanoate) binding in a heptadentate manner to three copper atoms [137].



(46)

A number of papers concerning polymeric complexes have been published and are included here. It is best to consider these examples as polymerised mononuclear complexes. The bridging agent is commonly halide [138], often organic ligands [139], and sometimes both ligand and halide or pseudohalide [140]. A theoretical treatment for the prediction of new stacking patterns of quasi-planar $Cu_nX_{2n}L_2$ oligomers (X = halide) is reported [141].

4.3 MONONUCLEAR COMPLEXES

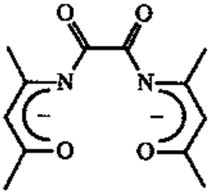
4.3.1 Mononuclear copper(II)

The vast number of structural studies on mononuclear copper(II) complexes is reflected in the extent of the entries in Table 1 at the end of the section. There is only space here to describe but a few of the more esoteric compounds. The table is designed for quick reference giving the donor chromophore, an indication of the geometry of the coordination sphere, and an indication of the nature of the ligands involved.

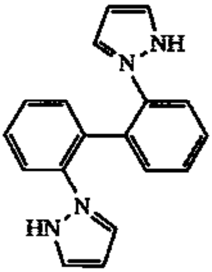
The structure of the copper(II) complex of a 9-membered N_2S-macrocycle, containing two pyridylmethyl arms pendant to the nitrogen donors [142], is described as square pyramidal with an axially positioned sulfur atom. The Cu-S bond is somewhat short and the N_4-basal plane is trapezoidally distorted; a strained conformation imposed by co-ordination requirements.

The square planar complex produced by the acyclic ligand **(47)**, gives rise to unusual electrochemical behaviour which is attributed to extensive delocalisation of metal electron density into the ligand π-system [143].

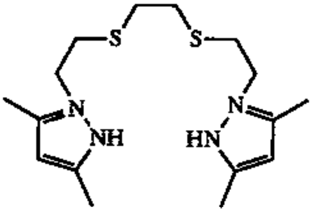
Pseudotetrahedral complexes are produced by the geometrical constraints of the bidentate ligand 2,2'-bis(2-imidazolyl)biphenyl **(48)** [144]. The ligand offers an N_4-chromophore to the copper atom, and in doing so exerts an "unprecedented" degree of geometric control over the co-ordination sphere of not only copper(II) but a range of other first-row late-transition metals. The dihedral angle of 87.2(2)° is close to ideal for a tetrahedron. Electrochemical and NMR techniques were used to examine electron exchange rates for the copper(I)/copper(II) pair, the slow value of which is ascribed to ineffective interaction of the unpaired electron with ligand orbitals.



(47)



(48)

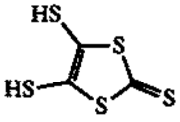


(49)

The co-ordination behaviour of the thioether function of the ligand (49) is reported as unusual in that in neither of the two forms of the complex [CuLCl$_2$] (the red form is *trans* square planar; the green form is tetrahedral) are the sulfur atoms involved in co-ordination, despite the fact that molecular mechanics calculations show no steric inhibition in this respect; the copper co-ordination sphere consists of two pyrazole nitrogens and two chlorides. The copper(I) analogues, on the other hand, do incorporate the thioethers within the co-ordination sphere [145].

Pseudo-macrocyclic ring formation, facilitated by hydrogen-bonding within a square planar complex, has been observed in an anionic species containing fluorinated alkoxide ligands [146].

The copper(II) complex of a Se$_4$-donor coronand (L) is reported as unstable in solution and spontaneously undergoes electron transfer to give copper(I), L$^+$, and L^{2+} [147]; crystallographic and redox studies are reported.



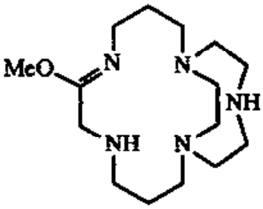
(50)

The reaction of 1,1'-dichalcogenolate complexes Cu(XX'CNEt$_2$)$_2$ (X = S, X' = S, Se), with (Bu$_4$N)$_2$[CuL$_2$], (H$_2$L = 1,3-dithiole-2-thione-4,5-dithiol, **50**), in acetone yields [CuL(XX'CNEt$_2$)] *via* a ligand exchange reaction [148]; ESR spectroscopy reveals that the 4-membered chelate ring, rather than the 5-membered ring, gains considerable electron density. In a related study, delocalisation of the unpaired electron was confirmed by the hyperfine splitting in a single-crystal and powder ESR spectroscopic study of a ^{63}Cu enriched complex [149].

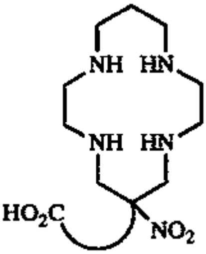
4.3.1.1 Copper(II) in synthesis

The involvement of copper(II) in ligand synthesis is usually in the form of a templating agent. Such reactions are a common feature of the co-ordination chemistry of macrocyclic ligands. New porphyrin-type macrocycles have been reported as being the result of a copper(II)-promoted cyclisation of acyclic tetrapyrroles [150]. The ring-closed product is extremely stable even in concentrated acid. The stabilising influence of the ion is emphasised by the ring expansion observed when the metal is removed. The condensation of glyoxal with (*N,N'*-bis(aminopropyl)-1,4,7-triazacyclononane)copper(II) results in the formation of the macrobicyclic product with evidence for co-ordination-stabilised imidate and enamine intermediates (**51**) [151]. Mannich-type reactions may also be copper-directed, such as the reaction of (4,7-diazadecane-1,10-diamine)copper(II) with formaldehyde and a variety of nitro-containing carboxylic acids to give new pendant-arm macrocycles (**52**) [152].

The Mannich [153] and Schiff-base [154] condensations are the most commonly found copper(II)-promoted ligand synthesis reactions. Where the template route is not available for complex ligands, prior synthesis followed by incorporation of copper(II) is necessary; this is illustrated in the recovery of the copper complexes of a range of pendant-arm macrocycles. Pendant N-heterocycles [155, 156], nitriles[157] and amines [158], as well as carboxyl [159], alcohol and ether groups [160-161]. Most frequently, the pendant group is attached to one of the precursor ligand N-donors [142, 155, 157-159, 161].

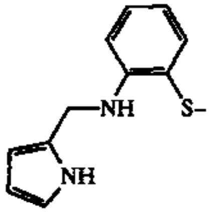


(51)

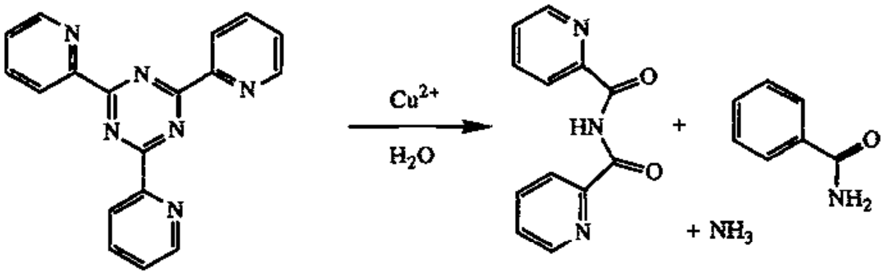


(52)

The electrochemical generation of complexes using a sacrificial copper anode is a useful addition to the synthetic repertoire when neutral complexes of anionic ligands are required [162]. CuL_2 (53), for example, has been produced in this way [163].

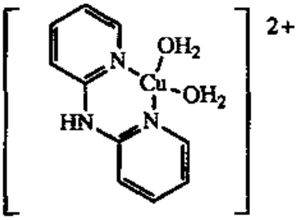


(53)



(54)

Several papers on copper(II)-assisted ligand hydrolysis reactions have appeared. The hydrolysis of a triazine ligand (54) has been studied [164]. Other work has shown that amide hydrolysis is facilitated by co-ordination of the amide carbonyl to the copper, with at least five substrates being acted upon by each copper [165]. The complex (55) is active in catalysing the hydrolysis of amides at neutral pH, in contrast to $Cu(OH_2)_6^{2+}$ [166].



(55)

4.3.1.2 Miscellaneous copper(II) studies

There has been some interest in the thermodynamics of the complexation of copper(II). Macrocycles feature prominently in these studies largely because of their relatively straightforward speciation in solution and their classical perception as size-based discriminators in the complexation of metal ions. In these studies, copper is usually only one of a series of metal ions examined. Size-based selectivity has been examined as a dependant of chelate ring size, rather than macrocyclic ring size, and found to be dominant in a carefully chosen series of structurally related ligands [167]; while a similar conclusion emerges from conformationally restricted open-chain amines [168]. Thus, for copper specificity, many interdependent variables need to be considered, with the result that molecular mechanics studies are a useful aid for the rationalisation of results [169]. A considerable macrocyclic effect is observed in the interaction of copper(II) with a series of N_3O_2-donor macrocyclic and related acyclic ligands [170]. A number of these macrocycles show a strong specificity for copper(II), with negligible complex formation with other late first-row transition-metal ions.

In selective transport studies, bis-benzimidazole ligands have been used as carriers to effect potentially useful discriminations between silver(I)/copper(II) and copper(II)/zinc(II) [171]. Other studies have examined the solution thermodynamic [172, 173, 174] and kinetic [173, 174] properties of copper(II).

An electrochemical examination of the copper(II)/copper(I) redox couple in DMSO finds that the formal potentials are approximately 0.15 V less positive relative to their aqueous analogues and concludes that this effect is due to solvation and complexation; reduced diffusion coefficients are attributed to the higher viscosity of the DMSO solutions [175].

In a continuing sequence of papers, the complexation of copper, within a γ-$Zr(HPO_4)_2.2H_2O$ matrix, is achieved with the intercalated ligands 2,2'-bipyridine and 1,10-phenanthroline, but when the ligand is the more bulky 2,9-dimethyl-1,10-phenanthroline, the copper atom is still included but is not complexed to the heterocyclic ligand [176]. Nevertheless, the importance of matrix-ligand interactions is emphasised by the unexpected order of copper uptake: 1,10 -phenanthroline > 2,9-dimethyl-1,10-phenanthroline > 2,2'-bipyridine.

The plasticity of the copper(II) co-ordination sphere for the CuN_2O_2-chromophore has been modelled using molecular mechanics calculations [177, 178]. Using the models, it has proved possible to reproduce the enantioselectivity effect of bis(*L-N,N*-dimethylvalinato)copper(II) [178]. Theoretical treatment of the weak magnetic exchange in one-dimensional halo-bridged copper(II) complexes has been examined [179].

