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THE CHEMISTRY OF COPPER AND SILVER IN THEIR HIGHER OXIDATION STATES

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CONTENTS

ABBREVIATIONS

R_2dtc	*N,N*-dialkyldithiocarbamate(1 –)
R_2tsc	*N,N*-dialkylthioselenocarbamate(1 –)
R_2dsc	*N,N*-dialkyldiselenocarbamate(1 –)
mnt	maleonitriledithiolate(2 –)
tdt	toluene-3,4-dithiolate(2 –)
pdt	3,4,5,6-tetramethylbenzene-1,2-dithiolate(2 –)

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xdt	*o*-xylene-4,5-dithiolate(2 −)
bdt	benzene-1,2-dithiolate(2 −)
tcdt	3,4,5,6-tetrachlorobenzene-1,2-dithiolate(2 −)
H_4Edta	ethylenediaminetetraacetic acid
Hdmg	dimethylglyoxime
TAAB	tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadiene
py	pyridine
pyz	pyrazine
2-Mepy,3-Mepy,4-Mepy	2-, 3-, 4-methylpyridine, respectively
*n*R-biH$_2$	*n*-alkylbiuret
bipy	2,2′-bipyridyl
phen	1,10-phenanthroline
diphos	*o*-phenylenebis(dimethylphosphine)
diars	*o*-phenylenebis(dimethylarsine)
terpy	2,2′,2″-terpyridyl
PhTuBu$_2$	*N*-phenyl-*N*′,*N*′-dibutylthiourea
SalenH$_2$	bissalicylaldehydeethylenediimine

The usual abbreviations for alkyl groups (Me, Et, etc.) are used. The abbreviations used for macrocycles, porphyrins and pyridine carboxylic acids are shown in Figs. 9, 27 and 20 respectively.

A. INTRODUCTION

High oxidation states * become increasingly unstable as one moves along the transition metal periods. Thermodynamic data to rationalise these changes are scarce or unavailable but contributing factors are increasing ionisation potentials and decreased bond energies as the metal orbitals contract with increasing nuclear charge. For the group 1B elements (sometimes called the first post-transition metal group), the common oxidation states are +1, +2 for copper, +1 for silver, and +1, +3 for gold (Tables 1 and 2). For many years other oxidation states were represented by a few often incompletely characterised compounds, but recent research has resulted in the characterisation of a considerable range of copper(III), silver(II), silver(III) complexes and these form the subject of the present review. Gold chemistry is treated only in a few cases for comparative purposes. Previous reviews covering aspects of this area are those of Margerum and Owens [Cu(III)-peptides] [3], Po [Ag(II) and Ag(III) *N*-macrocycles] [4], and McMillan [higher oxidation states of Ag] [5].

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* "High oxidation state" is a useful classification, but difficult to define precisely. The problems are discussed in ref. 1, and there are some interesting brief comments in ref. 2.

TABLE 1

Oxidation states of the group IB metals [a]

OS	Copper	Silver	Gold
+1	$\underline{d^{10}}$	$\underline{d^{10}}$	$\underline{d^{10}}$
+2	$\underline{d^{9}}$	d^{9}	d^{9}
+3	d^{8}	d^{8}	$\underline{d^{8}}$
+4	d^{7}	(d^{7})	(d^{7})
+5		(d^{6})	d^{6}

[a] Underlined states are the most important, states in parentheses are unconfirmed.

TABLE 2

Ionisation potentials (kJ mol^{-1}) [a]

	1	2	3	4	ΔH_{atom} [b]
Cu	745	1958	3545	5682	339
Ag	731	2072	3360	5012	286
Au	889	1980	2895	4192	368

[a] From R.V. Parish, The Metallic Elements, Longman, London, 1977. [b] Enthalpy of atomisation.

In addition to the coverage in standard works [6], review articles on other oxidation states of these elements useful for comparison are Cu(I) [7], Cu(II) [8], and a book on the chemistry of gold [9].

The review aims to discuss literature available to us up to December 1985, and although comprehensive literature citation is not the aim, it is hoped that reasonably complete coverage has been achieved.

B. COPPER(III) CHEMISTRY

Copper(III) is a d^8 ion and a useful starting point is to consider the extensive chemistry of the isoelectronic nickel(II) ion [10]. Comparison suggests that paramagnetic octahedral complexes are to be expected with weak field ligands, whilst increasing the field will promote diamagnetic square-planar or low spin five-coordination. Since increasing metal oxidation state produces an increased ligand field splitting, it is likely that diamagnetic compounds will predominate in copper(III) and this is observed in practice. Structurally characterised examples include $[CuF_6]^{3-}$ (paramagnetic octahedral), ${}^{1}_{\infty}[CuO_{4/2}]^{-}$ (planar and diamagnetic), and square-pyramidal diamagnetic $[Cu(o\text{-}C_6H_4(PMe_2)_2)_2Cl](ClO_4)_2$. Tetrahedral four-coordination and high spin five-coordination are unknown and probably unlikely.

(i) Fluorides and oxides

Copper trifluoride is unknown, but both $[CuF_6]^{3-}$ and $[CuF_4]^-$ have been characterised. Green $K_3[CuF_6]$ reported [11] in 1949 was for a number of years the most clearly established example of a copper(III) complex. More recently a series of hexafluorocuprates(III) $M_3[CuF_6]$ (M = Na–Cs), $M_2M'[CuF_6]$ (M = K–Cs, M' = Li–Cs) have been prepared by fluorination, in some cases under high pressure, of appropriate chlorocuprates(II) or alkali-halide/copper chloride mixtures [12–14]. All are green microcrystalline solids at room temperature, and undergo a curious reversible colour change to brown on heating [14]. They are very moisture sensitive, instantly decomposed to Cu(II) by water [11] and $K_3[CuF_6]$ in liquid HF evolves fluorine above 0°C [15]. The complexes have magnetic moments slightly above the spin-only values for octahedral d^8, ca. 2.9–3.0 BM, and obey the Curie–Weiss law with small θ values [14]. The diffuse reflectance spectrum of $KCs_2[CuF_6]$ has been reported [16] (Fig. 1) and analysed [$Dq = 1410$ cm^{-1}, β, 0.55]. The structures are cation dependent [14], e.g. $M_3[CuF_6]$

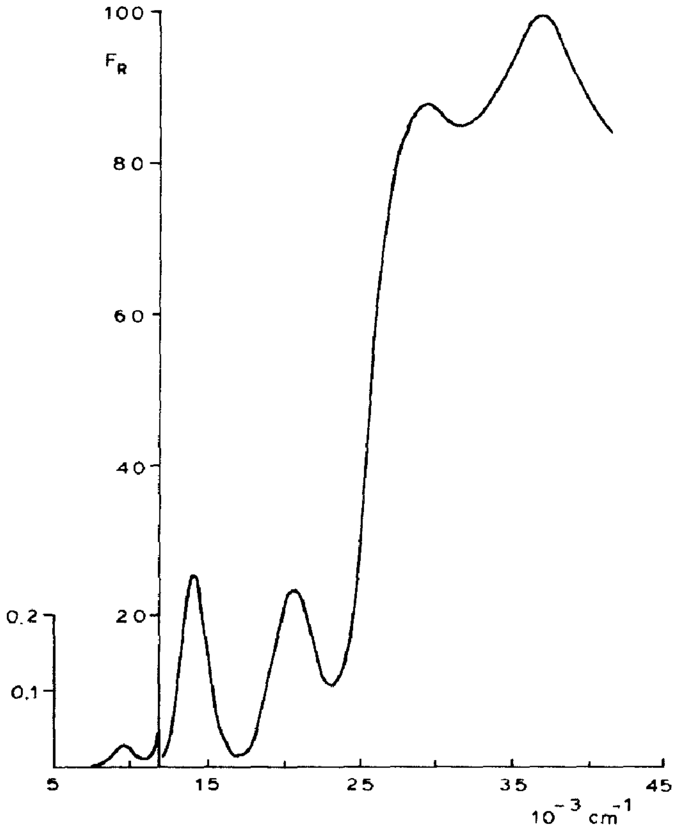


Fig. 1. The diffuse reflectance spectrum of $Cs_2K[CuF_6]$ from ref. 16.

(M = K–Cs) are of the $K_3[CrF_6]$ type, $Na_3[CuF_6]$ is monoclinic $[Na_3(AlF_6)]$, whilst $M_2M'[CuF_6]$ (M, M′ = K–Cs) are cubic elpasolites. Also reported are $CsZnCuF_6$ [17,18], $CsMgCuF_6$ [18], $CsBaCuF_6$ [14], and $CsCu^{II}Cu^{III}F_6$ [19]. Fluorination of $Cs[CuCl_3]$ was reported [20] to give "$CsCuF_{3.6}$", which is [19] a mixture of $CsCu^{II}Cu^{III}F_6$ and $Cs_2Cu^{II}_{0.5}Cu^{III}F_6$. The black $CsCu^{II}Cu^{III}F_6$ is obtained pure by high pressure fluorination [19], and is isostructural with $CsNi^{II}Ni^{III}F_6$.

The tetrafluorocuprates(III) $M[CuF_4]$ (M = K–Cs) have been obtained only recently, and the caesium salt alone has been described in detail [21]. High pressure fluorination (350 atm/400 °C) of $Cs[CuCl_3]$ affords the deep orange, diamagnetic $Cs[CuF_4]$, which has the $K[BrF_4]$ structure and hence contains square planar $[CuF_4]^-$ ions.

Reports of a reddish-brown higher oxide of copper, usually assumed to be $Cu_2O_3 \cdot nH_2O$ date back well over one hundred years. The preparations involve oxidation of $Cu(OH)_2$ in concentrated aqueous alkali with $S_2O_8^{2-}$, Cl_2, OBr^-, etc., the products being ill-defined cuprates(III) (below), which on washing with cold water, produce red-brown materials. These decompose on drying, and hence 'characterisation' rests on Cu : 'active' oxygen ratio in the crude products. The more recent studies have reported low active O : Cu ratios consistent with only small amounts of Cu(III). Certainly reports of anhydrous Cu_2O_3 are in error [22,23], but the constitution of these red-brown 'hydrates' remains unclear [24].

Oxocuprates(III) include the well-characterised blue-black M^ICuO_2 prepared by dry methods and the unstable red materials made by wet methods. Blue-black M^ICuO_2 (M = Na, K, Rb, Cs) were obtained by Klemm and co-workers [25,26] by heating CuO with the appropriate alkali-metal superoxide or peroxide (M = Na only) in oxygen. In water immediate decomposition to Cu(II) and evolution of oxygen occurs. The complexes are diamagnetic, and X-ray diffraction studies show that planar $^1_\infty[CuO_{4/2}]$ chains are present Cu–O = 1.84 Å, Cu–O–Cu = 94.6° ($KCuO_2$) [27,28]. Lithium oxocuprate(III) has not been obtained, but a black Na_3CuO_3 is formed by heating $NaCuO_2$ above 450 °C, or better from Na_2O_2 and CuO in oxygen at 630 °C. It is diamagnetic suggesting four-coordinate copper but the detailed structure is not known [29]. Black $Ba_2Cu_2O_5$ is produced by heating BaO_2 and $Cu(NO_3)_2$ at 580 °C in air or by heating $BaCuO_2$ at 600 °C under 400 atm of oxygen [30]. Strontium and calcium fail to produce analogous materials. The magnetic moment of $Ba_2Cu_2O_5$ ($\mu_{eff} = 3.06/300$ K) suggests octahedral coordination for the copper(III). The X-ray absorption spectrum of $Ba_2Cu_2O_5$ has been reported [31] and supports the presence of Cu(III).

Copper(III) is also present in $LaCuO_3$ [30,32], $YCuO_3$ [30], $SrLaCuO_4$ [33] and La_4LiCuO_8 [32], although details both of the structure of $LaCuO_3$ and its magnetic properties are disputed.

Unstable red oxocuprates made by wet methods are not well characterised. A red oxocuprate(III) is produced by NaOBr oxidation of $Cu(OH)_2$ in concentrated aqueous NaOH under carefully controlled conditions [22], and analysis of the wet product indicated a Na : Cu : active oxygen ratio of 1 : 1 : 0.5. The product slowly decomposes at room temperature, and more extensively on drying [34]. A more stable red-brown diamagnetic $Ba[CuO_2]_2 \cdot H_2O$ is formed by precipitation of the red solution formed on OBr^- oxidation of $Cu(OH)_2$ with $BaCl_2$ [22], and impure Ca and Sr analogues are known. Instability has prevented the establishment of the copper unit in these materials, but it clearly differs from the linear $^1_\infty[CuO_{4/2}]$ unit in the blue $M[CuO_2]$.