Table 1 Some structurally characterised copper(II) complexes

Structure[a,b]	Ligand type(L; L^1/L^2)	Complex	Notes	Ref
Oct (N_2O_4)	2-benzoylpyridine	$[CuL_2(OH_2)]^{2+}$		180
Oct (N_2O_4)	β-diketonato/diazole	$CuL^1_2L^2_2$		181
Oct (N_2O_4)	iminodiacetate /imidazole	CuL^1L^2MeOH		182
Oct (N_2O_3S)	alcohol-pendant glycinato	CuL(NCS)	polymer; bridging NCS^-	183
Oct (N_2S_2)$(BF_4)_2$	thio-imidazole	$CuL_2(BF_4)_2$	O_2/catalytic activity	184
Oct/sbp (N_4O_2)	oxadiazole-dipyridine	$[CuL_2]^{2+}$		185
Oct (N_4O_2)	purinyl/ethylamine	$CuL^1_2L^2_2(OH_2)_2$		186
Oct (N_4O_2)	N_4-macrocycle	$[CuL(OH_2)_2]^{2+}$		187
Oct (N_4O_2)	ethylenediamine	$[CuL_2(OH_2)_2]^{2+}$		187
Oct (N_4S_2)	imidazole-thioether	$[CuL_2]^{2+}$	electrochemistry	188
Oct (N_4S_2)	dioximate/thiourea	$Cu(L^1)_2L^2_2$		189
Oct (N_6)	2-(aminomethyl) pyridine	$[CuL_3]^{2+}$	Cl^- from nucl. attack on CH_2Cl_2	190
Oct (N_6)	terpyridine	$[CuL_2]^{2+}$	ESR study	191
Oct (O_6)	imidazolyl-*N*-oxide /acetylacetonato	$[CuL(hfac)_2]^+$	*N*-oxide bridge to second Cu	192
Oct (O_6)	pyrrolidinyl-*N*-oxide /acetylacetonato	$[CuL(acac)_2]^+$	one-dimen. chain; *N*-oxide bridge	193
Oct (Cl_6)	chloride	$[CuL_3]^-$	pseudo-1-D ferromagnet	194
Oct (Cl_6/Br_6)	halides	$[CuX_4]^{2-}$	bridging halide between sheets	195

Oct	4-methylpyridine	$[CuL_2(NCS)_2]_n$	3-co-ordination polyhedra	196
Oct	4-picoline	$CuL_2(NCS)_2$	3-co-ordination polyhedra	197
Spy (NO_4)	$^-OC_6H_4CH{=}NCH_2$-$CH_2SO_3^-$	$CuL(OH_2)$	-SO_3^- bridge (long range)	198
Spy (N_2O_3/ N_3O_2)	bipyridine /asparaginato	$CuL^1(HL^2)OH_2$ and CuL^1L^2		199
Spy (N_2O_3)	Schiff base/imidazole	CuL^1L^2	ESR study	200
Spy (N_2O_3)	diamine/formamide	$[CuL^1(L^2)_3]^{2+}$		201
Spy (N_2O_2Cl)	amino-phosphine oxide	$[CuL_2Cl]^+$		202
Spy (N_2OS)	imidazole-thioether	$CuL(ONO_2)$	electrochemistry	188
Spy (N_2O_2S)	Schiff-base dianion	$[CuL(NCS)]^-$	NCS^- bridge; ESR	203
Spy (N_2SBr_2)	1,5-bis(benzimidazol-2-yl)-3-thiapentane	$CuLBr_2$	mobility of biometallosites	204
Spy (N_3O_2)	N_3-macrocycle/*gem*-diol	CuL^1L^2		205
Spy (N_3O_2)	desferrithiocin	CuL_2		206
Spy/Spl	amino-alkoxides	CuL_2	volatile complexes	207
Spy/tbp (N_3O_2)	diethylenetriamine	$[CuL(O_2NO)]^+$		208
Spy (N_3Cl_2)	pyridyl-imidazolyl	$CuLCl_2$		209
Spy/tbp (N_3S)	imidazole-thioether	$CuL(NCS)_2$	electrochemistry; ESR	210
Spy (N_4O)	N_4-macrocycle benzoic acid (pendant)	$[CuL]^{2+}$ and $[CuL]^+$	ionised and unionised acid	211
Spy (N_4O)	diaza-dioxime	$[CuL(OH_2)]^+$		212
Spy (N_4Cl)	diamino-diimidazolyl	$[CuLCl]^+$		213

Spy (N_4Br)	2,3-di(2-pyridyl) quinoxaline	$[CuL_2Br]^+$		214
Spy (N_4I)	N_3-macrocycle-amine (pendant)	$[CuLI]^+$		215
Spy (N_4S)	glyoximato/thiourea	$Cu(L^1{}_2L^2$		216
Spy (N_5)	pyridyl-amino-amide-imidazole	$[CuL]^+$		217
Spy (N_5)	N_5-macrocycle	$[CuL]^{2+}$		218
Spy (N_5)	bipyridyl/cyanamide	$[CuL^1{}_2L^2]^{2+}$		219
Spy (O_5)	1,2,3-benzenetricarboxlato	$CuL_2(OH_2)_3$		220
Spy	amino-pyran-2-one /pyridine	$CuL^1{}_2L^2$		221
Spy	pyridyl-amino-thioacetamide	$[CuLX]^+$ $X = Br^-, N_3^-$	stereospecific	222
Spy	*L*-valinato	$CuL_2(OH_2)$	ESR	223
Tbp (N_2OS_2)	pyrazolyl-thioether	$[CuL(OH_2)]^{2+}$		224
Tby (N_2O_2S)	1,5-bis(benzimidazol-2-yl)-3-thiapentane	$CuL(NO_3)_2$	mobility of biometallosites	204
Tbp (N_4O)	bipyrimidine	$[CuL_2(OH_2)]^{2+}$		225
Tbp (N_4O)	diimino-diquinolinyl	$[CuL(OH_2)]^{2+}$		226
Tbp (N_4Cl)	bipyridyl	$[CuL_2Cl]^+$		227
Tbp (N_5)	diimino-diquinolinyl-amino	$[CuL]^{2+}$		226
Tbp (N_5)	purinyl/ethylamine	$[CuL^1{}_2L^2{}_3]^{2+}$		186
Tbp (N_5)	N_5-cage	$[CuL]^{2+}$		228
Spl (NO_3)	acetylacetonato/2-carbamoylpyrazine	$[CuL^1L^2]^+$		229
Spl (N_2O_2)	salicylaldimine	CuL_2	liquid crystalline	230

Spl (N_2O_2)	*L*-prolinato	CuL_2		231
Spl (N_2O_2)	imine-phenolate-pyridyl	CuL_2	pyridyl not co-ordinated	232
Spl (N_2O_2)	amino acid	$[CuL_2]^{2+}$		233
Spl (N_2O_2)	phenolate-imine-alcohol	CuL_2		234
Spl (N_2O_2)	*L*-2-aminobutyrato	CuL_2	ESR	235
Spl (N_2O_2)	salicylidenenaminato	CuL_2		236
Spl (N_2O_2)	salicylaldiminato	CuL_2		237
Spl (N_2Cl_2)	bipyridyl-dicarboxylic acid	$CuLCl_2$		238
Spl (N_4)	bis(methoxycarbimido)-aminato	CuL_2		239
Spl (N_4)	pyrrolylamino	CuL_2		240
Spl (N_4)	bipyridyl/cyanamide	$CuL^1L^2_2$	electrochemistry	219
Spl (N_4)	porphinato	CuL		241
Spl (O_4)	pyridyl-*N*-oxide	$CuL_2(ONO_2)_2$		242
Spl (S_4)	dithiocarbamato	CuL_2	long-range interactions	243
Spl	imino-*N*-oxide/imidazole	$[CuL^1L^2]^+$		244
Tet (N_4)	bis(bipyridyl)	$[CuL]^{2+}$	electrochemistry	245
Tet (N_4)	*o*-phenylendiminato /pyridine	$CuL^1L^2_2$		246
Tet (N_4)	amino-uracilato	CuL_2	ESR	247
Tet (Br_4)	bromide	$[CuL_4]^{2-}$		248

[a] Oct = octahedral; Spy = square pyramidal; Tbp = trigonal bipyramidal; Spl = square planar; Tet = tetrahedral

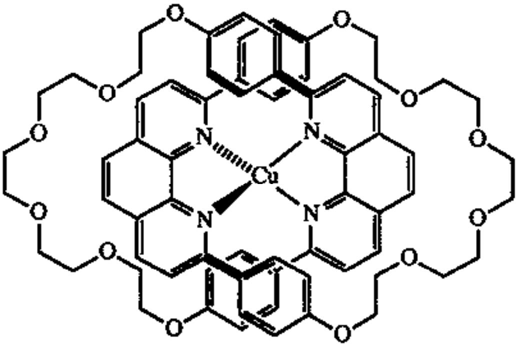
[b] expressions in parenthesis represent co-ordination sphere of donor atoms

4.3.2 Mononuclear copper(I)

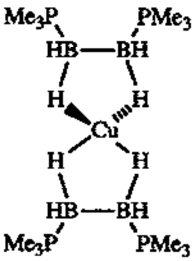
Numerous papers have appeared involving the copper(I) ion, and many of these have already been cited above. However, this section limits its remit only to mononuclear complexes and especially to cases where the complexes have been structurally characterised.

The synthesis of entwined ligands, or interlocked macrocycles (catenands), continued to be a productive area in 1990 [249]. The copper(I) ion is implicated in the templated organisation of such ligand arrangements. It is the copper(I)-enforced tetrahedral pre-organisation of the reacting functionalities of the precursor ligands that directs the reaction to produce the mechanically interlocked catenands (**56**). Studies of the chelating open-chain 'fragments' of the catenands suggest that interaction between the ligands within the copper(I) coordination sphere, such as mesomeric phenyl interactions, are also factors determining the stability of precursor pre-organisation [250].

Tripodal Schiff-base ligands, derived from tris(aminoalkyl)amines, give rise to trigonal pyramidal complexes with long bonds to the apical bridgehead nitrogen compared to the distances for the equatorial pendant nitrogens [251].



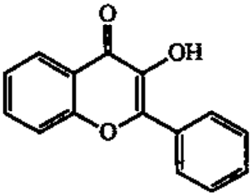
(56)



(57)

A most interesting structure for *bis*{*bis*(trimethylphosphine)-tetrahydroboron}copper(I) is reported as the tetrahedral ligation of copper(I) by means of two vicinal hydrogen atoms on each ligand (**57**) [252].

Ligands involving softer donors have also been examined. Tetrahedral complexes result with an N_2S_2-donor macrocycle [253]; while distorted tetrahedral complexes are characterised for $[Cu(PMe_3)]_4^+$ [254], and $[CuL(PPh_3)_2]$, where HL = 3-hydroxyflavone (**58**) [255]. Lower co-ordination numbers of three [256], and two [257] are also reported.



(58)

A number of remaining structurally characterised complexes are summarised in Table 2.

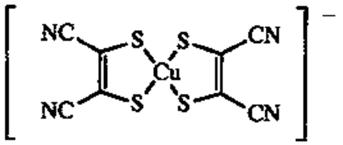
Table 2 Some structurally characterised copper(I) complexes.

Ligand (L)	Complex	Structure[a]	Notes	Ref.
2,5-dimethylpyrazine	$CuL_2(CF_3SO_3)$	Tet. (N_3O)	Polymeric; bridging L	258
1-methyl-1,3-imidazoline-2-thione	$CuL(PPh_3)_2Br$	Tet. (BrP_2S)	12 analogues also reported	259
pyridine-2-thione	$[CuL_2(PPh_3)_2]^+$	Tet. (P_2S_2)	8 analogues also reported	260
carbon monoxide	CuLCl	Tet. (Cl_3CO)	Cl^--bridged layers	261
dibenzotetrathia-fulvalene	$L[Cu(NCS)_2]$	Bent		262

[a] Tet. = tetrahedral; expression in parenthesis indicates co-ordination sphere

4.3.3 Mononuclear copper(III)

The oxidative addition of dibenzoyl peroxide to copper(I) chloride gives an isolable copper(III) product, $[CuCl(BzO)_2(Py)_2]$, which is shown by X-ray crystallography to have tetragonal pyramidal geometry [263]. Another structurally characterised copper(III) complex in the solid state, is that of the anion bis(*cis*-1,2-dicyanoethylenedithiolato)cuprate(III) (59) [264].



(59)

Other reports concerning copper(III) relate to solution studies, usually of short-lived species, and commonly involve the use of macrocyclic ligands. Thus, in a study of the spectral properties of copper(II) and copper(III) complexes of amide-containing macrocyclic ligands, it has been shown that, of the two states, the +3 ion is more sensitive to changes in ligand structure such as ring size and the nature of substituents [265]. A chlorine-bridged inner-sphere mechanism is proposed for the production of copper(III) species by oxidation of copper(II) tetraaza-macrocyclic complexes using photo-generated oxidants such as Cl^- and OCl^- [266]; axial co-ordination of chloride is said to stabilise the copper(III) state. In this connection, a kinetic study of diimine macrocyclic complexes also purports a similar stabilisation from axial halide co-ordination [267]. In a pulse-radiolysis study, the oxidation of copper(II) to copper(III) using methyl free-radicals in aqueous solution demonstrates the feasibility of the use of aliphatic free-radicals to generate very short-lived copper(III) species, and suggests that they may be implicated in the reported radiosensitisation effect of copper compounds [268]. Finally, a photochemical study of copper(II) macrocyclic complex, bound to poly(acrylic acid), shows the generation of a short-lived copper(III) intermediate [269].

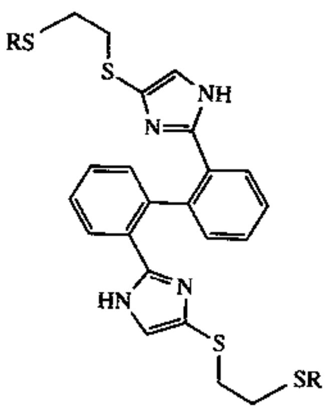
4.4 BIOLOGICAL COPPER

This section has been subdivided into three categories: model compounds; studies on natural systems; and, biologically related uses of copper compounds. Segregation of complexes classed as models for natural systems was problematic since many copper complexes are of relevance in this respect, but to varying degrees. Inclusion as a 'model' has been largely restricted to those compounds which have not already been described above, and which in addition, are overtly classified as models in either the title or the abstract of the paper.

4.4.1 Model complexes

4.4.1.1 Type I copper

Interest in this area remains steady, with the complex which will satisfactorily model several of the key type I features still remaining elusive. The topic was the subject of a 103-reference review [270] covering aspects of both the synthetic chemistry and the physical data of the compounds.

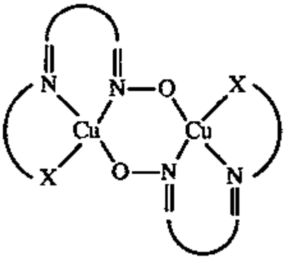


(60)

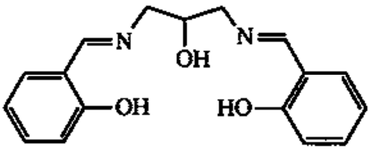
In a study of tetrahedral copper(II) complexes of hindered tris(pyrazolyl)-borate ligands, a thiolato derivative of the form $[Cu(SBu^t)L]$ has been isolated at low temperature [271]. The visible and ESR spectra of the compound are promising for a model, while the X-ray structure of the more stable analogue, [Cu(Cl)L], establishes the co-ordination environment as tetrahedral. A series of ligands with N_2S_2-donor sets, derived from the condensation of (1R)-3-hydroxymethyleneborane-2-thione and 2-aminothia-alkyl-1-methyl-benzimidazoles, gives rise to tetrahedral copper(II) complexes on the basis of visible and ESR spectral evidence [272]; electrochemical work shows that the copper(I) derivatives of these compounds are readily accessed. The nearly tetrahedral copper(I) complexes, [CuL], of **(60)** have been structurally characterised in the solid state, showing normal Cu-N distances while the Cu-S distances are long in comparison to related complexes, and short in comparison to the reduced form of plastocyanin [273]. In contrast, the copper(II) analogues form $[CuL_2]$ complexes, indicative of a switch to N_4-coordination. A stabilising effect of insulin on the copper(II) thiolate bond in intensely blue complexes of pentafluorothiophenol has been noted [274]. The kinetics of the reduction of copper(II) to copper(I) by hydroquinone in the presence of polydentate 8-mercaptoquinolyl phenols has also been examined with a view to model activity [275].

4.4.1.2 Type II and type(III) copper

The binuclear copper(I) complexes of **(31)** have already been described above as having exocyclic copper, as in **(22)**. This complex comes close to achieving two very important criteria in the modelling of type III copper: (i) the stabilisation of the Cu-O_2-Cu intermediate and, (ii) the moderation of the copper(II)/copper(I) potential to achieve reversible binding of dioxygen [66]. Thus, the macrocyclic 'platform', together with the bulk of *N*-pendant pyridyl groups, provides sufficient restriction of access to the coppers, as to severely limit the degree of dimer formation, and hence prevents full and irreversible 4-electron reduction of the dioxygen. Further, the pendant nature of the pyridyl ligands provides a low-energy pathway for geometrical changes that accompany redox processes, while the electronic properties of the group lend a considerable positive shift of potential relative to pendant amine groups. The uptake of dioxygen is quasi-reversible and corresponds to 0.75 of a molecule per dicopper site; this is attributed to a mixture of the 1:1 adduct which reversibly binds O_2, and a mixed-valence O_2-bridged dimer which is irreversible with respect to binding.



(61)



(62)

A series of model complexes are reported of the form $Cu_2L_2X_2$ **(61)** with a strictly planar 6-membered $Cu(ON)_2Cu$ core [276]. Extensive π-delocalisation within this core facilitates strong antiferromagnetic coupling between the metal centres to the extent that the complexes are rendered diamagnetic at all measurable temperatures up to 400 K. The strong coupling, together with other spectroscopic data, is compared with that of biological type III copper in oxidases. In addition, a further series of complexes based on the structure **(62)** is reported in the same paper. These complexes are models for the active site of ascorbate oxidase, now known to contain both type III and type II copper.

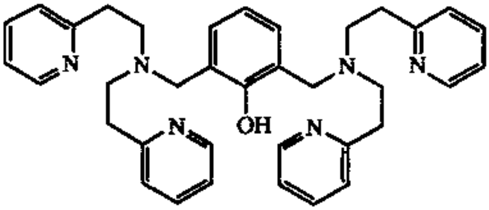
The remaining type III models are structurally very similar, being based on binucleating ligands with pendant bridging hydroxide groups; 1,3-diaminopropan-2-ol is a popular synthetic platform for the generation of such ligands by reaction at the primary amines. Thus, the importance of the plasticity of the co-ordination sphere of copper(I), in model studies using *N*-pendant imidazolyl ligands of this genre, emphasises that the superior ligand constraints imposed by the protein in the natural systems is improtant for the maintence of irregular geometries around copper(I) [277]. The closely related ligand derived from the Schiff-base condensation with acetylacetone yields a copper(II)-azido complex which is a model for metazidohaemocyanin [278]. Other model compounds examine the role of the endogenous bridge in oxyhaemocyanin [279], and the kinetics, and mechanism of ligand substitution [280].

4.4.13 Miscellaneous

Models for the metalloenzymes superoxide dismutase [281], cytochrome-c-oxidase [282, 283], the phenolase and catecholase activity of tyrosinase [55], and monooxygenases [284] appear.

In particular, a copper(III)-induced *C*-terminal oxidative *N*-dealkylation reaction of peptide-derived ligands has been proposed as a model for the copper enzyme peptidyl α-amidating monooxygenase [285]. The reaction of a trinuclear copper(I) complex, $Cu_3L(PF_6)_3$, with dioxygen, with complete 4-electron reduction, together with formation of a hexanuclear copper(II) cluster, $\{[Cu_3L(OH)]_2(\mu\text{-}OH)_2\}(PF_6)_6$, emphasises the importance of a 3-electron trinuclear copper(I) source for dioxygen reduction in model compounds of cytochrome-*c*-oxidase [283]. Other studies include models for metal ion-assisted molecular recognition using copper(II)-*D*/*L*-histidine complexes [286]; the biomimetic binding of azide and thiocyanate to copper [287], and the biomimetic reduction of copper(II) [288]. The deoxyrybonucleohelicates are double-stranded, double-helical (with the bases on the 'outside' of the helix) complexes which self-assemble under the directive influence of tetrahedral co-ordination to copper(I) [289]. These topologically interesting compounds are cited as useful structural and models for the formation of double helices, and also for the study of the selectivity of binding of complementary entities to the external bases.

The reaction of the mixed-valence compound, $[Cu_2L]PF_6$ in which HL = 2,6-bis(bis(2-pyridylethyl)aminomethyl)phenol (**63**), with $[NO]PF_6$ to give $\{Cu_2L(\mu\text{-}NO)\}(PF_6)_2.2CH_2Cl_2$ serves as a model for the ion-mediated nitrite reduction in enzymes [290].



(63)

4.4.2 Protein studies

The results of a comparative kinetic study of cyanide binding to haemocyanin and tyrosinase, indicate that the active site in the latter is much more accessible than that of the former

[291]. The effects of pH on the structure and reactivity of the blue-copper proteins, azurin and amicyanin, have been examined [292]. Intercalative binding to DNA by copper(II) complexes of porphyrinic ligands enhances unwinding relative to the metal-free porphyrin [293]. The hydrolytic cleavage of RNA oligomers by potentially redox-active copper(II) complexes of pyridine-derived ligands showed no significant difference from non-redox-active metal complexes [294]. pH-Dependant redox titrations of cytochrome-*c* oxidase ligated with cyanide are interpreted on the basis of an interaction between the haeme group and at least two other copper components [295]. The characterisation of a 0.5:1 carbon monoxide:copper(I) adduct of reduced dopamine β-hydroxylase provides "the first evidence" for structural non-equivalence in the copper(I) centres of the enzyme [296]. The uptake of copper(II) by brain tissue was found to be facilitated by complexation using histidine in a study of the uptake of complexed copper-67 by brain hypothalamic tissue [297]. A mechanism for the cellular uptake of copper from ceruloplasmin proposes that the protein never enters the cells, dissociation of the copper being necessary prior to uptake by the cell [298]. Formation of a copper(II) derivative of thioredoxin (from Escherichia coli) allowed crystallisation of the protein, and the resolution of a crystal structure at 1.68 Å with a crystallographic *R*-factor of 0.165 [299]. The structure, which gives important information about the active-site disulfide bridge, showed a distorted octahedral copper environment which facilitates essential packing interactions in the crystal.

4.4.3 Biologically relevant ligands

The stability of copper(II) complexation by ATP and AMP has been examined in a range of 1,4-dioxane-water mixtures in order to mimic the behaviour of resultant species in proteins [300]. The results suggest the extent of macrochelate formation is both variable and unpredictable, and indicates that at the protein-water interface, changes in polarity may cause structural changes in the complexes.

Schiff-base complexes, derived from the condensation of sulfophenylglycine with the vitamin-B_6 co-enzymes pyridoxal 5'-phosphate and 5'-deoxypyridoxal, have been shown to react with O_2 to produce the corresponding oximes as O_2-insertion products [301].

The interaction of copper with amino acids has been examined in a number of respects, ranging from structural: *L*-threonato [302], glycinato [303], cytosine [304]; to electronic: *L*-histidinato and *L*-asparaginato [305], histamine and adenosine [306]; to electrochemical: cysteine [307]; to ESR: histamine [306].