(ii) Group VIB donor ligands

Oxygen donors

As long ago as 1818, a yellow species produced by OCl^- oxidation of Cu(II) was observed [35], and the nature of the soluble species has usually been assumed to be $[Cu(OH)_4]^-$ [22,24,34,36] although the evidence is inconclusive. A recent detailed study [37] showed that $Cu(OH)_2$ catalyses the decomposition of OCl^- and OBr^- by two pathways, one of which produces a small amount of highly unstable yellow material for which a $[Cu_2^{III}O_n(OH)_{9-2n}]^{3-}$ formulation was proposed.

Pulse radiolysis has been used to produce aquocopper(III) species [38]; in neutral solution $[Cu(OH)_{3-n}(aq)]^{n+}$ ($n = 1, 2$) are present which decompose to Cu(II) and H_2O_2, and in acid solution decomposition may involve $OH^\cdot$ radicals. A later study [39] suggested $Cu(OH)_3$ as the predominant species when $pH \geqslant 4$ which has a half-life of ~ 2 ms at pH 4.4.

Periodate and tellurate complexes of copper(III) have been prepared by several authors [36,40–45] by chemical (OCl^-, $S_2O_8^{2-}$, MnO_4^-, OBr^-) or electrochemical oxidation of copper(II) in alkaline solution in the presence of tellurate or periodate ions. Similar complexes were not formed by selenate, antimonate or stannate ions [36]. All authors who obtained analytical data agreed with a Cu : "IO_6" or Cu : "TeO_6" ratio of 1 : 2, but reported materials with varying amounts of alkali metal ions, H^+ and degrees of hydration. Typical formulae reported were $Na_7Cu(IO_6)_2 \cdot 16H_2O$, $Na_5H_2Cu(IO_6)_2 \cdot 13H_2O$ and $Na_7H_2Cu(TeO_6)_2 \cdot 12H_2O$. Malatesta proposed that complex anions with the copper in a six-coordinate environment provided by two facially-bound periodate or tellurate groups were present [42]. All the materials were shown to be diamagnetic [43,44,46,47], which raises doubts about the octahedral environment which would be expected to lead to paramagnetism. A low precision X-ray crystal structure of $Na_3KH_3Cu(IO_6)_2 \cdot 14H_2O$ showed the copper environment to be planar with coordination to two bidentate IO_6 groups [48]. Subsequent studies have generally assumed Malatesta's [42] formulation of IO_6^{5-} and TeO_6^{6-} ligands, despite the need to incorporate nH$^+$ in the formulae of several salts to achieve neutrality. This was questioned for the Ag(III) analogues by Kirschenbaum et al. [49], and a detailed reinvestigation [50] of the Cu (and Ag) salts by analysis, IR spectroscopy and conductivity measurements provided strong evidence for their formulation as $[Cu(HIO_6)_2]^{5-}$ and $[Cu(H_2TeO_6)_2]^{5-}$. The electronic spectra of these complexes have been reported several times [50–56], and although the agreement between different studies is rather poor in detail, it is clear that an assignment based on L → Cu charge transfer type transitions is correct [55].

Oxidation of inorganic and particularly organic substrates by $[Cu(HIO_6)_2]^{5-}$ or $[Cu(H_2TeO_6)_2]^{5-}$ has received considerable attention; representative examples include primary alcohols to aldehydes [57,58], aldehydes [59, 60], ketones [61], iridium (analytically) [62], aliphatic amines [63] and carboxylic acids [64].

Only one example of a neutral oxygen donor complex is known, the deep purple, diamagnetic $[Cu(C_5H_5NO)_4](PF_6)_3$, made by electrochemical oxidation of the Cu(II) analogue in liquid sulphur dioxide [65]. Cyclic voltammetry indicates the oxidation potential is ≈ 1.6 V vs. SCE. The material is easily decomposed by moisture and almost certainly contains square-planar coordinated copper(III).

Sulphur donors

Many copper(III) complexes of sulphur donor ligands are known and some of this chemistry has been described in reviews of the chemistry of dithiocarbamates [66,67] and dithiolenes [68–70].

Dithiocarbamates

Steggerda and co-workers [71] have prepared the violet complex $[CuBr_2(n\text{-}Bu_2dtc)]$ by bromine oxidation of $[Cu(n\text{-}Bu_2dtc)]$ in CS_2 and have reported its crystal structure. The complex is planar to within the accuracy of the structure determination (with the exception of the butyl chains). The Cu–S bond length of 2.193(6) Å is comparable with that of another Cu(III) species $[Cu(mnt)_2]^-$ and considerably shorter than the Cu(II)–S distance of 2.30 Å in $[Cu(n\text{-}Bu_2dtc)_2]$ [72]. The Cu–Br bond length is also significantly shorter than those in copper(II) species, 2.311(4) Å as opposed to 2.40 Å in $CuBr_2$ [73], 2.46 Å in $[CuBr_4(H_2O)_2]^{2-}$ [74] and 2.54 Å in $[CuBr_2(NH_3)_2]$ [75]. There is considerable in-plane distortion, the angles S–Cu–S and Br–Cu–Br being 75.9° and 103.2° respectively. The shortest intermolecular Cu–S distance is 3.34 Å, differing from $[Cu(n\text{-}Pr_2dtc)_2]$ which is effectively five coordinate, with the fifth Cu–S distance being 2.85 Å.

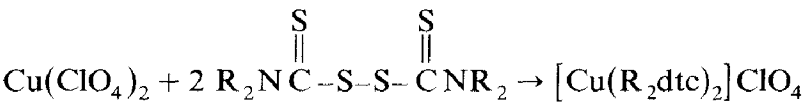
The complex was diamagnetic as would be expected for a square-planar d^8 complex. The infrared spectrum showed a shift in the C–N stretching frequencies from 1475 cm^{-1} in [Cu(dtc)] to 1560 cm^{-1} in this case, reflecting the changing bond order with changing metal oxidation state. The electronic spectrum showed bands at 330, 370 and 560 nm. No interpretation has been offered.

The complex $[CuCl_2(n\text{-}Bu_2dtc)]$ is noted as an intermediate in chlorine oxidation of $[Cu(n\text{-}Bu_2dtc)]$ in chloroform as a red-orange complex. No spectroscopic or physical data are reported [76]. Nigo et al. claim to have prepared $[CuI_2(Et_2dtc)]$ [77], but other workers have been unable to reproduce this result [66,78].

Complexes of the form $[Cu(RR'dtc)_2]X$, where X is a bulky anion, e.g. ClO_4^-, I_3^- or $FeCl_4^-$, are readily prepared. Brinkhoff reported the preparation of $[Cu(Et_2dtc)_2]^+I_3^-$ by oxidation of $[Cu(Et_2dtc)]$ or $[Cu(Et_2dtc)_2]$ with I_2 in $CHCl_3$ or CS_2 [78]. Conductivity studies in nitrobenzene showed it to be a 1 : 1 electrolyte and the half-wave potential, $E_{1/2}$, of the reversible one-electron oxidation of $[Cu(Et_2dtc)_2]$ (0.66 V) was the same as observed for the reduction of $[Cu(Et_2dtc)_2]^+I_3^-$. The infrared spectrum is very similar to that of the nickel(II) analogue and shows a striking increase in the Cu–S bond strength on oxidation from copper(II) to copper(III). This is explained on the basis of a molecular orbital scheme set up from an ESR study of $[Cu(Et_2dtc)_2]$ which showed the unpaired electron to be in a σ-antibonding orbital composed of predominantly copper and sulphur orbitals [79]. Removal of this electron results in an increase in the σ-bond strength as expected from the IR data.

A crystal structure determination of $[Cu(Bu_2dtc)_2]^+I_3^-$ [80] has shown the complex to be square planar with Cu–S bond lengths of 2.22 Å compared with 2.30 Å in $[Cu(Bu_2dtc)_2]$.

Several methods have been employed by different groups of workers to prepare complexes of this type. Kaul and Pandeya [81] made use of the oxidising properties of thiuram disulphide in the preparation of $[Cu(morphdtc)_2]ClO_4$ and $[Cu(cy_2dtc)_2]ClO_4$ as shown below, because the copper(II) complexes of these ligands were insoluble.



$$Cu(ClO_4)_2 + 2\,R_2N\overset{\overset{S}{\|}}{C}\text{–S–S–}\overset{\overset{S}{\|}}{C}NR_2 \rightarrow [Cu(R_2dtc)_2]ClO_4$$

The shifts in the infrared spectra of these complexes confirmed that the complexes were copper(III) dithiocarbamates and not thiuram disulphide complexes, the Cu–S and C–N stretches being characteristic for the different configurations. The electronic spectra were almost identical to those of the analogous nickel(II) complexes. These showed a *d–d* band in the region of 15,500 cm^{-1} and also two bands at 23,000 and 27,000 cm^{-1} which were thought to be charge-transfer bands.

Golding and co-workers [82] produced copper(III) dithiocarbamates by reaction of copper(II) dithiocarbamates with metal salts in the following ways

$$Cu(R_2dtc)_2 + 2\ FeCl_3 \rightarrow [Cu(R_2dtc)_2]^+[FeCl_4]^- + FeCl_2$$

$$Cu(R_2dtc)_2 + Fe(ClO_4)_3 \rightarrow [Cu(R_2dtc)_2]^+ClO_4^- + Fe(ClO_4)_2$$

An interesting copper(II) disproportionation has been noted [83,84] where $Cu(BF_4)_2$ or $Cu(ClO_4)_2$ oxidise $[Cu(R_2dtc)_2]$ to copper(III) complexes. The reaction stoichiometry has been deduced from plots of optical density vs. mole fraction of reactants (Job's method) to be

$$4[Cu(R_2dtc)_2] + 2\ CuX_2 \rightarrow 3[Cu(R_2dtc)_2]X + Cu_3(R_2dtc)_2X$$

Both reaction products were isolated [84].

The following reaction has also been noted [85].

$$Cu(BF_4)_2 + Mn(R_2dtc)_3 \rightarrow [Cu(R_2dtc)_2]BF_4 + \text{“}Mn^{II}\text{”}$$

Four copper(III) complexes have been isolated in this way, namely those of Et_2dtc, Bz_2dtc, MePhdtc and pyrrdtc. The manganese(II) species has not been isolated as it spontaneously oxidises to manganese(III) in the presence of dithiocarbamate.

The electron transfer reactions of these complexes have been studied electrochemically [86] and it has been shown that $[Cu(R_2dtc)_2]$ undergoes single one-electron oxidation and reduction steps at a platinum electrode. These have been established to be

$$[Cu^I(R_2dtc)_2]^- \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Cu^{II}(R_2dtc)_2] \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Cu^{III}(R_2dtc)_2]^+$$

These redox processes have been characterised for sixteen different substituents R by normal pulse voltammetry, cyclic voltammetry, spectroelectrolysis and coulometry. The oxidation process was monitored by the change in electronic absorption spectrum and showed isosbestic points at 464 and 328 nm for the $[Cu(i\text{-}Pr_2dtc)_2] \rightarrow [Cu(i\text{-}Pr_2dtc)_2]^+$ process. The plot of oxidation potential vs. reduction potential is approximately linear showing that substituents which enhance ease of oxidation (e.g. R = cyclohexyl or isopropyl) make reduction more difficult and vice versa. The product of oxidation of $[Cu(i\text{-}Pr_2dtc)_2]$ gave an almost identical electronic spectrum to that of $[Cu(i\text{-}Pr_2dtc)_2]BF_4$. The oxidation potentials ranged from 0.574 V for $[Cu(cy_2dtc)_2]$ to 0.755 V for $[Cu(Bz_2dtc)_2]$. These results were confirmed more generally by Chant et al. [87] who found that there existed a considerable dependence of oxidation potential on the alkyl substituents present, with oxidation potentials in the order $Bz_2 > {}^iBu_2 > cy_2$. They also noted a dependence of the potentials on d^n configuration concluding that the electron transfer processes were predominantly metal based.

Interestingly, a number of mixed valence dithiocarbamate complexes have been reported. Copper(II) and copper(III) are found together in the complexes $[Cu_3(Bu_2dtc)_6](MBr_3)_2$ (M = Zn, Cd, Hg) [88], $Cu_2(Bu_2dtc)_4I_3$ [66] and $Cu_2(R_2dtc)_3Br_2$ [89], while the complexes $[Cu(R_2dtc)_2]^+[Cu_{n-1}Br_n]^-$ [90] and $[Cu(Pr_2dtc)_2]_2^+[Cu_2Br_4]^{2-}$ [66] contain copper(I) and copper(III).