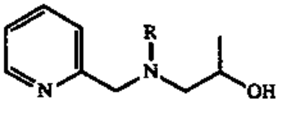
The interaction of copper with a range of other biologically relevant ligands of industrial and medicinal significance are mentioned. Saccharin, as saccharinate, with copper has been examined both structurally [308], and electronically [309]. The antiinflammatory drugs tolmetin, ibuprofen and naproxen deprotonate to ligate copper(II) as the monomeric and dimeric complexes $CuL_2(py)_2$ and $Cu_2L_4(DMSO)_2$ [310]; while the antiflammatory drug piroxicam binds copper(II) through amide and pyridyl nitrogens to form $CuL_2(DMF)_2$ [311]. The reaction of streptomycin with $CuCl_2$ in aqueous solution afforded the copper(II) complex of the hydrolysed product stretidine [312]. A *trans*-square planar complex of formula $CuL_2(py)_2$, where L = the antidiabetic drug acetohexamide, has also been reported [313]. Reports appear on the interaction of copper(II) with the herbicide acifluorfen [314], and the mutagenic agent 5-bromouracil [315].

4.4.4 *Biologically Applied Studies*

Kinetically stable complexes of tetraazamacrocycle-monoclonal antibody conjugates, containing both copper-64 and copper-67, have been developed and studied with a view towards their potential as tumour targetting agents [316]. The serum stability of copper-67 complexes of bifunctional chelating agents and macrocyclic ligands has been reported [317]. Computer simulations of the blood plasma distribution of a number of metal complexes of diethylenetriamine pentaacetic acid, including copper(II), which are potential contrast agents in NMR imaging have been undertaken [318]. The antifungal properties of copper(II) complexes of thiosemicarbazones derived from 2-acetylpyridine have been examined along with other first-row transition metals [319].

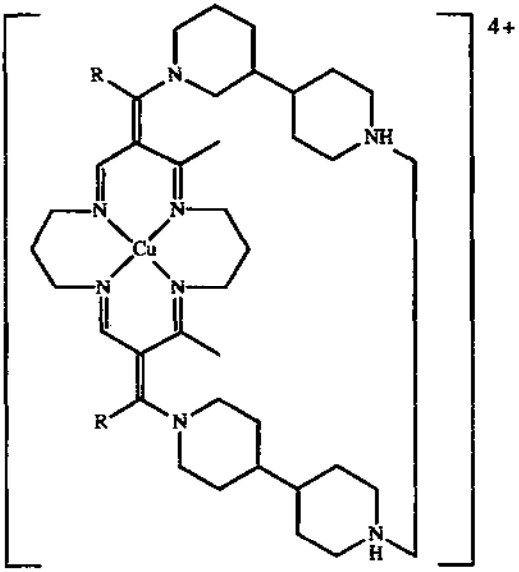
4.5 *SUPRAMOLECULAR CHEMISTRY*

The incorporation of metal chelates, including copper, into bilayer membranes, either as a component of the bilayer, or as a guest molecule, has been the subject of a short review [320]. A 30-reference review discusses the interlacing of molecular threads, with particular emphasis on the exploitation of copper co-ordination chemistry [321]. Studies on the formation of molecular vesicles, by the liquid surfactant dihexadecyl[5-(1-imidazolyl)-3-oxapentyl]methylammonium chloride, have shown that copper(II) initiates vesicle formation through co-ordination within the bilayers [322]. Hydrolytic metallomicelles, made up of ligand (64) (with R = $^{n}C_{16}H_{33}$) and copper(II), show catalytic properties in the cleavage of the *p*-nitrophenyl ester of picolinic acid [323]. The importance of the supramolecular assembly is demonstrated through the lack of activity for the analogous complex with R = Me.



(64)

Inclusion complexes of alcoholic guests in vaulted macrocyclic copper complexes (65) are reported to be regiospecific and driven by hydrophobic interactions in aqueous media [324]; crystallographic and NMR spectroscopic results are reported.



(65)

REFERENCES

1. I. Castro, J. Faus, M. Julve, F. Lloret, M. Verdaguer, O. Kahn, S. Jeannin, Y. Jeannin, and J. Vaissermen, *J. Chem. Soc., Dalton Trans.*, (1990) 2207.
2. D.A. Firmin, E.R. Quilano, R. Cameron, A.K. Pant, E.D. Stevens, C.J. O'Connor, O. Kahn, and T. Mallah, *Inorg. Chim. Acta*, 172 (1990) 211.
3. O.J. Gelling, A. Meetsma, and B.L. Feringa, *Inorg. Chem.*, 29 (1990) 2816.
4. I. Castro, J. Faus, M. Julve, M. Verdaguer, A. Monge, and E. Gutierrez-Puebla, *Inorg. Chim. Acta*, 170 (1990) 251.
5. G. Christou, S.P. Perpeles, K. Folting, J.C. Huffman, R.J. Webb, and D.N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, (1990) 746; G. Christou, S.P. Perpeles, E. Libby, K. Folting, J.C. Huffman, R.J. Webb, and D.N. Hendrickson, *Inorg. Chem.*, 29 (1990) 3657.
6. (a) N. Kitajima, K. Fujisawa, and Y. Morooka, *Inorg. Chem.*, 29 (1990) 357; (b) N. Kitajima, T. Koda, Y. Iwata, and Y. Morooka, *J. Am. Chem. Soc.*, 112 (1990) 8833.
7. D. Liao, Q. Zhao, and G. Wang, *Sci. China, Ser. B*, 33 (1990) 914.
8. M. Drillon, A. Grand, and P. Rey, *Inorg. Chem.*, 29 (1990) 771.
9. F. Demartin, M. Manassero, L. Naldini, A. Panzanelli, and M.A. Zoroddu, *Inorg. Chim. Acta*, 171 (1990) 229.
10. T. Lindgren, R. Sillanpaa, K. Rissanen, L.K. Thompson, C.J. O'Connor, G.A. Van Albada, and J. Reedijk, *Inorg. Chim. Acta*, 171 (1990) 95.
11. S. Brooker and V. McKee, *Inorg. Chim. Acta*, 173 (1990) 69.
12. A. Tosik, M. Bukowska-Strzyzewska, and J. Mrozinski, *J. Coord. Chem.*, 21 (1990) 253.
13. J.V. Folgado, P. Gomez-Romero, F. Sapina, and D. Beltran-Porter, *J. Chem. Soc., Dalton Trans.*, (1990) 2325.
14. A. Caneschi, F. Ferraro, D. Gatteschi, P. Rey, and R. Sessoli, *Inorg. Chem.*, 29 (1990) 1756.
15. R.G. Bhirud and T.S. Srivastava, *J. Inorg. Biochem.*, 40 (1990) 331.
16. J.P. Costes and M.I. Fernandez-Garcia, *Inorg. Chim. Acta*, 173 (1990) 247.
17. T.N. Doman, D.E. Williams, J.F. Banks, R.M. Buchanan, H.R. Chang, R.J. Webb, and D.N. Hendrickson, *Inorg. Chem.*, 29 (1990) 1058; T. Kamiusuki, H. Okawa, N. Matsumoto, and S. Kida, *J. Chem. Soc., Dalton Trans.*, (1990) 195.
18. H. Oshio and U. Nagashima, *Inorg. Chem.*, 29 (1990) 3321; A.W. Maverick, M.L. Ivie, J.H. Waggenspack, and F.R. Fronczek, *Inorg. Chem.*, 29 (1990) 2403.

19. S.M. Peng and H.F. Chen, *Bull. Inst. Chem. Acad. Sin.*, 37 (1990) 49; K. Bertoncello, G.D. Fallon, and K.S. Murray, *Polyhedron*, 9 (1990) 2867; T.C.W. Mak, W.H. Yip, C.H.L. Kennard, and G Smith, *Polyhedron*, 9 (1990) 1667; T. Tokii, N. Watanabe, N.M. Nakashima, Y. Muto, M. Morooka, S. Ohba, and Y Saito, *Bull. Chem. Soc. Jpn.*, 63 (1990) 364; T. Tokii, M. Nakashima, T. Furukawa, Y. Muto, and R.L. Lindvedt, *Chem. Lett.*, (1990) 363; H.D. Nguyen, B. Viossat, A. Busnot, A.G. Sicilia Zafra, J.M. Gonzalez Perez, J. Niclos Gutierrez, *Inorg. Chim. Acta*, 169 (1990) 9; L.P. Battaglia, A. Bonamartini Corradi, and M.A. Zoroddu, *J. Crystallogr. Spectrosc. Res.*, 20 (1990) 161; M. Melnik, Z. Sabova, J. Morzinski, and A. Szymasek, *J. Mol. Struct.*, 240 (1990) 285; L. Menabue and M. Saladina, *J. Chem. Soc., Dalton Trans.*, (1990) 1581.
20. A. Deeg, D. Mootz, and H. Wunderlich, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1927.
21. S. Alverez, M. Julve, and M Verdaguer, *Inorg. Chem.*, 29 (1990) 4500.
22. X. Solans, M. Aguilo, A. Gleizes, J. Faus, M. Julve, M. Verdaguer, *Inorg. Chem.*, 29 (1990) 775.
23. K. Matsumoto, S. Ooi, W. Mori, and Y Nakao, *J. Chem. Soc., Dalton Trans.*, (1990) 3117.
24. T. Rojo, J.I.R. Larramendi, I. Duran, J.L. Mesa, J. Via, and M.I. Arriotua, *Polyhedron*, 9 (1990) 2693.
25. A.E. Mauro, S.I. Klein, J.S. Saldana, C.A. De Simone, J. Zukerman-Schpector, and E.E. Castellano, *Polyhedron*, 9 (1990) 2937.
26. J. Sletten, and A. Soerensen, *Acta Chem. Scand.*, 44 (1990) 1018.
27. N. Kitajima, K. Fujisawa, T. Koda, S. Hikichi, and Y. Morooka, *J. Chem. Soc., Chem. Commun.*, (1990) 1357.
28. P.D. Ackrivos, M.N. Christanopoulou, N. Baumgarten, and P. Kokorotsikos, *Spectrochim. Acta, Part A*, 46A (1990) 363.
29. M.L. Brader, E.W. Ainscough, E.N. Baker, A.M. Brodie, and S.L. Ingham, *J. Chem. Soc., Dalton Trans.*, (1990) 2785.
30. H. Okawa, N. Matsumoto, M. Koikawa, K. Takeda, and S. Kida, *J. Chem. Soc., Dalton Trans.*, (1990) 1383.
31. S. Ferrer, J. Borras, C. Miratvilles, and A. Fuertes, *Inorg. Chem.*, 29 (1990) 206.
32. E.O. Schlemper, J Stunkel, and C. Patterson, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1226; Y.M. Wang, C.C. Wang, S.L. Wang, and C.S. Chung, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1770.
33. D. Luneau, H. Oshio, H. Okawa, M. Koikawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, 63 (1990) 2212.
34. N.D. Kulkarni, M. Jacob, K.V. Patel, and P.K. Bhattacharya, *Synth. React. Inorg. Met.-Org. Chem.*, 20, 937.
35. S.K. Mandal, L.K. Thompson, M.J. Newlands, E.J. Gabe, and F.L. Lee, *Inorg. Chem.*, 29 (1990) 3556.
36. C.M. Mikulski, G. Borges (Jr.), A. Renn, and N.M. Karayannis, *J. Coord. Chem.*, 21 (1990) 89.
37. E. Dubler, G. Haenggi, and H. Schmalle, *Inorg. Chem.*, 29 (1990) 2518.
38. A. Mederos, P. Gili, S. Dominguez, A. Benitez, P.M. Soledad, M. Hernandez-Padilla, P. Martin-Zarza, M.L. Rodriguez, C. Ruiz-Perez, F.J. Lahoz, L.A. Oro, F. Brito, J.M. Arrieta, M. Vlassi, and G. Germain, *J. Chem. Soc., Dalton Trans.*, (1990) 1477; C. Ruiz-Perez, M.L. Rodriguez, F.V. Rodriguez-Romero, A. Mederos, P. Gili, and P. Martin-Zarza, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1405.
39. H. Adams, N.A. Bailey, W.D. Carlisle, and D.E. Fenton, *Acta Crystallogr., Sect. C: Cryst.Struct. Commun.*, C46 (1990) 1439.
40. H. Oshio, *J. Chem. Soc., Dalton Trans.*, (1990) 2985; H. Oshio, K. Toriumi, and Y. Hayashi, *J. Chem. Soc., Dalton Trans.*, (1990) 293.
41. H Adams, G. Candeland, J. D. Crane, D.E. Fenton, and A.J. Smith, *J. Chem. Soc., Chem. Commun.*, (1990) 93.
42. A. Markiewicz, K.S. Murray, I.L. Swann, and S.R. Pickering, *Aust. J. Chem.*, 43 (1990) 1407.
43. C.R. Lucas, S. Liu, and L.K. Thompson, *Inorg. Chem.*, 29 (1990) 85.
44. P.G. Graham, D.C. Weatherburn, F.C. March, and W.T. Robinson, *Inorg. Chim. Acta*, 178 (1990) 227.
45. P. Chaudhuri and K. Oder, *J. Chem. Soc., Dalton Trans.*, (1990) 1597.
46. M. Fujiwara, H. Wakita, T. Matshushita, and T. Shono, *Bull. Chem. Soc. Jpn.*, 63 (1990) 3443.
47. C. Harding, D. McDowell, J. Nelson, S. Raghunathan, C Stevenson, M.G.B. Drew, and P.C. Yates, *J. Chem. Soc., Dalton Trans.*, (1990) 2521.
48. R. Menif, A.E. Martell, P.J. Squatritto, and A. Clearfield, *Inorg. Chem.*, 29 (1990) 4723.