$[Cu_3(Bu_2dtc)_6](MBr_3)_2$ compounds were prepared by mixing solutions of bromine in chloroform, MBr_2 in ethanol and $[Cu(Bu_2dtc)_2]$ in chloroform in a 1 : 2 : 3 molar ratio followed by precipitation with petroleum ether (40–60°) of a crystalline product. Magnetic susceptibility measurements of 1500, 1560 and 1650×10^{-6} c.g.s. for M = Cd, Hg and Zn, respectively, at 293 K correspond with one unpaired electron in the system. The Curie–Weiss law was followed in the temperature range 100–293 K with $\theta = -10$ K for $(CdBr_3)^-$ salt. A single crystal ESR study showed four broad lines in all directions with principal g-values of $g_1 = 2.0907(2)$, $g_2 = 2.0252(2)$, $g_3 = 2.0505(2)$ and the principal hyperfine values $A_x = 26.0(7)$, $A_y = 43.1(7)$, $A_z = 154.8(1) \times 10^{-4}$ cm^{-1} in good agreement with results for $[Cu(Et_2dtc)_2]$ [79]. Values of g and A suggest the electron is localised on one metal centre only. The infrared data show C–N and Cu–S stretching frequencies in the ranges of both copper(II) and copper(III) dithiocarbamates (Table 3) again confirming the presence of both oxidation states. Conductivity studies in nitrobenzene showed that the complexes dissociated in solution to give $[Cu(Bu_2dtc)_2]$, $[Cu(Bu_2dtc)_2]^+$ and $(MBr_3)^-$ in a 1 : 2 : 2 ratio. A single crystal X-ray structure determination showed the complex to consist of two centrosymmetric ions, $[Cu_3(Bu_2dtc)_6]^{2+}$ and $[Cd_2Br_6]^{2-}$. The cation contains three $Cu(Bu_2dtc)_2$ units, one with Cu–S distances very similar to those in $Cu(Et_2dtc)_2$ and two with much shorter Cu–S distances which are the same as those in $[Cu(Bu_2dtc)_2]^+I_3^-$. The three units are piled on top of each other at very short distances, such that the copper(II) ion is six coordinate and the two copper(III) ions are five coordinate. The Cu(II)–S intermolecular distance is 3.19 Å and the Cu(III)–S distance is 2.88 Å (Table 4). Spek [93,94] has determined the structure of $[Cu_3(Bu_2dtc)_6][Hg_2Br_6]$ at low temperatures, at −80°C and −40°C. A reversible transition point is seen at −50°C. The structures were essentially isomorphous at the two temperatures, with the major changes occurring in the packing of the butyl chains. The bond lengths are not significantly different from the determination of Cras et al. [88] (Fig. 2).

$[Cu_2(Me_2dtc)_3Br_2]$ was prepared by stirring CuBr and Me_4tds (tetramethylthiuram disulphide) in equimolar amounts in chloroform for 1 h. The product is obtained in quantitative yield as a black microcrystalline solid.

TABLE 3

Copper dithiocarbamate complexes, IR data

Complex	ν(Cu–S) (cm^{-1})	ν(C–N) (cm^{-1})	Ref.
$[Cu(Et_2dtc)_2]$	345, 370	1490	82
$[Cu(Et_2dtc)_2]ClO_4$	385, 410	1570	82
$[Cu(Bu_2dtc)_2]$	352	1500	90
$[Cu(Bu_2dtc)_2][CdBr_3]$	411	1551	90
$[CuBr_2(Bu_2dtc)]$	– [a]	1560	71
$[Cu(morphdtc)_2]$	342	1440	81
$[Cu(morphdtc)_2]ClO_4$	375, 400	1530	81
$[Cu(Cy_2dtc)_2]$	350	1470	81
$[Cu(Cy_2dtc)_2]ClO_4$	388, 400	1520	81
$[Cu(Bz_2dtc)_2]$	315, 380	1474	83
$[Cu(Bz_2dtc)_2]ClO_4$	392, 412	1510	83
$[Cu(BzMedtc)_2]$	358	1509	83
$[Cu(BzMedtc)_2]ClO_4$	392, 408	1545	83
$[Cu(BzEtdtc)_2]$	332, 345	1480	83
$[Cu(BzEtdtc)_2]ClO_4$	395, 410	1505	83
$[Cu(Me_2dtc)_2]$	350	1520	90
$Cu_2(Me_2dtc)_3Cl_2$	360, 385	1545, 1565	89
$Cu_2(Me_2dtc)_3Br_2$	357, 386	1545, 1565	89
$[Cu(Me_2dtc)_2][CdBr_3]$	402	1575	90
$Cu_2(Et_2dtc)_3Br_2$	355, 391	1515, 1535	89
$[Cu(Et_2dtc)_2][CdBr_3]$	399	1545	89
$[Cu(Me_2dtc)_2]^+[Cu_2Br_3]^-$	400	1570	90
$[Cu(Et_2dtc)_2]^+[Cu_4Br_5]^-$	392	1535	90
$[Cu(Pr_2dtc)_2]^+[Cu_4Br_5]^-$	392/400 [b]	1545	90
$[Cu(Br_2dtc)_2]^+[Cu_6Br_7]^-$	393	1530	90

[a] Not reported. [b] Unambiguous assignment not possible.

The complexes are paramagnetic with $\mu = 1.77$–1.86 BM, equivalent to one unpaired electron per formula unit. A single crystal ESR spectrum showed only a single sharp line as a result of exchange interaction of the unpaired electrons of neighbouring molecules. The infrared spectra of these complexes again show C–N and Cu–S stretching frequencies commensurate with both copper(II) and copper(III) dithiocarbamates (Table 3). The crystal structure of $Cu_2(Et_2dtc)_3Br_2$ showed the complex to consist of chains of alternating $[Cu(Et_2dtc)_2]^+$ and $[Cu(Et_2dtc)Br_2]^-$ units. The coordination of both copper atoms can be described as distorted octahedral with bridging sulphur and bromine atoms between units at long distances (Cu–Br = 2.97 Å, Cu–S = 3.27 Å for the $[Cu(Et_2dtc)_2]^+$ unit and Cu–S = 2.94 and 3.00 Å for the $[Cu(Et_2dtc)Br_2]^-$ unit).

$Cu_2(Bu_2dtc)_4I_3$ has a magnetic moment at room temperature which suggests one unpaired electron for every two copper atoms and infrared

TABLE 4

Summary of bond lengths (Å) observed in copper dithiocarbamate complexes

	Oxidation state						
	$[Cu(Bu_2dtc)Br_2]$	$[Cu(Bu_2dtc)]^+I_3^-$	$[Cu_3(Bu_2dtc)_6][Cd_2Br_6]$		$[Cu_2(Et_2dtc)_3Br_2]$		$[Cu(Et_2dtc)_2]$
	III	III	III	II	III	II	II
Cu–S	2.193 (6)	2.23 (2) 2.22 (2) 2.22 (2) 2.21 (2)	2.22 (1) 2.23 (1) 2.21 (1) 2.23 (1)	2.30 (1) 2.35 (1)	2.16 (2) 2.20 (2) 2.19 (2) 2.26 (2)	2.27 (2) 2.29 (2)	2.317 (2) 2.297 (2) 2.301 (2) 2.339 (2)
Cu–Br	2.311 (4)	–	–	–	–	2.40 (2)	–
Cu–S (intermolecular)	3.34	–	2.88 (1)	3.19 (1)	3.27 (3)	3.00 (3)	2.85
Reference	71	80	88		89		72

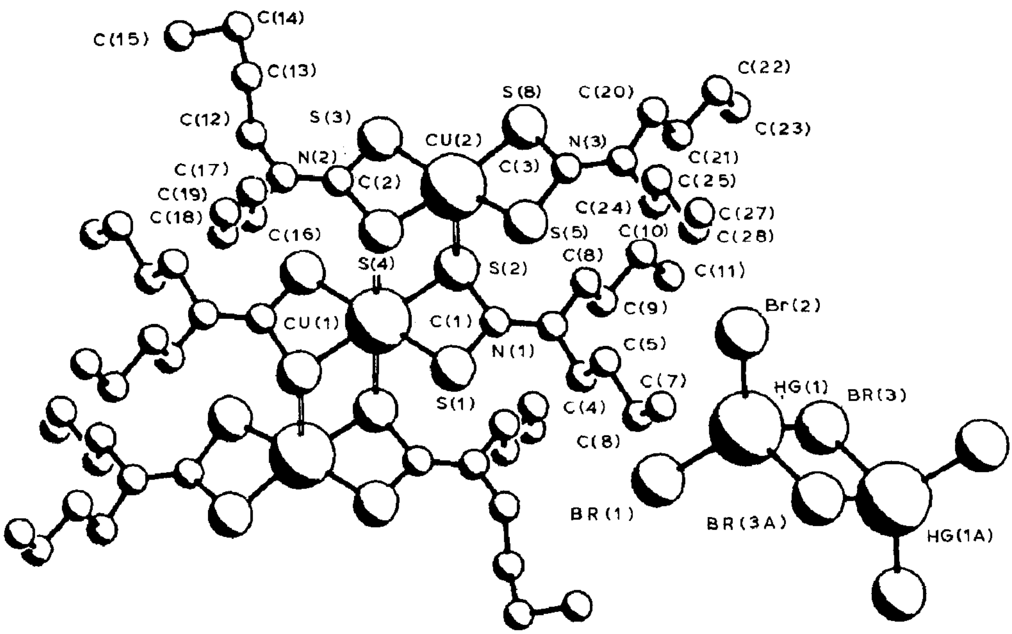


Fig. 2. The structure of $[Cu_3(Bu_2dtc)_6][Hg_2Br_6]$ from ref. 94.

spectra suggest the presence of $[Cu(Bu_2dtc)_2]$ and $[Cu(Bu_2dtc)_2]^+$ units. No further data are available.

The complexes $[Cu_2Au(Bu_2dtc)_6][MBr_3]_2$ (M = Zn, Cd or Hg) also contain copper in both II and III oxidation states [91]. They were found to be isomorphous with $[Cu_3(Bu_2dtc)_6][MBr_3]_2$. A crystal structure showed that there is a central $Cu(II)(Bu_2dtc)_2$ unit which is in an apically distorted octahedral environment while the Cu(III)/Au(III) position is disordered. The observed bond lengths around this disordered position (mean value 2.265 Å) are close to an average Cu(III)–S/Au(III)–S distance given as 2.272 Å, obtained by calculating the mean value of Au(III)–S and Cu(III)–S distances in other dithiocarbamate complexes. Infrared data are not conclusive, but seem to agree with this information.

The complexes of form $Cu_n(R_2dtc)_2Br_n$ (R = Me, $n = 3$; R = Et, Pr, $n = 5$; R = Bu, $n = 7$) are examples of copper in oxidation states III and I co-existing. The compounds are insoluble in all common solvents, rendering solution state measurements impossible. They are prepared by mixing CuBr and R_4tds in appropriate stoichiometries in dichloromethane. Infrared spectra (both C–N and Cu–S stretching frequencies (Table 3)) point to the presence of the $[Cu(R_2dtc)_2]^+$ unit, while magnetic susceptibility measurements show the complexes to be diamagnetic. ESCA results for $Cu_7(Bu_2dtc)_2Br_7$ show that copper is present in two oxidation states in the ratio 1 : 6. The complexes are formulated as $[Cu(R_2dtc)_2]^+[Cu_{n-1}Br_n]^-$. The

n-values are clearly dependent on the alkyl chain length and the anions are thought to fill the gaps between the alkyl chains. The complex $[Cu(Pr_2dtc)_2]^+[Cu_2Br_4]^{2-}$ is also reported but no further data were given.

Reaction of $[Cu(Bu_2dtc)_2]$ and $ZnCl_2$ in diethyl ether results in several products [92], including the species $[Cu_3(Bu_2dtc)_6]^{2+}[ZnCl_3]_2^-$ and $[Cu(Bu_2dtc)_2]^+[ZnCl_3]^-$ similar to those complexes already mentioned. Reaction with $ZnBr_2$ resulted in the bromo analogues being formed.