49. S.K. Mandal, L.K. Thompson, M.J. Newlands, E.J. Gabe, and K Nag, *Inorg. Chem.*, 29 (1990) 1324.
50. P. Comba, G.A. Lawrance, T.M. Manning, A. Makiewicz, K.S. Murray, M.A. O'Leary, B.W. Skelton, and A.H. White, *Aust. J. Chem.*, 43 (1990) 69.
51. I. Murase, I. Ueda, N. Marubayashi, S. Kida, N. Matsumoto, M. Kudo, M. Toyohara, K. Hiate, M. Mukuriya, *J. Chem. Soc., Dalton Trans.*, (1990) 2763.
52. G. Vuckovic, E. Asato, N. Matsumoto, and S, Kida, *Inorg. Chim. Acta*, 171 (1990) 45.
53. Y. Nishida, *Z. Naturforsch., B: Chem. Sci.*, 45 (1990) 39.
54. M. Munakata, M.Maekawa, S. Kitagawa, M. Adachi, and H. Masuda, *Inorg. Chim. Acta*, 167 (1990) 181.
55. M. Reglier, C. Jorand, B. Waegall, *J. Chem. Soc., Chem. Commun.*, (1990) 1752.
56. G.A. Ardizzoia, M.A. Angaroni, G. La Monica, N. Masciocchi, and M. Moret, *J. Chem. Soc., Dalton Trans.*, (1990) 2277; M.P. Gamasa, J. Gimeno, E. Lastra, J.M. Rubio Gonzalez, and S. Garcia-Granda, *Polyhedron*, 9 (1990) 2603.
57. S.W. Lee, and W.C. Trogler, *Inorg. Chem.*, 29 (1990) 1659.
58. J. Diez, P. Gamasa, J. Gimeno, M. Lanfranchi, and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, (1990) 1027.
59. P. Karagiannidis, S.K. Hadjikakou, P. Aslanidis, amd A. Hountas, *Inorg. Chim. Acta*, 178 (1990) 27.
60. X. Jin, K. Tang, Y. Han, A. Camus, N. Marsich, *J. Coord. Chem.*, 22 (1990) 1.
61. F Olbrich, J. Kopf, E. Weiss, A. Krebs, and S. Mueller, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1650.
62. A.J. Blake, R.O. Gould, A.J. Holder, A.J. Lavery, and M. Shroeder, *Polyhedron*, 9 (1990) 2919.
63. A.J. Blake, A. Taylor, and M. Schroeder, *Polyhedron*, 9 (1990) 2911.
64. P.M. Ngwenya, A.E. Martell, and J Reibenspies, *J. Chem. Soc., Chem. Commun.*, (1990) 1207.
65. D. Mac Dowell and J. Nelson, *Tett. Lett.*, (1988) 385.
66. E. Asato, S. Hashimoto, N. Matsumoto, and S. Kida, *J. Chem. Soc., Dalton Trans.*, (1990) 1741.
67. T.A. Wark and D.W. Stephan, *Inorg. Chem.*, 29 (1990) 1731.
68. Z.J. Zhong, N. Matsumoto, H. Okawa, and S Kida, *Chem. Lett.*, (1990) 87.
69. K. Nakatani, O. Kahn, C. Mathoniere, Y. Pei, C. Zakine, and J.P. Renard, *New. J. Chem.*, 14 (1990) 861.
70. P.J. Van Koningsbruggen, O. Kahn, K. Nakatani, Y. Pei, J.P. Renard, M. Drillon, and P Legoll, *Inorg. Chem.*, 29 (1990) 3325.
71. M.C. Munoz Roca, D. Beltran, J.A. Real, A. Mosset, and J. Galy, *J. Chem. Soc., Dalton Trans.*, (1990) 1131.
72. M.A. El-Sayed, and G. Davies, *Inorg. Chim. Acta*, 173 (1990) 163.
73. A. El-Dissouky, and G.B. Mohamad, *Inorg. Chim. Acta*, 168 (1990) 241.
74. D. Chen, Z. Liu, W. Tang, A. Dai, W. Liu, B. Wang, M. Wang, and P Zheng, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1426.
75. K. Mochizuki, A. Iijima, Y. Endoh, and Y. Ikeda, *Bull. Chem. Soc. Jpn.*, 63 (1990) 565.
76. Z.Y. Zhang, D.Z. Liao, K.H. Jiang, S.Q. Hao, X.K. Yao, H.G. Wang, and G.L. Wang, *Inorg. Chim. Acta*, 173 (1990) 201.
77. H. Oshio, K.Toriumi, S. Bandow, K. Miyagawa, and S. Kurita, *J. Chem. Soc., Dalton Trans.*, (1990) 1013.
78. N. Matsumoto, M. Sakamoto, H. Tamaki, H. Okawa, and S. Kida, *Chem. Lett.*, (1990) 853.
79. M. Sato, M. Katada, S. Nakashima, H. Sano, and S. Akabori, *J. Chem. Soc., Dalton Trans.*, (1990) 1979.
80. D.L. Kepert, *Chemtracts: Anal., Phys., Inorg. Chem.*, 2 (1990) 328; B.F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 112 (1990) 1546.
81. J.C. Chambron and J.P. Sauvage, *New J. Chem.*, 14 (1990) 883.
82. R.W. Gable, B.F. Hoskins, and R. Robson, *J. Chem. Soc., Chem. Commun.*, (1990) 762.
83. L.P. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B. Hathaway, C. Simmons, and P. Thornton, *J. Chem. Soc., Dalton Trans.*, (1990) 3835.
84. M.R, Godfrey, T.P. Newcombe, B.M. Hoffman, and J.A. Ibers, *J. Am. Chem. Soc.*, 112 (1990) 7260.
85. D. Luneau, H. Oshio, H. Okawa, and S. Kida, *J. Chem. Soc., Dalton Trans.*, (1990) 2283.
86. W. Vreugdenhill, J.G. Haasnoot, J. Reedijk, and J.S. Wood, *Inorg. Chim. Acta*, 167 (1990) 109.
87. R. Sillanpaa, and K. Rissanen, *Acta Chem. Scand.*, 44 (1990) 1013.
88. K. Smolander and K. Liesto, *Inorg. Chim. Acta*, 169 (1990) 151.
89. H. Okawa, M. Koikawa, S. Kida, D. Luneau, and H. Oshio, *J. Chem. Soc., Dalton Trans.*, (1990) 469.