1,2-Dithiolates

There has been considerable controversy in the literature regarding the assignment of metal oxidation states in the complexes of these ligands, especially where "high" metal oxidation states are concerned. Numerous resonance forms can be written with the metal in varying oxidation states. From the molecular orbital scheme proposed by Gray et al. [95] (Fig. 3), it was suggested that the complex in which the $4b_{2g}$ and $4a_g$ levels were filled could be correctly represented as containing dianionic dithiolato ligands with the metal ion in the classical oxidation state appropriate to the overall charge of the molecule [68]. The diamagnetic complexes of copper, $[Cu(dithiolate)_2]^-$, can therefore be regarded as genuine d^8, copper(III) species.

The earliest reported example of a copper(III) dithiolate was $[Cu(mnt)_2]^-$, prepared by Davison et al. in 1963 [96]. This was made by oxidation of $[Bu_4N]_2^+[Cu(mnt)_2]^{2-}$ with $[NiS_4C_4(CF_3)_4]$ in hot dichloromethane. Recrystallisation from ethanol/dichloromethane yielded dark-red crystals of the complex. The X-ray powder pattern showed the complex to be isomorphous with analogous complexes of nickel, cobalt, palladium and platinum which were known to be planar species. A full structural determination confirmed this [97]. The $[Cu(mnt)_2]^-$ ion is approximately square planar, but the four sulphur atoms are twisted irregularly from the plane with deviations between 0.02 Å and 0.11 Å from the ideal. The S–Cu–S angles in the chelate rings are 92°. The four Cu–S bonds are crystallographically non-equivalent, being 2.158, 2.170, 2.174 and 2.177 Å. The $[Cu(mnt)_2]^-$ units are stacked along the a-axis (Fig. 4) with the copper–copper nearest neighbour distances being 4.026 and 4.431 Å. There is no close approach of a fifth sulphur atom unlike some of the dithiocarbamate complexes previously mentioned. This structure is as would be expected for a four coordinate d^8 species and is consistent with other data obtained (Table 5).

The complex $[Ph_4As]^+[CuS_4C_4(CF_3)_4]^-$ was prepared from $[(PPh_3)CuI]_4$ and $(CF_3)_2C_2S_2$ followed by addition of Ph_4AsCl. Recrystallisation of the product thus formed from boiling isobutyl alcohol/cyclohexane yielded olive-green crystals. The complex is again diamagnetic and conductivity measurements show it to be a 1 : 1 electrolyte [98].

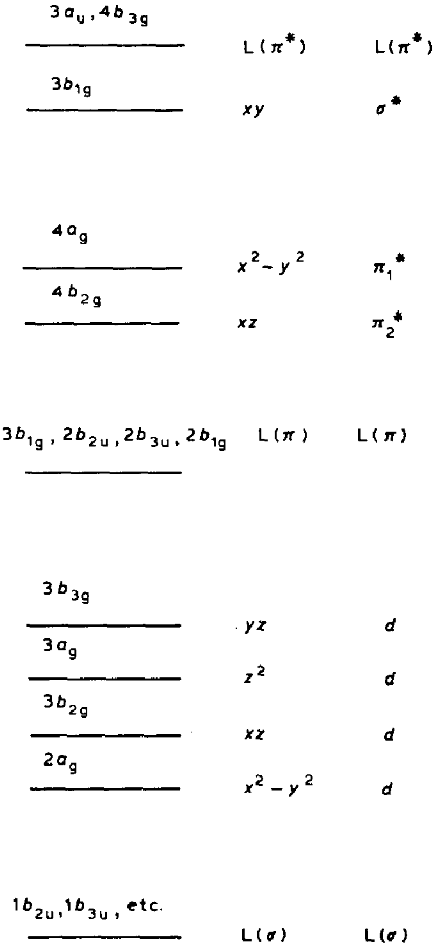


Fig. 3. MO scheme for $[Cu(mnt)_2]^{n-}$ after Gray et al. [95].

Gray and co-workers have prepared a series of copper(III) complexes of benzene dithiolate and related ligands [99,100] which are diamagnetic and planar. Physical and spectroscopic data are shown in Table 5. Electronic spectra in various solvents including those which are strongly coordinating show a remarkable lack of perturbation indicating that there is no significant interaction in the fifth and sixth coordinating positions.

Quite detailed studies of the electronic structure of these complexes have been made. Gray et al. [95] have proposed an orbital scheme based on MO calculations for the $[Ni(mnt)_2]^{n-}$ ion which may be used as a basis for discussion for the copper species mentioned. The orbitals L(π) and L(π^*) are essentially pure ligand orbitals whilst the orbitals π_1, π_2 and σ^* have contributions from both M and L. π_1 and π_2 are predominantly ligand in character and σ^* has enough metal character to be viewed as a substantially

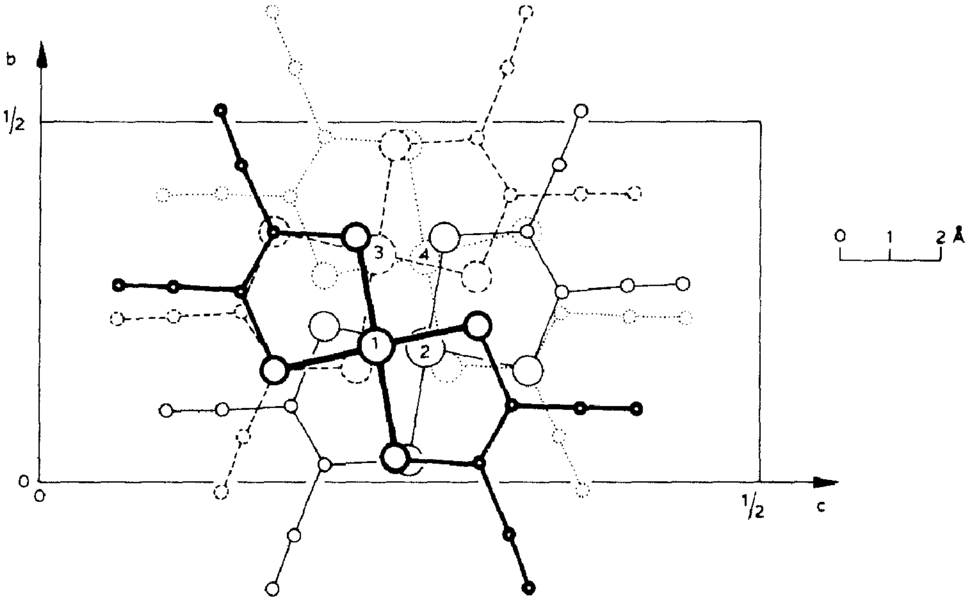


Fig. 4. The structure of $[\mathrm{Cu(mnt)}_2]^-$ from ref. 96.

TABLE 5

Copper(III) dithiolate complexes

Complex	Colour	Magnetic properties	Conductivity, Λ (cm^2 ohm^{-1} M^{-1})	Polarographic reduction potential $E_{1/2}$/V (DMF)	UV/visible spectra $\nu_{\max}(\epsilon_{\max})$/ cm^{-1} (dm^3 mol^{-1} cm^{-1})
$[\mathrm{Cu(mnt)}_2]^-$	Dark red	Diamagnetic	69	−0.201	13,000 (110) 6400 (337)
$[\mathrm{CuS_4C_4(CF_3)_4}]^-$	Green	Diamagnetic	–	−0.010	–
$[\mathrm{Cu(tdt)}_2]^-$	Green	Diamagnetic	68	−1.15	15,600 (318) 8090 (382)
$[\mathrm{Cu(pdt)}_2]^-$	Green	Diamagnetic	58	−1.41	15,500 (350) 8425 (260)
$[\mathrm{Cu(xdt)}_2]^-$	Green	Diamagnetic	59	−1.21	15,000 (320) 7800 (420)
$[\mathrm{Cu(bdt)}_2^n]^-$	Green	Diamagnetic	74	−1.14	15,900 (310) 8300 (300)
$[\mathrm{Cu(tcdt)}_2]^-$	Green	Diamagnetic	60	−0.752	17,200 (300) 8875 (200)
$[\mathrm{Cu(QDT)}_2]^-$	Brown	Diamagnetic	71	–	17,650 (670) 11,230 (450)

metal-based orbital in these complexes. It is these three orbitals which are used in assignment of low energy bands in the electronic spectra of these complexes. The separation of π_1 and σ^* is called Δ_1 and the $\pi_2 \rightarrow \pi_1$ separation Δ_2. The copper(III) complexes have ground state $(\pi_2)^2(\pi_1)^2$ and the first two low energy transitions are assigned to the transitions $\pi_1 \rightarrow \sigma^*$ and $\pi_2 \rightarrow \sigma^*$ respectively. In general it is found that Δ_1 increases as the electron-withdrawing nature of the substituents increases and a similar trend is observed for Δ_2. These bands are weak ($\epsilon = 200$–400) since they are parity forbidden. The available data are presented in Table 5.

A diamagnetic copper(III) complex of 2,3-quinoxalinedithiol, $[\text{n-Bu}_4\text{N}]^+[\text{Cu(QDT)}_2]^-$ was prepared by bubbling air through a methanolic solution of $[\text{n-Bu}_4\text{N}]_2^+[\text{Cu(QDT)}_2]^{2-}$. The ESR spectrum of the copper(II) complex confirmed that the ligand was *S,S′* coordinated rather than some mixture of *S* and *N*. Half-wave potentials showed that $[\text{Cu(QDT)}_2]^{2-}$ is much more readily oxidised than other $[\text{Cu(dithiolate)}_2]^{2-}$ complexes and also more readily than the nickel complex, the reverse of the trend for most complexes.

Complexes containing both 1,1-dithiocarbamate and 1,2-dithiolene ligands, $[\text{Cu(mnt)(R}_2\text{dtc)}]$ where R = Et, Bu, Ph, have been prepared by addition of $[\text{CuBr}_2(\text{R}_2\text{dtc})]$ solution to a suspension of Na_2mnt in CH_2Cl_2 giving an immediate green solution which on treatment with ether and cooling yielded dark-green crystals of the complexes [102,103]. Voltammetric studies showed that substituents had little effect on the oxidation potential of $[\text{Cu(mnt)(R}_2\text{dtc)}]^-$ unlike the bis 1,1-dithiocarbamate complexes giving a value of $\epsilon_{1/2} = 0.33$ V. This one-electron transfer is reversible.

Coucouvanis et al. have prepared a complex of the ligand 1,1-dicarboethoxy-2,2-ethylenedithiolate (DED) and reported its crystal structure [104,105]. The complex $\text{K}^+[\text{Cu(DED)}_2]^-$ is prepared by oxidation of $\text{K}_2^+[\text{Cu(DED)}_2]^{2-}$ by H_2O_2 or excess Cu(II) ions in aqueous media and is precipitated as a green solid. The $[\text{Cu(DED)}_2]^{2-}$ ion undergoes a reversible one-electron electrochemical oxidation at -0.50 V in CH_2Cl_2 vs. Ag/AgI with Bu_4NClO_4 as the supporting electrolyte. The electronic spectrum was very similar to those of the isoelectronic nickel(II) complexes. The crystal structure of $\text{K[Cu(DED)}_2] \cdot \text{OEt}_2$ shows the complex to be rigorously square planar with Cu–S distances of 2.190(5) Å and 2.199(5) Å comparing well with the values of 2.19(1) Å in $\text{CuBr}_2(\text{Bu}_2\text{dtc})$ and 2.22(2) Å in $[\text{Cu(Bu}_2\text{dtc)}_2]^+\text{I}_3^-$. There is no interaction in the axial sites. It is interesting to note that one of the carboethoxy groups lies in the plane of the molecule whilst the other is twisted about the single C–C bond forming a large angle with the C_4S_2 backbone of the ligand.

A complex of the dithiooxalate (Dto) ligand $[\text{Cu(Dto)}_2]^-$ has been prepared [106] by adding $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in acetone to $[\text{Cu(Dto)}_2]^{2-}$ in

CH_2Cl_2 and crystallising with a 3:1 pentane/ether mixture. A red, light sensitive solid was prepared. IR spectra of this complex revealed *S*-coordinated dithiooxalate ligands with ν(C=O) = 1640 and 1590 cm^{-1}. Repeated scans showed the appearance of a band at 2055 cm^{-1} and addition of PPh_3 to solutions of these complexes resulted in liberation of gaseous COS. It seems that light promotes a 2-electron Dto → Cu^{III} transfer with cleavage of the C–C bond forming COS. The reaction scheme proposed is:

$$[Cu^{III}(Dto)_2]^- \xrightarrow{h\nu} [Cu^{I}(Dto)(COS)_2]^- \xrightarrow{PPh_3} [Cu(Dto)(PPh_3)_2]^- + 2\,COS$$

The crystal structure determination of $[(Ph_3P)_2N]^+[Cu(Dto)_2]^-$ showed the complex to be square planar with Cu–S bond lengths of 2.164(1) Å and 2.178(1) Å, significantly different from the values of 2.253(2) Å and 2.268(2) Å in the copper(II) analogue [107].

Cras and co-workers [108] detected copper(III) thioureido complexes using cyclic voltammetry but failed to isolate them. Oxidation at a constant potential (+0.85 V) or with I_2 of $Cu^{II}(PhtuBu_2)_2$ resulted only in decomposition products of a further reaction indicated by the decrease in concentrations of both the copper(II) and copper(III) complexes.

Selenium ligands

Only one copper(III) complex with selenium donor atoms has been isolated [109]. $[Cu(Et_2dsc)_2]^+I_3^-$ was prepared by iodine oxidation of $[Cu(Et_2dsc)_2]$ as a purple diamagnetic solid. IR spectra showed ν(Cu–Se) to increase from 240 cm^{-1} in the copper(II) complex to 310 cm^{-1} in the

TABLE 6

Oxidation potentials of $[CuL_2]$ and $[Cu(mnt)L]^-$ in acetonitrile (L = dithio-, thioseleno- and diselenocarbamate)

Ligand, L	$E_{1/2}$ of species oxidised (V)	
	$[CuL_2]$	$[Cu(mnt)L]^-$
Et_2dtc	0.33	0.27
Et_2tsc	0.20	0.19
Et_2dsc	0.07	0.12
Bz_2dtc	0.41	0.32
Bz_2tsc	0.25	0.23
Bz_2dsc	0.13	0.16
Cy_2dtc	0.20	0.20
Cy_2tsc	0.08	0.12
Cy_2dsc	−0.04	0.04

copper(III) complex and ν(C–N) to increase from 1500 to 1535 $\mathrm{cm^{-1}}$. The electronic spectrum closely resembles that of the sulphur analogue. The complex can be prepared by electrochemical oxidation of $[\mathrm{Cu(Et_2dsc)_2}]$ in $\mathrm{CH_2Cl_2}$. The reversible redox reaction has $E_{1/2} = 0.24$ V vs. SCE compared with 0.44 V for the sulphur analogue.

The oxidations of copper(II) dithio, thioseleno and diselenocarbamate complexes have been compared [110,111] and the $E_{1/2}$ values are tabulated in Table 6. The oxidation potential is dependent on the substituent ($\mathrm{Bz_2} > \mathrm{Et_2} > \mathrm{Cy_2}$) and the donor atoms ($\mathrm{S_2} > \mathrm{SSe} > \mathrm{Se_2}$). None of these complexes has been isolated.

(iii) Group VB donor ligands

Copper(II) complexes of some imine-oxime ligands (Fig. 5) are readily oxidised to copper(III) complexes. The complex of ligand A is oxidised by $\mathrm{S_2O_8^{2-}}$, $\mathrm{IO_4^-}$ and $\mathrm{IrCl_6^{2-}}$ [112] giving an intense blue product which absorbs strongly at 581 nm ($\epsilon = 6 \times 10^3$ $\mathrm{M^{-1}\ cm^{-1}}$) in the electronic spectrum arising from a L → M charge transfer. The copper(II) complex exhibits quasi-reversible electrochemical behaviour with $E_0 = 0.08$ V vs. NHE. The copper(II) complex of B was oxidised by $\mathrm{S_2O_8^{2-}}$, $\mathrm{IO_4^-}$ and $\mathrm{PbO_2}$ [113] and gave a red complex absorbing at 515 nm ($\epsilon = 1.25 \times 10^4$ $\mathrm{M^{-1}\ cm^{-1}}$). This complex was surprisingly stable and was isolated as black, shiny crystals. The E_0 values of this complex and the copper(III) complex of ligand C were found to be pH dependent consistent with eqns. (1) and (2)

$$[\mathrm{Cu^{III}(L)}]^+ + \mathrm{e^-} + \mathrm{H^+} \rightleftharpoons [\mathrm{Cu^{II}(LH)}]^+ \tag{1}$$

$$E = E_0 - 0.059\ \mathrm{pH} \tag{2}$$

Solutions of the copper(III) complex of ligand B oxidised iodide, ascorbic acid and sulphite with regeneration of the copper(II) complex. A study of the kinetics of oxidation of hydroquinone by this complex [114] showed the rate constant to be first order in each of the reactants while the second order

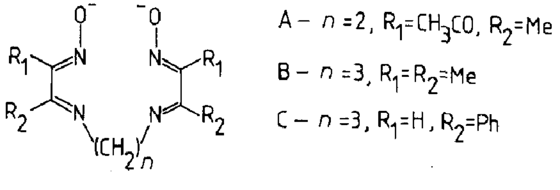


Fig. 5. Imine-oxime ligands.

rate constant varied with $[\mathrm{H}^+]$ according to eqns. (3)

$$K_2 = K_2' + K_3[\mathrm{H}^+] \tag{3}$$

$$K_2' = (2.4 \pm 1.3) \times 10^3\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

$$K_3 = (9.13 \pm 0.80) \times 10^7\ \mathrm{dm^6\ mol^{-1}\ s^{-2}}$$

The oxidation of $[\mathrm{Co^{II}(EDTA)}]^{2-}$ solutions by copper(III) complexes of A and B [115] has been found to proceed via rapid electron transfer and the formation of long-lived intermediates which are thought to arise from coordination of one or both of the oxime oxygens to the cobalt(II) complex prior to electron transfer. Monitoring by electronic absorption spectra showed rapid formation of the long-lived intermediates and slow decomposition. The oxidation is thought to be an inner sphere process.

The oxidation of iodide by copper(III) complexes of ligands A and B has also been studied [116]. The reaction is first order in $[\mathrm{Cu}^{3+}]$ and is thought to proceed via two pathways, one first order in $[\mathrm{I}^-]$ and one second order in $[\mathrm{I}^-]$ such that

$$K_{\mathrm{obs}} = 2K_2[\mathrm{I}^-] + 2K_3[\mathrm{I}^-]^2$$

The iodide could be oxidised by an inner sphere mechanism whereby the iodide associates rapidly in an axial position followed by electron transfer and dissociation. The copper(III) complexes are reduced to the copper(II) complexes.

Morphurgo and Tomlinson [117] have shown that copper(II) complexes of dimethylglyoxime are oxidised by peroxodisulphate to copper(III) species in neutral or weakly alkaline solutions. Varying pH and the Cu : L ratio results in different copper(II) species being present in solution, so identifying the oxidised species is not easy. Oxidation at pH 7.90 resulted in a band at 520 nm in the electronic spectrum, while at pH 10.90 the spectrum was characterised by a band at 950 nm. Between these extremes of pH, both species co-exist. It is thought that the species absorbing at 950 nm is $[\mathrm{Cu^{III}Cu^{II}(Hdmg)_2(OH)_2}]_2$ which is an hydroxyl-bridged tetramer (Fig. 6). No structure has been suggested for the other species.

Datta and Chakravorty [118] have prepared a mixed valence oxime complex with a $\mathrm{Cu^{III}Cu^{II}_2O}$ core (Fig. 7) by electrochemical oxidation of the $\mathrm{Cu^{II}_3O}$ analogue. Oxidation of a number of these complexes was performed but the most stable, that of α-isonitrosobenzyl phenyl n-propylketimine, was chosen for isolation and characterisation. The one electron oxidation was reversible. A crystal structure determination of the $\mathrm{Cu^{II}_3O}$ complex [119] confirmed the trimeric nature of the complex and showed it to be almost co-planar with the exception of the central oxygen atom which was raised out of the plane forming a weak inter-trimer bond. The electrochemical, IR

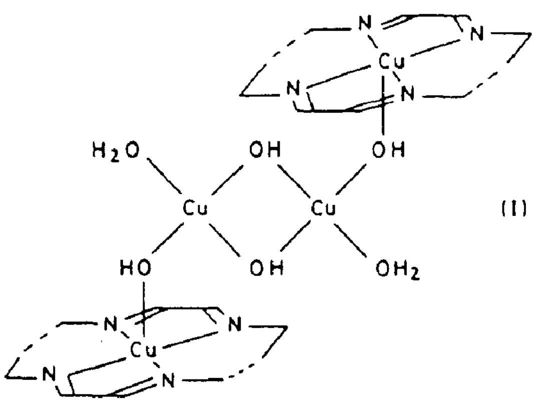


Fig. 6. Proposed structure of $[Cu_2(Hdmg)_2(OH)_2]_2$ from ref. 117.

and NMR data confirm that the $Cu^{III}Cu^{II}_2O$ complex has essentially the same structure. The complex is diamagnetic as a result of interaction of the three copper $d_{x^2-y^2}$ orbitals with the ligands. The electronic spectrum shows two allowed bands at ~ 840 and ~ 700 nm. These are at too low an energy to be L → M charge transfer bands and have been assigned to $Cu^{II}(d_{x^2-y^2}) \rightarrow Cu^{III}(d_{x^2-y^2})$ transitions.

Copper(III) complexes of biuret (bi) and oxamide (oxam) have been reported [120,121] with formulae $K[Cu(bi)_2]$ and $K[Cu(oxam)_2]$ respectively. The biuret complex was initially obtained as a brown solid by oxidation of $K_2[Cu(bi)_2]$ with $K_2S_2O_8$ in 5N KOH solution [120] but Levitzki and Anbar [122] performed the oxidation under milder conditions using $[IrCl_6]^{2-}$ or $[Fe(phen)_3]^{3+}$ at pH 11. The reaction was instantaneous and thought to proceed via a direct electron transfer mechanism. The ion $[OsCl_6]^{2-}$, however, did not oxidise the copper(II) complex and it was concluded that the redox potential of the couple Cu^{II}/Cu^{III} in this system lay between 0.85 and

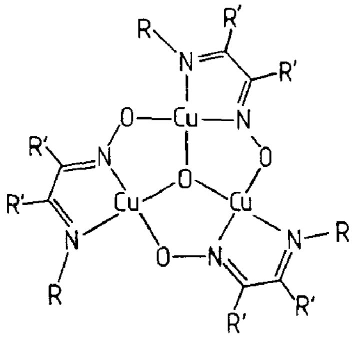


Fig. 7. Proposed structure of $[Cu^{III}Cu^{II}_2O(L)_3]$ where L is an isonitrosoketimine ligand.

1.07 V. Reaction of this complex in acidified KI yielded two equivalents of I_2 per mole $K[Cu(bi)_2]$, while reactions with aqueous HCl and H_2SO_4 yielded Cl_2 and O_2 respectively. Alkyl-substituted biuret complexes were prepared in order to increase the solubility [121]. NMR and IR data showed these complexes to be bonded via the N-atoms while the UV–visible data showed a striking similarity to those of the corresponding Ni(II) complexes, supporting the idea that they are structurally very similar. A complex $KCu(3R\text{-}bi)_2(1R\text{-}biH_2)_2$ was also formed, but the NMR spectrum showed this to be $K[Cu(3R\text{-}bi)_2]$ with the 1-alkyl-biuret as a non-coordinated entity which had also not been deprotonated. It is thought that these are H-bonded to the 3-alkyl-biuret ligands. The oxamide complex $K[Cu(oxam)_2]$ was prepared electrochemically from excess ligand and the copper(II) salt in 0.1 N KOH. The yellow product was diamagnetic and decomposed in light. Again the striking similarity with the nickel(II) analogue led to the conclusion that it had a similar structure, namely square-planar coordination of the ligands about the metal centre. The structural aspect has been confirmed by Birker [123,124] who prepared a copper(III) complex of *o*-phenylenebis(biuret) by iodine oxidation of the parent copper(II) complex. The copper atom was found to be surrounded by an approximately square-planar arrangement of nitrogen atoms (Fig. 8) as would be expected, with deviations from the least-squares plane being approximately 0.1 Å. The four nitrogen atoms are at 1.82(1), 1.85(1), 1.86(1) and 1.89(1) Å from the copper atom, short

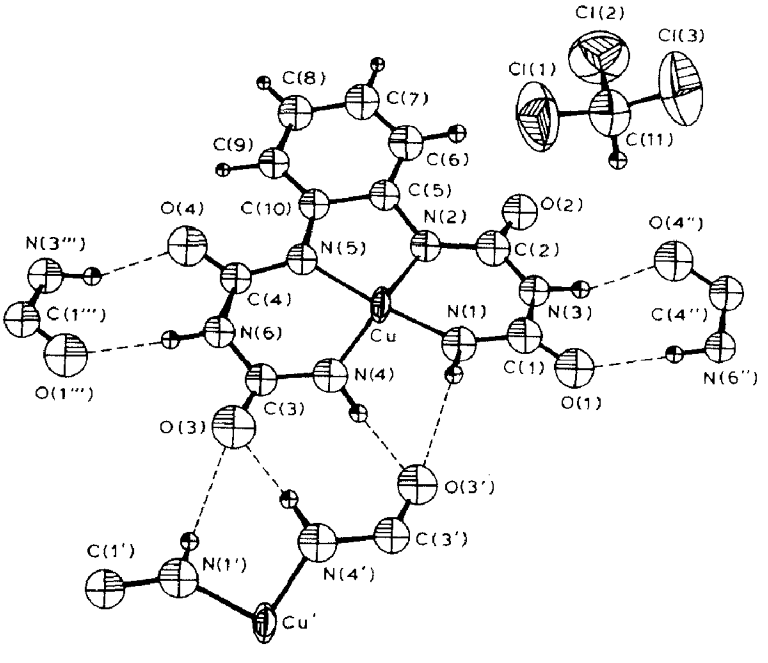


Fig. 8. Structure of $[Cu^{III}(o\text{-phenbisbiuret})]^-$ from ref. 124.

distances compared with 1.93 Å in $K_2[Cu(bi)_2]$ [125] and bond lengths of other N_4-coordinated copper(II) complexes.