90. A. Garcia, R. Costa, and J. Ribas, *Inorg. Chim. Acta*, 168 (1990) 249; Y. Journaux, F.Llauret,and O. Kahn, *Inorg. Chem.*, 29 (1990) 3048; R. Bariz, C. Bremard, G. Nowogrocki, and S. Sueur, *Polyhedron*, 9 (1990) 2663.
91. C. Fukuhara, K. Tsuneyoshi, N. Matsumoto, S. Kida, M. Mikuriya, and M. Mori, *J. Chem. Soc., Dalton Trans.*, (1990) 3473.
92. S.A. Mbogo, W.R. McWhinnie, and, T.S. Lobana, *Inorg. Chim. Acta*, 172 (1990) 221.
93. M.R. Bond, R.D. Willett, R.S. Rubins, P. Zhou, C.E. Zaspel, S.L. Hutton, and J.E. Drumheller, *Phys. Rev. B: Condens. Matter*, 42 (1990) 10280.
94. G.A. Bowmaker, A. Camus, R.D.Hart, J.D. Kildea, B.W. Skelton, and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1990) 3753.
95. M.K. Ehlert, S.J. Rettig, A. Storr, R.C. Thompson, and J. Trotter, *Can. J. Chem.*, 68 (1990) 1444.
96. M. Angaroni, G.A. Ardizzoia, T. Beringhelli, G. La Monica, D. Gatteschi, M. Massciocchi, and M. Moret, *J. Chem. Soc., Dalton Trans.*, (1990) 3305.
97. P Chaudhuri, M. Winter, P. Fleischhauer, W. Haase, U Floerke, and H.J. Haupt, *J. Chem. Soc., Chem. Commun.*, (1990) 1728.
98. J. Ribas, C. Diaz, R. Costa, Y. Journaux, C. Mathoniere, O. Kahn, and A. Gleizes, *Inorg. Chem.*, 29 (1990) 2042.
99. V. Ahsen, A. Gurek, A. Gul, and O. Bekaroglu, *J. Chem. Soc., Dalton Trans.*, (1990) 5.
100. G.P. Gupta, G. Lang, C.A. Koch, B. Wang, W.R. Scheidt, and C.A. Reed, *Inorg. Chem.*, 29 (1990) 4234.
101. M. Bracci, C. Ercolani, B. Floris, M. Bassetti, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.*, (1990) 1357.
102. N. Zhu, Y. Zheng, and X. Wu, *Inorg. Chem.*, 29 (1990) 2705.
103. D.M. Knotter, W.J.J. Smeets, A.L. Spek, and G. Van Koten, *J. Am. Chem. Soc.*, 112 (1990) 5895.
104. R.L. Lindvedt, and J.K. Zehetmair, *Inorg. Chem.*, 29 (1990) 2204.
105. E. Gojon, J.M. Latour, S.J. Greaves, D.C. Povey, V. Ramdas, and G.W. Smith, *J. Chem. Soc., Dalton Trans.*, (1990) 2043.
106. T.J.R. Weakly, and R.G. Finke, *Inorg. Chem.*, 29 (1990) 1235.
107. J.A. Samuels, B.A. Vaarstra, J.C. Huffman, K.L. Trojan, W.E. Hatfield, and K.G. Caulton, *J. Am. Chem. Soc.*, 112 (1990) 9623.
108. H.M. Handler, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 2054.
109. D.J. Brauer, G. Hessler, P.C. Kneuppel, and O. Stelzer, *Inorg. Chem.*, 29 (1990) 2370.
110. A. Erdonmez, J.H. Van Diemen, R.A.G. De Graaff, and J. Reedijk, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 402.
111. E. Ramli, T.B. Rauchfuss, and C.L. Stern, *J. Am. Chem. Soc.*, 112 (1990) 4043.
112. X. Bao, and E.M. Holt, *J. Crystallogr. Spectrosc. Res.*, 20 (1990) 339.
113. B. Becker, W. Wojnowski, K. Peters, E.M. Peters, and H.G. Von Schnering, *Polyhedron*, 9 (1990) 1659.
114. M.M. Olmstead, and P.P. Power, *J. Am. Chem. Soc.*, 112 (1990) 8008.
115. E. Colacio, J.P. Costes, R. Kivekas, J.P. Laurent, and J. Ruiz, *Inorg. Chem.*, 29 (1990) 4240.
116. E. Block, H. Kang, G. Ofori-Okai, and J. Zubieta, *Inorg. Chim. Acta*, 167 (1990) 147.
117. E. Bouwman, W.L. Dreissen, J. Reedijk, C. Smykalla, J.M.M. Smits, P.T. Beurskens, F. Laschi, and P. Zanello, *Inorg. Chem.*, 29 (1990) 4881.
118. M. Haakansson, and S. Jagner, *J. Organomet. Chem.*, 397 (1990) 383.
119. J. Sletten, A. Soerensen, M. Julve, and Y. Journaux, *Inorg. Chem.*, 29 (1990) 5054.
120. M.A. El-Sayed, and G. Davies, *Inorg. Chem.*, 29 (1990) 4891; M.A. El-Sayed, A. El-Toukhy, K.Z. Ismael, and A.A. El-Maradne, *Inorg. Chim. Acta*, 177 (1990) 155.
121. M. Baumgartner, H. Schmalle, and E. Dubler, *Polyhedron*, 9 (1990) 1155.
122. Y. Zang, Z. Yin, G. Wang, C. Zeng, A. Dai, and Z. Zhou, *Inorg. Chem.*, 29 (1990) 560.
123. X. Lei, Z.H. Huang, M. Hong, Q. Liu, and H. Liu, *Jiegou Huaxue*, 9 (1990) 53.
124. N. Zhu, Y. Zheng, and X. Wu, *J. Chem. Soc., Chem. Commun.*, (1990) 780.
125. Z. Huang, X. Lei, B. Kang, J. Liu, Q. Liu, M Hong, H. Liu, *Inorg. Chim. Acta*, 169 (1990) 25.
126. C. Benelli, A. Caneschi, D. Gateschi, O. Guillou, and L. Pardi, *Inorg. Chem.*, 29 (1990) 1750; C. Benelli, A. Caneschi, D. Gateschi, O. Guillou, and L. Pardi, *J. Magn. Magn. Mater.*, 83 (1990) 522.
127. F. Lloret, Y. Journaux, and M. Julve, *Inorg. Chem.*, 29 (1990) 3967.
128. M. R. Bond, R.D. Willet, and G.V. Rubenacher, *Inorg. Chem.*, 29 (1990) 2713.
129. A. Mueller, E. Krickemeyer,and M. Penk, *J. Chem. Soc., Chem. Commun.*, (1990) 321.
130. B. F. Hoskins, R. Robson, and P. Smith, *J. Chem. Soc., Chem. Commun.*, (1990) 488.

131. S. Kitagawa, M. Munakata, H. Shimono, S. Matsuyama, and H. Masuda, *J. Chem. Soc., Dalton Trans.*, (1990) 2105.
132. P. Espinet, J.Fornies, F. Martinez, M. Tomas, E. Lalinde, M.T. Moreno, A. Ruiz, and A.J. Welch, *J. Chem. Soc., Dalton Trans.*, (1990) 791.
133. S.S.D. Brown, I.D. Salter, T. Adatia, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, (1990) 799.
134. H. Liu, R. Cao, X.Lei, D. Wu, G. Wei, Z. Huang, M. Hong, and B. Kang, *J. Chem. Soc., Dalton Trans.*, (1990) 1023.
135. T.A. Annan, R. Kumar, and D.G. Tuck, *Inorg. Chem.*, 29 (1990) 2475.
136. G. Attilio Ardizzoia, M.A. Angaroni, G. La Monica, F. Cariati, M. Moret, and N. Masciocchi, *J. Chem. Soc., Chem. Commun.*, (1990) 1021.
137. R.E. Norman and R.E. Stenamp, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 6.
138. N. Dodoff, J. Macicek, O. Angelova, S. Varbanov, N. Spassovska, *J. Coord. Chem.*, 22 (1990) 219; R.M. El-Shazly, M.M. Bekheit, F.I. Taha, A.A.Y. Tawansi, *Transition Met. Chem. (London)*, 15 (1990) 337; B. Bremer, A.A. Pinkerton, and J.A. Walmsley, *Inorg. Chim. Acta*, 174 (1990) 27; B. Chiari, O. Piovesana, T. Tarantelli, and P.F. Zanazzi, *Inorg. Chem.*, 29 (1990) 1172.
139. O.P. Anderson, K.K. Brito, and S.K. Laird, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1600; M.L. Brader, E.W. Ainscough, E.N. Baker, A.M. Brodie, and D.A. Lewandoski, *J. Chem. Soc., Dalton Trans.*, (1990) 2089.
140. S. Lindross and P. Lumme, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 2039; F. Bigoli, M. Lanfranchi, and M.A. Pellinghelli, *J. Chem. Res., Synop.*, (1990) 214; M.B. Hursthouse, K.J. Izod, M.A. Mazid, and P Thornton, *Polyhedron*, 9 (1990) 535.
141. R.D. Willet, M.R. Bond, G. Pon, *Inorg. Chem.*, 29 (1990) 4160.
142. K. Wasielewski and R. Mattes, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1826.
143. G. Cros, A. Gleizes, J.P. Laurent, and M.H. Darbieu, *Inorg. Chim. Acta*, 174 (1990) 33.
144. S. Knapp, T.P. Keenan, X. Zhang, R. Fikar, J.A. Potenza, and H.J. Schugar, *J. Am. Chem. Soc.*, 112 (1990) 3452.
145. W.G. Haanstra, W.A.J.W. Van der Donk, W.L. Dreissen, J. Reedijk, J.S. Wood, and M.G.B. Drew, *J. Chem. Soc., Dalton Trans.*, (1990) 3123.
146. R. Hynes, N.C. Payne, and C.J. Willis, *J. Chem. Soc., Chem. Commun.*, (1990) 744.
147. R.J. Bachelor, F.W.B. Einstein, I.D. Gay, J.H. Gu, B.M. Pinto, and X.M. Zhou, *J. Am. Chem. Soc.*, 112 (1990) 3706.
148. W. Dietzsch, S. Rauer, R.M. Olk, R, Kirmse, K. Koehler, L. Golic, and B. Olk, *Inorg. Chim. Acta*, 169 (1990) 55.
149. R. Kirmse, K. Koehler, R.M. Olk, W. Dietzch, E. Hoyer, and G. Zwanenburg, *Inorg. Chem.*, 29 (1990) 4073.
150. P.A. Liddell, M.M. Olmstead, and K.M. Smith, *J. Am. Chem. Soc.*, 112 (1990) 2038.
151. D.G. Fortier and A. McAuley, *J. Am. Chem. Soc.*, 112 (1990) 2640.
152. G.A. Lawrance, M. Maeder, M.A. O'Leary, and F.H. Woon, *Polyhedron*, 9 (1990) 2227.
153. P.W. Wade and R.D. Hancock, *J. Chem. Soc., Dalton Trans.*, (1990) 1323; P.V. Bernhardt, G.A. Lawrance, B.W. Skelton, and A.H. White, *Aust. J. Chem.*, 43 (1990) 399.
154. R Singh, *Bull. Electrochem.*, 6 (1990) 834.
155. K.P. Balakrishnan, H.A.A. Omar, P Moore, N.W. Alcock, and G.A. Pike, *J. Chem. Soc., Dalton Trans.*, (1990) 2965; R. Bilewicz and M. Pietrazkiewicz, *Polyhedron*, 9 (1990) 2353; G. De Martino Norante, M.F. Di Vaira, S. Mazzi, and P. Stopioni, *Inorg. Chem.*, 29 (1990) 2822.
156. E. Kimura, Y. Kotake, T. Koike, M. Shionoya, and M. Shiro, *Inorg. Chem.*, 29 (1990) 4991.
157. R.W. Hay, M.T. Tarafder, *Transition Met. Chem. (London)*, 15 (1990) 490.
158. A. Schiegg and T. A. Kaden, *Helv. Chim. Acta*, 73 (1990) 716.
159. M. Studer, T.A. Kaden, and H.R. Maecke, *Helv. Chim. Acta*, 73 (1990) 149.
160. N.A. Bailey, D.E. Fenton, and D.J. Winter, *J. Chem. Soc., Dalton Trans.*, (1990) 15; W.N. Setzer, E.L. Cacioppo, Q. Guo, G.L. Grant, D.D. Kim, J.L. Hubbard, and D.G. Van der Veer, *Inorg. Chem.*, 29 (1990) 2672; Y.N. Belokon, L.K. Pritula, V.I. Tararov, V.I. Bakhmutov, Y.T. Struchkov, T.V. Timofeeva, and V.M. Belikov, *J. Chem. Soc., Dalton Trans.*, (1990) 1867.
161. U. Auerbach, U. Eckert, K. Weighardt, B. Nuber, and J. Weiss, *Inorg. Chem.*, 29 (1990) 938.
162. T.A. Annan, C, Peppe, and D.G. Tuck, *Can. J. Chem.*, 68 (1990) 1598.
163. J.Castro, J. Romero, J.A. Garcia-Vazquez, M.L. Duran, A. Castineiras, A. Sousa, and D.E. Fenton, *J. Chem. Soc., Dalton Trans.*, (1990) 3255.
164. I. Castro, J. Faus, M. Julve, J.M. Amigo, J. Sletten, and T. Debaerdemaeker, *J. Chem. Soc., Dalton Trans.*, (1990) 891.

165. B.F. Duerr and A.W. Czarnik, *J. Chem. Soc., Chem. Commun.*, (1990) 1707.
166. J. Chin, V.Jubian, and K. Mrejen, *J. Chem. Soc., Chem. Commun.*, (1990) 1326.
167. R.D. Hancock, P.W. Wade, M.P. Ngwenya, A.S. De Sousa, and K.V. Damu, *Inorg. Chem.*, 29 (1990) 1968.
168. R.D. Hancock, M.P. Ngwenya, A. Evers, P.W. Wade, J.C.A. Boeyans, and S.M. Dobson, *Inorg. Chem.*, 29 (1990) 264.
169. P.W. Wade, R.D. Hancock, J.C.A. Boeyens, and S.M. Dobson, *J. Chem. Soc., Dalton Trans.*, (1990) 483.
170. K.R. Adam, S. Donnelly, A.J. Leong, L.F. Lindoy, B.J. McCool, A. Bashall, M.R. Dent, B.P. Murphy, M. McPartlin, D.E. Fenton, and P.A. Tasker, *J. Chem. Soc., Dalton Trans.*, (1990) 1635.