A comparison of the XPS spectra of copper(III) and copper(II) biuret complexes has been made [126]. The $2P_{3/2}$ binding energy for the +3 oxidation state (934.5 eV) is higher than for the +2 oxidation state (933.7 eV) as would be expected, but it is lower than binding energies in some other copper(II) systems. This is probably a result of the strong electron donating properties of the biuret ligand. These complexes also show satellite structure in the spectra, but this has not been explained.

Oxidation of copper(II) complexes of 1-(2-hydroxyphenyl)biuret ($PhbiH_2$) and 1-(2-pyridylmethylene)biuret ($pybiH_2$) was attempted [127]. The complex $[Cu(PhbiH)_2]$ had an oxidation potential of 0.440 V in DMSO compared with −0.310 for $[NBu_4]_2[Cu(bi)_2]$ though the product was not isolable. The complex of $pybiH_2$ was not oxidised in the experimental range available.

Meyerstein [128] has reported the radiolytic oxidation of CuL_2^{2+} where L is an amine or amino acid. The complexes formed give electronic spectra very similar to Cu(III)aq, with a slight shift (10–20 nm) to lower energy and the absorption coefficients suggest a L → M charge-transfer process though some doubt is cast on this since the change in ligand might not be expected to cause such a large fluctuation in λ_{max}. Both $[Cu^{III}(NH_3)_n]^{3+}$ and $[Cu^{III}(en)_2]^{3+}$ decompose via a second-order pathway. The latter reaction rate increases with pH. This is thought to arise from the formation of $^{\cdot}OH$ radicals as a decomposition intermediate in alkaline solution. The amino acid complexes, however, decompose via a first order reaction in which the first step may be electron transfer from the carboxylate group to the copper atom.

Copper(III) complexes of cyclic amines have been studied extensively. Olson and Vasilevskis [129] isolated complexes of the ligands *trans*-TETRAMINE, L_{13}, and *trans*-DIENE, L_{14} (Fig. 9) of type $[Cu(L)]^{3+}X_3^- \cdot 2CH_3CN$ ($X = BF_4^-$, ClO_4^-). These orange-red complexes were prepared by electrochemical oxidation of the corresponding copper(II) complex in CH_3CN at temperatures below −14°C in the presence of Et_4NX. The presence of CH_3CN was apparent in the IR spectrum and the formulation was made by analogy with the nickel(III) complexes. At room temperature the copper(III) complexes decomposed spontaneously in acetonitrile with the liberation of acid. The decomposition was monitored spectrophotometrically, and the presence of isosbestic points showed that only one reaction product was formed while the nitrile bands in the IR spectrum disappear on decomposition. No organic matter is released. If Cu(*trans*-TETRAMINE)$^{2+}$ is continuously oxidised at an electrode at 41°C the final product is Cu(*trans*-DIENE)$^{2+}$. The internal redox process shown in Fig. 10 accounts for this.

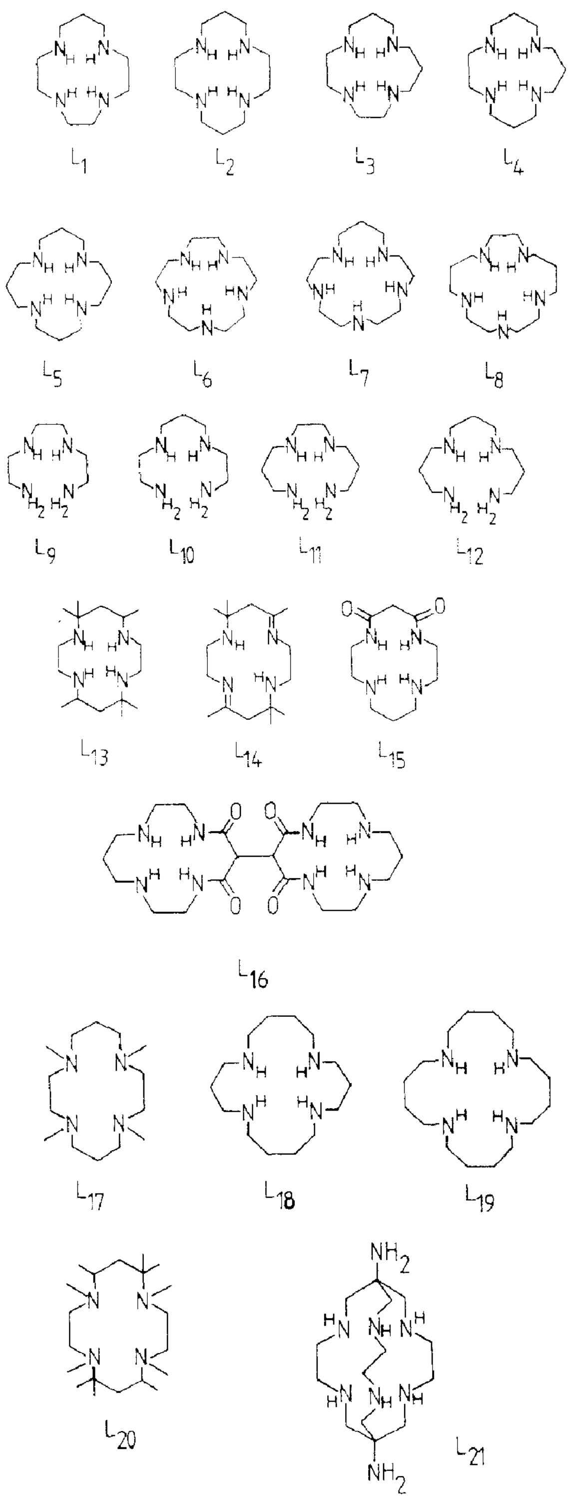


Fig. 9. Macrocyclic ligands and their abbreviations.

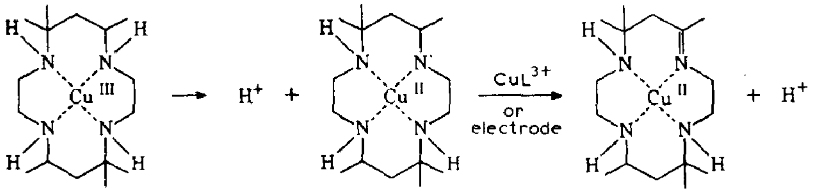


Fig. 10. The reduction of a copper(III) macrocycle.

Endicott and co-workers produced these copper(III) complexes electrochemically but did not isolate them [130] reporting $E_{1/2}$ of 1.64 V for the *trans*-DIENE complex and 1.68 V for the *trans*-TETRAMINE complex.

Fabbrizzi and co-workers have studied the electrochemistry of a large number of tetraazamacrocycles and their open chain analogues (Fig. 9). Their study of 14-membered macrocycles [131] showed that at high scan rates the process was an uncomplicated one-electron transfer process but at lower scan rates the species primarily electrogenerated reacts forming species which are further oxidised in a complicated process which is not fully understood. It is thought that cleavage of the ring system with subsequent release of the Cu^{2+} ion occurs. Varying ring size and denticity [132] of the ligands caused considerable changes in ease of attainment of the +3 oxidation state and in the stability of that oxidation state once attained (Table 7). The symmetrical 14-membered macrocyclic ligand L_2 gives the most readily formed copper(III) complex. Contraction to 13 members and

TABLE 7

Electrochemical data for copper(II) aza macrocycles and their open-chain analogues

Ligand	Ring size	Denticity	Oxidation potential $E_{1/2}$ (V [a])	$t_{1/2}$ (CuL_n^{3+}) (s)
L_1	13	4	+1.00	3
L_2	14	4	+0.99	7
L_3	14	4	+1.03	60
L_4	15	4	+1.12	38
L_5	16	4	+1.23	3
L_6	15	5	+1.07	0.20
L_7	16	5	+1.12	0.02
L_8	17	5	+1.22	0.004
L_9	–	4	+1.07	0.6
L_{10}	–	4	+1.09	1.9
L_{11}	–	4	+1.05	1.8
L_{12}	–	4	+1.1	–

[a] Vs. ferrocenium–ferrocene.

expansion to 15 or 16 members causes an increase in oxidation potential. It is found that the oxidation potential and enthalpy of complexation ΔH^0_{aq} (Cu^{2+} + L) are roughly correlated, the greater the exothermicity the smaller the oxidation potential. It seems that the ligand cavity size and the metal ion radius are closely involved in these trends. The quinquidentate ligands L_6–L_8 form much less stable copper(III) complexes and progressive ring expansion makes oxidation more difficult.

A comparison has been made between the tetraaza macrocycles and their open chain analogues L_9–L_{12} [133]. Ease of attainment of the +3 oxidation state seems to be almost independent of ligand size in the open chain analogues unlike the macrocyclic complexes. The copper ion radius decreases drastically on oxidation from +2 to +3 oxidation states and the flexible open-chain ligands can accomodate this change more readily than the more rigid macrocyclic ligands. The open-chain ligand complexes are much less stable than those of the macrocycles as indicated by the half lives in Table 7. It is concluded that a macrocyclic effect [134] exists in the sense that the reactivity of the macrocyclic complex is reduced with respect to that of the corresponding open chain complex.

It has also been established [135] that in the presence of strong acid the decomposition of copper(III) macrocyclic complexes is dramatically retarded. This is not surprising in view of the mechanism proposed by Olson and Vasilevskis [129] (Fig. 10) and the discovery of protons in electrochemical solutions after decomposition of the products [132]. The half life of Cu(*trans*-TETRAMINE)$^{3+}$ was ~ 87 min in 10 M $HClO_4$.

A comparison of the deprotonated amido and the amino group have shown that the former stabilises the copper(III) oxidation state more readily [136]. A copper(III) complex of dioxocyclam (L_{15}, Fig. 9) persists in water for hours [137] whereas the attempted formation of a copper(III) cyclam (L_2) complex resulted in instant decomposition [138]. The cyclic voltammetry investigation showed that the dioxocyclam complex had an $E_{1/2}$ (Cu^{II}/Cu^{III}) value of +0.15 V compared with +0.99 V for the cyclam complex a difference of 19.4 kcal mol^{-1}, expressing quantitatively the effect of replacement of two amine groups with deprotonated amido groups.

Kimura et al. [139] have confirmed much of this work having studied the oxidation of copper(II) complexes of 13–15 membered macrocycles, with 0–3 deprotonated amido groups and with different extra-planar groups. They found that the oxidation became more difficult as ring size increased. With the same ligand size but with an increase in the number of deprotonated amido groups the oxidation potential decreased from 0.86 V in the mono-amido complex to 0.43 V in the tri-amido complex. It has been suggested that axially-coordinated water is lost on oxidation from copper(II) to copper(III). The effect of appended substituents on the electrode poten-

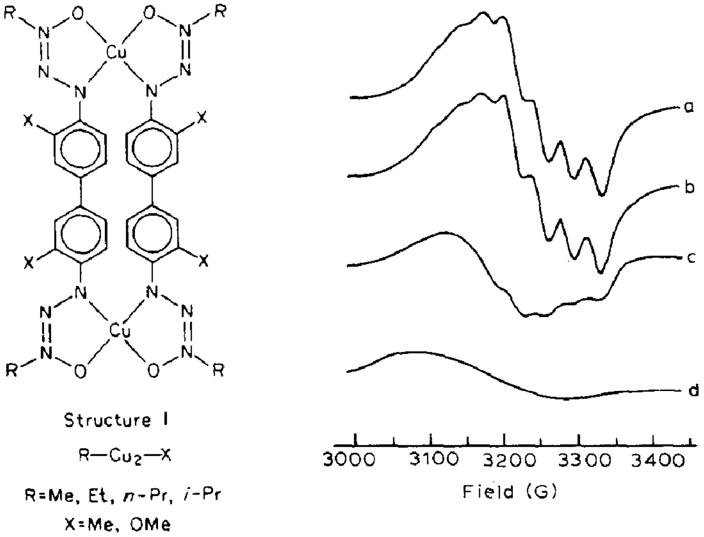


Fig. 11. Proposed structure of R–Cu_2–X and ESR spectra after varying degrees of electrochemical oxidation from ref. 141.

tials is very small in the case of phenyl and pyridyl substituents, but pyridine *N*-oxide causes the oxidation potential to drop to 0.04–0.2 V (depending on the ligand) such that the copper(II) complexes are air oxidised in alkaline solution, though the species formed are very unstable.

Fabbrizzi and co-workers [140] have studied the oxidation of a copper(II) complex of bisdioxocyclam, a double ring octaaza macrocycle (L_{16}, Fig. 9). Mono- or di-metallic species may be formed by varying the ligand-to-metal ratio. Differential pulse voltammetry (DPV) of the dimetallic species gave rise to two one-electron oxidations at 0.578 and 0.681 V vs. SCE arising from the consecutive one-electron oxidation of each metal centre. The difference in oxidation potential may arise from repulsive electrostatic effects between the copper(II) and copper(III) ions. Investigation of the 1 : 1 complex was not conclusive as a number of species are present in solution.

Zacharias and Ramachandraiah [141] report the two step oxidation of binuclear copper(II) complexes R–Cu_2–X (Fig. 11(a)) where X = OMe. The electrochemical data show two consecutive redox processes (Table 8) which are one-electron, nearly reversible processes. Constant potential electrolysis coupled with ESR and electronic spectra measurements confirm the processes involved to be

$$\text{R–Cu}_2^{\text{II}}\text{–OMe} \rightleftharpoons \text{R–Cu}^{\text{II}}\text{Cu}^{\text{III}}\text{–OMe} \qquad \text{(couple A)}$$

$$\text{R–Cu}^{\text{II}}\text{Cu}^{\text{III}}\text{–OMe} \rightleftharpoons \text{R–Cu}_2^{\text{III}}\text{–OMe} \qquad \text{(couple B)}$$

The large separation of the oxidation potentials (250 mV) suggests that

TABLE 8

Electrochemical data for R–Cu_2–X systems

Complex	Couple A E^0/V [a]	Couple B E^0/V [a]
Me–Cu_2–OMe	0.515	0.750
Et–Cu_2–OMe	0.530	0.743
n-Pr–Cu_2–OMe	0.535	0.763
i-Pr–Cu_2–OMe	0.495	0.725

[a] Scan rate = 50 mV s^{-1}.

there is weak copper–copper interaction in these complexes. On electrolysis at 0.0 V the ESR and electronic spectra remained constant, at 0.65 V the ESR signal diminished and at 0.85 V both the ESR spectrum and the 11,000 cm^{-1} band in the electronic spectrum disappeared as expected for square planar copper(III) complexes (Fig. 11(b)).

Reduction of yellow-green $[Cu^{II}(TAAB)]Cl_2$ by H_2 or Hg yield a royal-blue complex [142–144] which may be represented as either $[Cu^I(TAAB)]^+ X^-$ or $[Cu^{III}(TAAB)^{2-}]^+X^-$ ($X = Cl^-$, PF_6^- or $HgCl_3^-$). The latter formulation is favoured on a number of counts. Infrared spectra show that the ligand is not hydrogenated since there are no bands observed in the N–H stretching region. All bands in the C=N stretch region show a shift of 25 cm^{-1} to low energy on 'reduction' supporting the contention that the ligand is reduced to $TAAB^{2-}$. The complexes are diamagnetic. The ligand strongly prefers to adopt a square-planar conformation, which is unfavourable for d^{10} copper(I) but highly favoured in d^8 copper(III). In addition to this the reduced ligand $TAAB^{2-}$ is a 34π electron system which is aromatic and is favoured because of resonance energy considerations. So the formulation as a copper(III) complex is most likely.

Cupric salts form intensely coloured products in the presence of oxalodihydrazide and certain aldehydes and ketones. This colouration is caused by copper(III) macrocyclic complexes if oxygen is present. There has been some confusion regarding the characterisation of these complexes [145,146] but it has now been established that a copper(III) macrocyclic complex (Fig. 12) is formed [147]. Oxidation of the orange copper(II) complex is effected by oxygen or ferricyanide, resulting in a violet complex which is ESR silent, NMR active and absorbs at 540 nm in the electronic spectrum. The crystal structure of this complex [146] showed Cu–N bond lengths of 1.86(1) Å, considerably shorter than in comparable copper(II) complexes. The XPS spectrum of this complex [148] did not show the characteristic 'shake up' satellite of paramagnetic copper species confirming its diamagnetism. Verification of the oxidation state by comparison with copper(II) complexes is not

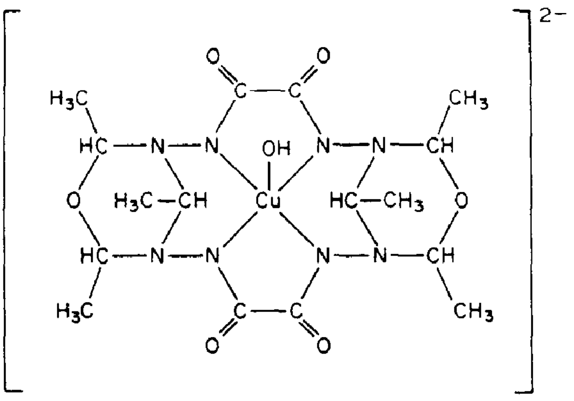


Fig. 12. Structure of a copper(III) macrocycle from ref. 147.

entirely foolproof, but a value 0.4 eV greater than $Cu^{II}O$ is consistent with the assignment made. When acetaldehyde was used as the source of carbonyls it was found that a deep blue colour ($\lambda_{max} = 600$ nm, $\epsilon = 16{,}000$) was seen and could be retained if an excess of aldehyde was avoided [149]. A crystal structure determination revealed a square-planar complex rather than the five-coordinate structure seen for the purple complex. Short Cu–N bond lengths (1.881 to 1.896 Å) are seen, commensurate with the high oxidation state of the copper, but otherwise the structural details were quite normal. The complex was stable in aqueous solutions of pH 8–9 for long periods and was ESR silent.

A comprehensive review of copper(III) tri- and tetra-peptide complexes by Margerum and Owens [3] has covered this area up to 1981. Some of the unpublished work reported therein has since appeared. This includes studies of self-exchange electron-transfer by ^1H NMR line broadening [150], electron-transfer reactions between $IrCl_6^{2-}$ and copper(II) peptides [151], reactions of the copper(III) complex of cyclo(β-alanylglycyl-β-alanylglycyl) [152], mechanism and kinetics of copper(III) tetraglycine reactions with sulphite [153], photochemistry of copper(III) complexes of polypeptides with α-amino isobutyric acid residues [154] and the electron transfer kinetics of reactions between copper(III/II) and nickel(III/II) deprotonated peptide complexes [155].

Since this review the first report of a copper(III) peptide in the solid state has been made [156]. The crystal structure of the complex of tri-α-amino-isobutyric acid, $Cu^{III}(H_{-2}Aib_3) \cdot 2H_2O \cdot 1.5NaClO_4$ has been determined. The coordination sphere has a square-planar array of three nitrogen atoms and an oxygen atom, deviating from the least squares plane by ~ 0.05 Å (Fig. 13) with a slight tetrahedral distortion. The M–N bond lengths are 1.90 Å for the amino nitrogen, 1.80 Å for the peptide nitrogens and 1.83 Å for

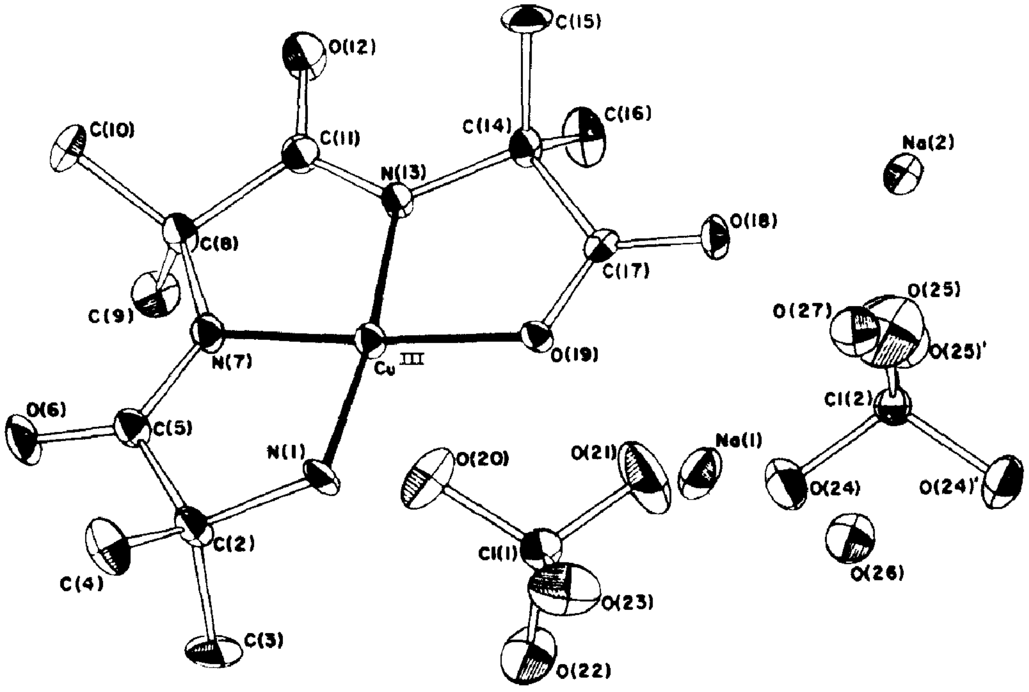


Fig. 13. Structure of $[Cu^{III}(H_{-2}Aib_3)]\cdot 2\ H_2O\cdot 1.5\ NaClO_4$ from ref. 156.

the M–O bond, all considerably shorter than for analogous copper(II) bonds. The nearest perchlorate atom in an axial position is at 2.91 Å and is not considered to interact significantly.

Also reported are electron transfer reactions with ruthenium(II) amine complexes and with hexacyanoferrate(II) [157]. From self-exchange rates for copper(III/II) peptide complexes the rates of reduction by $Ru(NH_3)_6^{2+}$, $Ru(NH_3)_5(py)^{2+}$ and $Ru(NH_3)_5(pic)^{2+}$ were accurately predicted from the Marcus theory. It is thought that the redox process takes place by an outer sphere mechanism in view of the absence of bridging ligands and the adherence to Marcus theory [157a]. In contrast the redox process with $Fe(CN)_6^{4-}$ is thought to proceed via an inner sphere mechanism with a cyanide bridged intermediate complex followed by coordination of water in the two axial positions in the resulting copper(II) complex [157b].

McAuliffe et al. have prepared copper(III) complexes of Schiff bases of type $[Cu(SB)(H_2O)_2]ClO_4$ where SB = salen and related ligands [158]. These are prepared as red-brown solids by oxidation of the corresponding copper(II) salts with air or H_2O_2 in ethanolic solution. These complexes are paramagnetic ($\mu_{eff} = 2.85$–3.12 BM) suggesting an octahedral complex. The electronic spectra are very similar to those of octahedrally-coordinated nickel(II) complexes while ESR measurements at 93 K exhibit a four-line isotropic signal with $g = 2.29$–2.17 and $g = 2.10$–2.06. These are some of the few genuinely octahedrally-coordinated copper(III) complexes.