171. K.I. Kinnear, J.C. Lockhart, and D.J. Rushton, *J. Chem. Soc., Dalton Trans.*, (1990) 1365.
172. P.K. Bhattacharya, M.R. Ullah, R.A. Khalii, S.J. Kitchen, and D.E. Fenton, *Polyhedron*, 9 (1990) 2239.
173. M. Shionoya, E.Kimura, and Y. Iitaka, *J. Am. Chem. Soc.*, 112 (1990) 9237.
174. C.H. Len and C.S. Chung, *J. Chem. Soc., Dalton Trans.*, (1990) 1755.
175. M.D. Benari and G.T. Hefter, *Aust. J. Chem.*, 43 (1990) 1791.
176. C. Ferragina and M.A. Massucci, *J. Chem. Soc., Dalton Trans.*, (1990) 1191.
177. J. Sabolovic and N. Raos, *Polyhedron*, 9 (1990) 1277.
178. J. Sabolovic and N. Raos, *Polyhedron*, 9 (1990) 2419.
179. P. Alemany and S. Alvarez, *Chem. Mater.*, 2 (1990) 723.
180. M.A.S. Goher, R.J. Wang, and T.C.W. Mak, *J. Crystallogr. Spectrosc. Res.*, 20 (1990) 265.
181. T. Kogane, M. Ishii, K. Harada, R. Hirota, and M. Nakahara, *Bull. Chem. Soc. Jpn.*, 63 (1990) 1005.
182. N.H. Dung, B. Viossat, A. Busnot, J.M. Gonzalez Perez, J. Niclos Gutierrez, F. Gardette,*Inorg. Chim. Acta*, 174 (1990) 145.
183. H. Yamaguchi, Y. Inomata, T. Takeuchi, *Inorg. Chim. Acta*, 172 (1990) 105.
184. A.H.J. Tullemans, E. Bouwman, R.A.G. De Graaff, W. L. Driessen, and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 109 (1990) 70.
185. J.P. Wignacourt, S. Sueur, and M. Lagrenee, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 394.
186. M. Parvez and W.J. Birdsall, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1775.
187. J. Emsley, M. Arif, P.A. Bates, and M.B. Hursthouse, *J. Mol. Struct.*, 220 (1990) 1.
188. A.C. Van Steenbergen, E. Bouwman, R.A.G. De Graaff, W.L. Driessen, J. Reedijk, and P. Zanello, *J. Chem. Soc., Dalton Trans.*, (1990) 3175.
189. M. Koman, M. Mariassy, and G. Ondrejovic, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 2041.
190. A.W. Maverick, M.L. Ivie, and F.R. Fronzek, *J. Coord. Chem.*, 21 (1990) 315.
191. J.V. Folgado, W. Henke, R. Allmann, H. Stratemeier, D. Beltran-Porter, T. Rojo, and D. Reinen, *Inorg. Chem.*, 29 (1990) 2035.
192. C.I. Cabello, A. Caneschi, R.L. Carlin, D. Gatteschi, P. Rey, and R. Sessoli, *Inorg. Chem.*, 29 (1990) 2582.
193. P.T. Matsunaga, D.T. McCall, M.D. Carducci, and R.J. Doedens, *Inorg. Chem.*, 29 (1990) 1655.
194. D.M. Nilsen, R.D. Larsen, K. Emerson, G.V. Rubenacker, Z. Ping, and J.E. Drumheller, *Inorg. Chem.*, 29 (1990) 2887.
195. J.K. Garland, K. Emerson, and M.R. Pressprich, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1603.
196. M. Kabesova, Z. Koziskova, and M. Dunaj-Jurco, *Collect. Czech. Chem. Commun.*, 55 (1990) 1184.
197. Z. Koziskova, J. Kozisek, and M. Kabesova, *Polyhedron*, 9 (1990) 1029.
198. M. Salo, R. Hamalainen, U. Turpeinen, and M. Lehtinen, *Arch. Pharm., (Weinheim, Ger.)*, 323 (1990) 31.
199. G. Battistuzzi Gavioli, M. Borsari, L. Menabue, M. Saladini, M. Sola, L.P Battaglia, C.A. Bonamartini Corradi, and G. Pelosi, *J. Chem. Soc., Dalton Trans.*, (1990) 97.
200. J. Sivy, V. Kettmann, J. Kraetsmar-Smogrovic, O. Svajlenova, C. Friebal, and G. Pelsch, *Z. Anorg. Allg. Chem.*, 583 (1990) 55.
201. C.C. Su, H.L. Tsai, S.R. Li, S.L. Wang, and C.Y. Cheng, *Transition Met. Chem. (London)*, 15 (1990) 454.
202. J.G.H. Du Preez, B.J.A.M. Van Brecht, and I. Warden, *Inorg. Chim. Acta*, 171 (1990) 121.

203. J. Sivy, F. Pavelcik, J. Kraetsmar-Smogrovic, M. Zemlicka, and V. Seressova, *Collect. Czech. Chem. Commun.*, 55 (1990) 2924.
204. J.C. Lockhart, W. Clegg, H.M.S. Hill, and D.J. Rushton, *J. Chem. Soc., Dalton Trans.*, (1990) 3541.
205. P. Bradford, R.C. Hynes, N.C. Payne, and C.J. Willis, *J. Am. Chem. Soc.*, 112 (1990) 2647.
206. C. Maichle, W. Hiller, J. Straehle, T. Schechinger, and U. Weser, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 747.
207. S.C. Goel, K.S. Kramer, M.Y. Chiang, and W.E. Buhro, *Polyhedron*, 9 (1990) 611.
208. R. Allmann, M. Krestl, C. Bolos, G. Manoussakis, and G. Nikolov, *Inorg. Chim. Acta*, 175 (1990) 255.
209. G. Bernardinelli, G. Hopfgartner, and A.F. Williams, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1642.
210. M. Zoeteman, E. Bouwman, R.A.G. De Graaf, W.L. Driessen, J. Reedijk, and P Zanello, *Inorg. Chem.*, 29 (1990) 3487.
211. M. Studer, A. Reisen, and T.A. Kaden, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 741.
212. T.J. Lee, Y. Chang, C,S. Chung, and Y.M. Wang, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 2360.
213. K. Inoue, N. Matsumoto, H. Okawa, and S. Kida, *Mem. Fac. Sci., Kyushu Univ., Ser. C,* 17 (1990) 225.
214. K.V. Goodwin, W.T. Pennington, and J.D. Petersen, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 898.
215. A. Wojtczak, M. Kaskolski, and T Ossowski, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1918.
216. M. Koman, M. Mariassy, and G. Ondrejovic, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 561.
217. R.E. Shepherd, T. J. Lomis, R.R. Koepsel, R. Hegde, and J.S. Mistry, *Inorg. Chim. Acta*, 171 (1990) 139.
218. J.C.A. Boeyens, S.M. Dobson, and E.L. Oosthuizen, *J. Crystallogr. Spectrosc. Res.*, 20 (1990) 407.
219. R.J. Crutchley, R. Hynes, and E.J. Gabe, *Inorg. Chem.*, 29 (1990) 4921.
220. R. Pech and J. Pickhardt, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1928.
221. O. Carugo, C. Bisi Castellani, and M. Rizzi, *Polyhedron*, 9 (1990) 2061.
222. P.J. Toscano, K.J. Fordon, D. Macherone, S. Liu, and J. Zubieta, *Polyhedron*, 9 (1990) 2375.
223. C.A. Steren, R. Calvo, E.E. Castellano, M.S. Fabiane, and O.E. Piro, *Physica B (Amsterdam)*, 164 (1990) 323.
224. W.G. Haanstra, W.A.J.W. Van der Donk, W.L. Driessen, J. Reedijk, M.G.B. Drew, and J.S. Wood, *Inorg. Chim. Acta*, 176 (1990) 299.
225. G. De Munno, G. Bruno, M. Julve, and M. Romeo, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1828.
226. H. Elias, E. Hilms, B. Wannowuis, and H. Paulus, *Inorg. Chim. Acta*, 178 (1990) 93.
227. P. Nagle, E. O'Sullivan, B.J. Hathaway, and E. Muller, *J. Chem. Soc., Dalton Trans.*, (1990) 3399.
228. A. Bencini, A. Bianchi, A. Borselli, S. Chimichi, M. Ciampolini, P. Dapporto, M. Micheloni, N. Nardi, P.Paoli, and B. Valtancoli, *Inorg. Chem.*, 29 (1990) 3282.
229. Z. Zhong, N. Matsumoto, H, Okawa, and S Kida, *Mem. Fac. Sci., Kyushu Univ., Ser. C,* 17 (1990) 221.
230. N. Hoshino, H. Murakami, Y. Matsunaga, T. Inabe, and Y. Maruyama, *Inorg. Chem.*, 29 (1990) 1177.
231. M.M.A.F. de C.T. Carrondo, M.T.L.S. Duarte, M.L.S. Goncalves, P. O'Brien, and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1990) 213.
232. A. Castineiras, W. Hillier, J. Straehle, J. Romero, R. Bastida, and A. Sousa, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 770.
233. M.B. Hursthouse, M. Motevalli, P. O'Brien, and P.B. Nunn, *J. Chem. Soc., Dalton Trans.*, (1990) 1985.
234. W. Maniukiewicz and M. Bukowska-Strzyzewska, *J. Crystallogr. Spectrosc. Res.*, 20 (1990) 363.
235. P.R. Levstein, R. Calvo, E.E. Castellano, O.E, Piro, and B.E. Rivero, *Inorg. Chem.*, 29 (1990) 3918.
236. M. Carotenuto, P. Iannelli, A. Immirzi, U. Caruso, A. Roviello, and A. Sirigu, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 2031.

237. V. Manriquez, J. Costmagna, J. Vargas, H.G. Von Schnering, and K. Peters, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1823.
238. R. Goddard, B. Hemalatha, and M.V. Rajasekharan, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 33.
239. J. Kozisek, M. Hvastijova, and J. Kohout, *Inorg. Chim. Acta*, 168 (1990) 157.
240. M. Parvez and W.J. Birdsall, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1434.
241. T. Nagata, A. Osuka, K. Maruyama, and K. Toriumi, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1745.
242. T. Aoyama, M. Yamanaka, S. Ohba, and Y. Saito, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 762.
243. W.E. Hatfield, P. Singh, and F. Nepveu, *Inorg. Chem.*, 29 (1990) 4214.
244. S. Gou, X. You, Z. Xu, K. Yu, and Z. Zhou, *Polyhedron*, 9 (1990) 2981.
245. T. Garber, S. Van Wallendael, D.P. Rillema, M. Kirk, W.E. Hatfield, J.H. Welch, and P. Singh, *Inorg. Chem.*, 29 (1990) 2863.
246. P.H. Cheng, H.Y. Cheng, C.C. Lin, S.M. Peng, *Inorg. Chim. Acta*, 169 (1990) 19.
247. V. Ravichandran, K.K. Chacko, A. Aoki, H. Yamazaki, J. Ruiz-Sanches, J. Saurez-Verela, J.D. Lopez-Gonzalez, J.M. Salas-Peregrin, and E. Colacio-Rodiguez, *Inorg. Chim. Acta*, 173 (1990) 107.
248. G. Madariaga, M.M. Alberdi, and F.J. Zuniga, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 2363.
249. M. Geoffroy, M. Wermeille, C.O. Buchecker, J.P. Sauvage, and G. Bernardinelli, *Inorg. Chim. Acta*, 167 (1990) 157; C. Dietrich-Buchecker and J.P. Sauvage, *Tetrahedron*, 46 (1990) 503.
250. F.K. Klemens, C.E.A. Palmer, S.M. Roland, P.E. Fanwick, D.R. McMillin, and J.P. Sauvage, *New J. Chem.*, 14 (1990) 129.
251. E.C. Alyea, G. Ferguson, M.C. Jennings, and Z. Xu, *Polyhedron*, 9 (1990) 739; E.C. Alyea, G. Ferguson, M.C. Jennings, and Z. Xu, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 2347; E.C. Alyea, G. Ferguson, M.C. Jennings, B. Li, Z. Xu, X. You, and S. Liu, *Polyhedron*, 9 (1990) 2463.
252. M. Shimoi, K. Katoh, H. Tobita, and H. Ogino, *Inorg. Chem.*, 29 (1990) 814.
253. K.P. Balakrishnan, A. Riesen, A.D. Zuberbuehler, and T.A. Kaden, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1236.
254. G.A. Bowmaker, P.C. Healy, L.M. Engelhardt, J.D. Kildea, B.W. Skelton, and A.H. White, *Aust. J. Chem.*, 43 (1990) 1697.
255. G. Speier, V. Fulop, and L. Parkanyi, *J. Chem. Soc., Chem. Commun.*, (1990) 512.
256. J. Zukerman-Schpector, E.E. Castellano, and G. Oliva, *Inorg. Chim. Acta*, 175 (1990) 1; M.S. Hussain, A.R. Al-Arfaj, and M.L. Hossain, *Transition Met. Chem. (London)*, 15 (1990) 264.
257. J.A. Bowmaker, A. Camus, B.W. Skelton, and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1990) 727; G.O. Tan, K.O. Hodgson, B. Hedman, G.R. Clark, M.L. Garrity, and T.N. Sorrell, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1773.
258. T. Otieno, S.J. Reitig, R.C. Thompson, and J Trotter, *Can. J. Chem.*, 68 (1990) 1901.
259. P. Karagiannidis, P. Aslanidis, S. Papastefanou, D. Mentzafos, A. Hountas, and A. Terzis, *Polyhedron*, 9 (1990) 981.
260. P. Karagiannidis, P. Aslanidis, S. Papastefanou, D. Mentzafos, A. Hountas, and A. Terzis, *Polyhedron*, 9 (1990) 2833.
261. M. Haakansson and S Jagner, *Inorg. Chem.*, 29 (1990) 5241.
262. W.H. Watson and R.P. Kashyap, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 2312.
263. G. Speier and V. Fulop, *J. Chem. Soc., Chem. Commun.*, (1990) 905.
264. B.R. Serr, C.E.L. Headford, C.M. Elliott, and O.P. Anderson, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 500.
265. Y.D. Lampeka and S.P. Gavrish, *J. Coord. Chem.*, 21 (1990) 351.
266. M.A. Khalifa, *J. Chem. Soc., Pak.*, 12 (1990) 8.
267. M.A. Khalifa and A.G. El-Kourashy , *Bull. Chem. Soc. Ethiop.*, 4 (1990) 19.
268. M.Masarwa, H. Cohen, R. Glaser, and D. Meyerstein, *Inorg. Chem.*, 29 (1990) 5031.
269. E. Baumgartner, S. Ronco, and G. Ferraudi, *Inorg. Chem.*, 29 (1990) 4747.
270. E. Bouwman, W.L. Driessen, and J. Reedijk, *Coord. Chem. Rev.*, 104 (1990) 143.
271. N. Kitajima, K. Fujisawa, and Y. Morooka, *J. Am. Chem. Soc.*, 112 (1990) 3210.
272. L. Casella, M. Gullotti, E. Suardi, M. Sisti, R. Pagliarin, and P. Zanello, *J. Chem. Soc., Dalton Trans.*, (1990) 2843.
273. S. Knapp, T.P. Keenan, J. Liu, J.A. Potenza, and H.J. Schugar, *Inorg. Chem.*, 29 (1990) 2189.
274. M.L. Brader and M.F. Dunn, *J. Am. Chem. Soc.*, 112 (1990) 4585.

275. J. Labuda and V.V. Pavlishchuk, *J. Coord. Chem.*, 21 (1990) 263.
276. R.J. Butcher, E. Sinn, and G.M. Mockler, *Proc. - Indian Acad. Sci., Chem. Sci.*, 102 (1990) 209.
277. M.G. Patch, H.K. Choi, D.R. Chapman, R. Bau, V. McKee, and C.A. Reed, *Inorg. Chem.*, 29 (1990) 110.
278. Y. Nakao, Y. Takagi, H. Okazaki, T. Itho, W. Mori, and S. Susuki, *Inorg. Chim. Acta*, 175 (1990) 17.
279. K.D. Karlin, I. Sanyal, A. Farooq, R.R. Jacobson, S.N. Shaikh, and J. Zubieta, *Inorg. Chim. Acta*, 174 (1990) 13.
280. S. Schindler, H. Elias, and H. Paulus, *Z. Naturforsch., B: Chem. Sci.*, 45 (1990) 607.
281. Q. Lu, Q.H. Luo, A.B. Dai, Z.Y. Zhou, and G.Z. Hu, *J. Chem. Soc., Chem. Commun.*, (1990) 1429.
282. K. Cynthia, K. Akabori, K. Spartalian, W.E. Hatfield, and B.R. Rohrs, *Inorg. Chem.*, 29 (1990) 2663.
283. K.D. Karlin, Q.F. Gan, A. Farooq, S. Liu, and J. Zubieta, *Inorg. Chem.*, 29 (1990) 2549.
284. O.J. Gelling and B.L. Feringa, *J. Am. Chem. Soc.*, 112 (1990) 7599.
285. K.V. Reddy, S.J. Jin, P.K. Arora, D.S. Sfeir, S.C.F. Maloney, F.L. Urbach, and L.M. Sayre, *J. Am. Chem. Soc.*, 112 (1990) 2332.
286. G. Borghesani, F. Pulidori, M. Remelli, R. Purello, and E. Rizzarelli, *J. Chem. Soc., Dalton Trans.*, (1990) 2095.
287. L. Casella, M. Gullotti, G. Pallanza, and M. Buga, *Biol. Met.*, 3 (1990) 137.
288. V.V. Pavilshchuk, P.E. Strizhak, K.B. Yatsimirskii, and J. Labuda, *Inorg. Chim. Acta*, 167 (1990) 47.
289. U. Koert, M.M. Harding, and J.M. Lehn, *Nature (London)*, 346 (1990) 339.
290. P.P. Paul, Z. Tyeklar, A. Farooq, K.D. Karlin, S. Liu, and J Zubieta, *J. Am. Chem. Soc.*, 112 (1990) 2430.
291. M. Beltramini, M. Santamaria, B. Salvato, and K. Lerch, *Biol. Met.*, 3 (1990) 93.
292. G.W. Canters, A. Lommen, M. Van de Kamp, and C.W.G. Hoitink, *Biol. Met.*, 3 (1990) 67; A. Lommen and G.W. Canters, *J. Biol. Chem.*, 265 (1990) 2768.
293. J.A. Strickland, L.G. Marzilli and W.D. Wilson, *Biopolymers*, 29 (1990) 1307.
294. M.K. Stern, J.K. Bashkin, and E.D. Sall, *J. Am. Chem. Soc.*, 112 (1990) 5357.
295. A.J. Moody and P.R. Rich, *Biochim. Biophys. Acta*, 1015 (1990) 205.
296. N.J. Blackburn, T.M. Pettingill, K.S. Seagraves, and R.T. Shigeta, *J. Biol. Chem.*, 265 (1990) 15383.
297. B.M. Katz and A. Barnea, *J. Biol. Chem.*, 265 (1990) 2017.
298. S.S. Percival and E.D. Harris, *Am. J. Physiol.*, 258 (1990) C140.
299. S.K. Katti, D.M. Le Master, and H. Eklund, *J. Mol. Biol.*, 212 (1990) 167.
300. G. Liang and H. Sigel, *Inorg. Chem.*, 29 (1990) 3631.
301. A.E. Martell and V.M. Shanbhag, *J. Chem. Soc., Chem. Commun.*, (1990) 352.
302. J. Li and C. Ge, *Cryst. Res. Technol.*, 25 (1990) K237.
303. R.E. Norman and N.J. Rose, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1.
304. Q.D. Tran and E. Palacios, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C46 (1990) 1220.
305. J. Li and C. Ge, *Cryst. Res. Technol.*, 25 (1990) K241.
306. M. Strasak and Z Durcova, *J. Coord. Chem.*, 22 (1990) 99.
307. M.J. Pena, I. Alarcon, and V. Lopez, *Electrochim. Acta*, 35 (1990) 47.
308. E.W. Ainscough, E.N. Baker, A.M. Brodie, R.G. Cresswell, J.D. Ranford, and J.M. Waters, *Inorg. Chim. Acta*, 172 (1990) 185.
309. J. Li, Y. Zhang, and J. Fan, *Cryst. Res. Technol.*, 25 (1990) 977.
310. C. Dendrinou-Samara, D.P. Kessissoglou, G.E. Manoussakis, D. Mentzafos, and A. Terzis, *J.Chem. Soc., Dalton Trans.*, (1990) 959.
311. R. Cini, G. Giorgi, A. Cinquantini, C. Rossi, and M. Sabat, *Inorg. Chem.*, 29 (1990) 5197.
312. M. Barba-Behrens, J.L. Bautista, M.E. Ruiz, P. Joseph-Nathan, A. Flores-Parra, and R. Contreras, *J. Inorg. Biochem.*, 40 (1990) 201.
313. A. Pezeshk and V. Pezeshk, *J. Inorg. Biochem.*, 38 (1990) 185.
314. H. Kozlowski, A. Pusino, J. Swiatek, J. Spychala, T. Glowiak, G. Micera, and C. Gessa, *J. Agric. Food Chem.*, 38 (1990) 1989.
315. U.P. Singh, R. Ghose, and A.K. Ghose, *Bull. Chem. Soc. Jpn.*, 63 (1990) 1226.
316. J.R. Morphy, D. Parker, R. Kataky, M.A.W. Eaton, A.T. Millican, R. Alexander, A. Harrison, and C. Walker, *J. Chem. Soc., Perkin Trans. 2*, (1990) 573.
317. M.K. Moi, S.J. DeNardo, and C.F. Meares, *Cancer Res.*, 50 (1990) 789s.
318. M.C. Gennaro, S. Aime, E. Santucci, M. Causa, and C. De Stefano, *Anal. Chim. Acta*, 233 (1990) 85.

319. D.X. West, C.S. Carlson, A.C. Whyte, and A.E. Liberta, *Transition Met. Chem. (London)*, 15 (1990) 43.
320. T. Kunitake and Y. Ishikawa, *J. Macromol. Sci., Chem.*, A27 (1990) 1157.
321. J.C. Chambron, C. Dietrich-Buchecker, C. Hemmert, A.K. Khemiss, D. Mitchell, J.P. Sauvage, and J. Weiss, *Pure Appl. Chem.*, 62 (1990) 1027.
322. J.H. Van Esch, A.L.H. Stols, and R.J.M. Nolte, *J. Chem. Soc., Chem. Commun.*, (1990) 1658.
323. G. De Santi, P. Scrimin, and U. Tonellato, *Tetrahedron Lett.*, 31 (1990) 4791.
324. T.J. Meade, N.W. Alcock, and D.H. Busch, *Inorg. Chem.*, 29 (1990) 3766.