Warren and Bennett [159] have prepared the only reported complexes of copper(III) tertiary phosphines and arsines. They report complexes $[Cu(L{-}L)_2](ClO_4)_3$ and $[Cu(L{-}L)_2Cl](ClO_4)_2$ where L–L = o-$C_6H_4(PMe_2)_2$ and o-$C_6H_4(AsMe_2)_2$ (diphos and diars respectively). The square-planar complexes are prepared by oxidation of the copper(I) analogues with concentrated nitric acid whilst the five-coordinate complexes are prepared by addition of chloride ions to the square-planar complexes. These are all yellow or orange diamagnetic solids which show charge-transfer bands between 320 and 420 nm in the electronic spectrum. Attempts to generate an octahedral $[Cu(L{-}L)_2Cl_2]^+$ species were not successful though a red colouration on the crystal surface when treated with Me_4NCl at -80°C has been ascribed to transient formation of this species. An X-ray crystal structure determination on $[Cu(diphos)_2Cl](ClO_4)_2$ revealed a square-pyramidal complex with Cu–P bond lengths being 2.263 Å, Cu–Cl = 2.461(1) Å and a long perchlorate contact in the sixth position of 2.889(4) Å.

In addition to these complexes we have recently prepared copper(III) phosphines and arsines of the type $[Cu(L{-}L)Cl_2]X$ (where X = Cl, BF_4 and L–L = bidentate phosphine or arsine ligands including o-$C_6H_4(PPh_2)_2$, o-$C_6H_4(AsPh_2)_2$, $Ph_2P(CH_2)_2PPh_2$, $Ph_2As(CH_2)_2AsPh_2$) by chlorine oxidation of dichloromethane solutions of copper(I) complexes $[Cu(L{-}L)_2]X$ [160]. The yellow/orange products are stable for several weeks in a dry atmosphere, but are immediately decomposed in solution by H_2O or ethanol. These complexes have been characterised by elemental analyses, ^1H and ^{31}P NMR, UV–visible and infrared spectroscopy. The analogy with the iso-electronic nickel(II) complexes $[Ni(L{-}L)Cl_2]$ is quite striking [161,162] and on this basis we expect the copper(III) complexes to be four-coordinate square planar species.

(iv) Groups IIIB and IVB donor ligands

Copper formally in the +3 oxidation state is found in some sandwich complexes of carboranes. The complex $[Cu^{III}(B_{10}H_{10}CH)_2]^{3-}$ was reported [163], prepared by reaction of copper(II) acetylacetonate and $Na_3B_{10}H_{10}CH$ in THF. No physical data were given. Warren and Hawthorne [164] have prepared the red $[Ph_3MeP]^+[Cu^{III}(\pi\text{-}(3)\text{-}1,2\text{-}B_9H_{11}C_2)_2]^-$ by air oxidation of the corresponding copper(II) complex and crystallisation with Ph_3PMe^+ Br^-. Cyclic voltammetry showed a reversible one-electron redox process at -0.35 V. It is interesting to note that the copper(III) complex is most stable. The electronic spectrum of this species showed absorptions at 205 and 492 nm and the ^1H NMR of the tetraphenylarsonium salt contained a phenyl

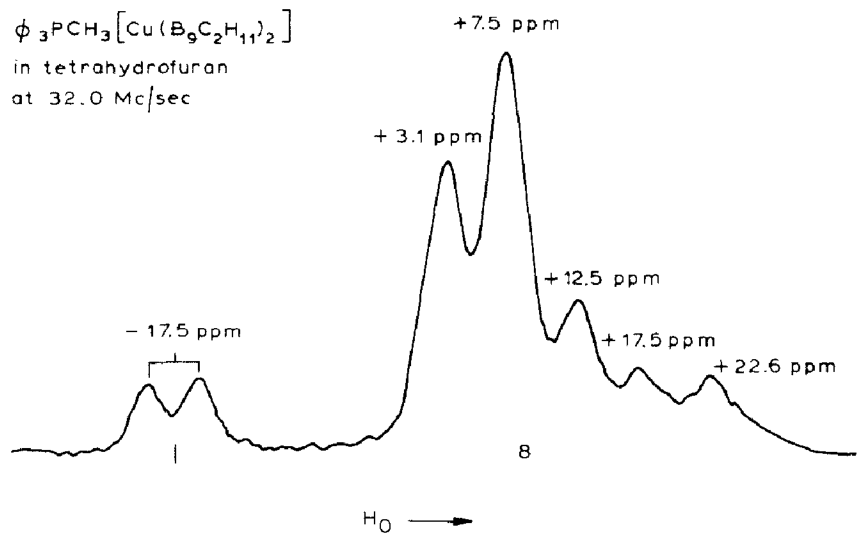


Fig. 14. ^{11}B NMR spectrum of $[Cu^{III}(B_9H_{11}C_2)_2]^-$ from ref. 165.

resonance at $\delta + 8.07$ ppm and a carborane C–H proton resonance at +3.91 ppm in a 5 : 1 ratio as expected. The ^{11}B NMR spectrum (Fig. 14) contains a high-field doublet characteristic of the d^8 species of this type which has been tentatively assigned to the unique boron atom in the open face of the ligand. A crystal structure determination of $[Ph_3MeP]^+[Cu(B_9H_{11}C_2)_2]^-$ [165] revealed an unusual geometry (Fig. 15) with a 'slip distortion' placing the copper atom closer to the ligand boron atoms (2.11 Å) than to the carbon atoms (2.52 Å) forming a highly distorted bis π-allyl type sandwich. In contrast to this [166,167] a σ-bonded complex $[Et_4N]^+[Cu[(B_{10}H_{10}C_2)_2]_2]^-$ has been prepared as a yellow diamagnetic solid. It is thought to be a square planar (Fig. 16) complex with four Cu–C σ-bonds. No C–H protons from the carborane were seen either in the ^1H NMR spectrum or in the infrared spectrum as expected. The ^{11}B spectrum consisted of two overlapping doublets centred at +3.9 and −0.5 ppm relative to $BF_3 \cdot OEt_2$. The electronic spectrum showed high intensity bands at 374, 272 and 200 nm. This complex could be reduced to its copper(II) analogue with lithium or zinc metal in the presence of Et_4NBr and cyclic voltammetry in dry CH_3CN gave a reversible wave at +0.15 V vs. SCE for a reversible Cu^{III}/Cu^{II} couple. More general aspects of bonding in these complexes is discussed in a recent book on the subject [168].

There has been speculation in recent years that copper(III) species may be formed as metastable intermediates in a number of organic reactions [169]. This is not unreasonable in view of experimental evidence of oxidation of copper(II) ions to copper(III) by organic radicals. Meyerstein and Freiberg

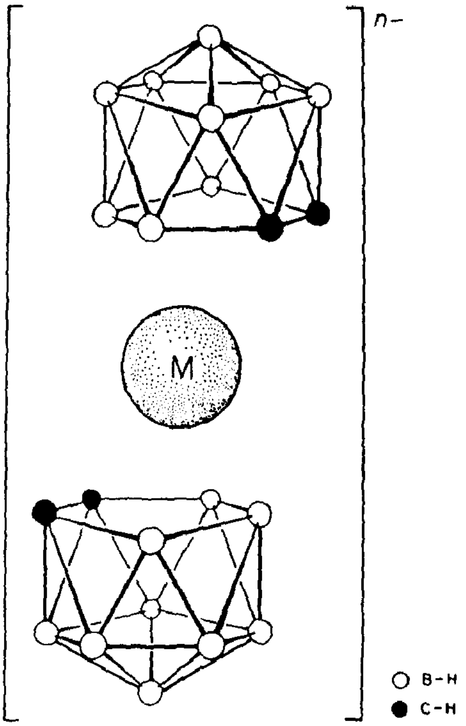


Fig. 15. Structure of $[Cu^{III}(B_9H_{11}C_2)_2]^-$ from ref. 165.

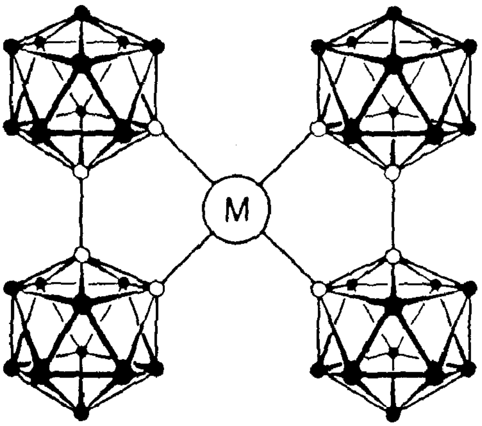


Fig. 16. Proposed structure of $[Cu^{III}[(B_{10}H_{10}C_2)_2]_2]^-$ from ref. 166.

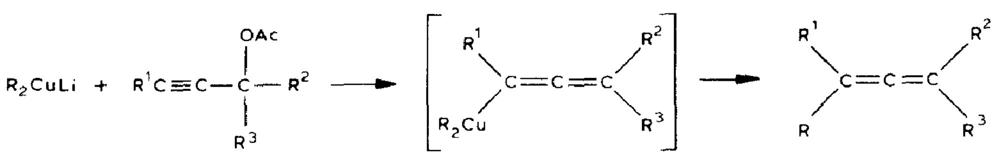
[170] have studied the reaction of $^{\bullet}CH_2CO_2^-$ with Cu^{2+} by pulse radiolysis. A strong absorbance near 320 nm is ascribed to the presence of $Cu(CH_2CO_2)^+$ and of $(CH_3CO_2)Cu(CH_2CO_2)$ which decompose with rates of $2.8 \pm 0.3\ s^{-1}$ and $90 \pm 5\ s^{-1}$ respectively. Similar results are obtained with $Me\dot{C}HCO_2^-$ and $^{\bullet}CHCl_2$ or $^{\bullet}CCl_3$, but not with $R_2\dot{C}OH$ or $^{\bullet}CO_2^-$ radicals. Radiolysis of solutions containing a copper(II) triglycyl Cu(GGG) complex and NaBr, Me_3COH or $MeCO_2Na$ led to formation of relatively long-lived intermediates absorbing at 385 ± 5 nm ($\epsilon = 4200 \pm 600\ dm^3\ mol^{-1}\ cm^{-1}$) with NaBr, 320 nm ($\epsilon = 5000 \pm 700\ dm^3\ mol^{-1}\ cm^{-1}$) with Me_3COH and a broader band $\lambda_{max} < 350$ nm with $MeCO_2Na$. These are thought to be due to $Cu^{III}(GGG)$, $Cu^{III}(GGG){-}CH_2CMe_2OH$ and $Cu^{III}(GGG){-}CH_2CO_2^-$ respectively [171]. Ferraudi [172] has reported the formation of $CuMe^{2+}$ (absorbing at < 350 nm) by reaction of methyl radicals and copper(II) ions.

Margerum [3] has reviewed the involvement of copper(III) intermediates in organic reactions. These reactions include the oxidation of alkyl radicals to alkenes and substituted alkyl groups by copper(II) ions [173], aromatic diazonium decomposition induced by copper(I) ions [174], catalysis of the cross-coupling of alkyl groups [175–177], reaction of alkyl and aryl halides with copper(I) salts [178] and the copper(I)-induced Ullmann coupling of aryl halides to form biaryls [179,180]. In addition to this a copper(III) intermediate is proposed in the formation of allenes by reaction of organocuprates with acetylated [181,182] and tosylated [183,184] acetylenes as shown below

$$\text{“}CH_3Cu^I\text{”}\ R{-}C{\equiv}C{-}CH_2{-}OTs \xrightarrow{-60\,^{\circ}C,THF} [R(CH_3Cu^{III})C{=}C{=}CH_2]^+$$

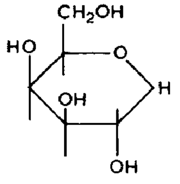
$$\rightarrow R(CH_3)C{=}C{=}CH_2$$

(where “CH_3Cu^I” is generated by addition of CuBr to RMgX in at least equimolar quantities) and



(v) Biological role of copper(III)

The possibility that Cu(III) may be involved in certain metalloenzyme systems has been proposed several times [3], but not surprisingly given the complexity of the systems, proof has been difficult to obtain and alternative interpretations have been advanced. One of the more studied systems is the oxidation of **A**



(A)

to the corresponding aldehyde by the enzyme galactose oxidase which contains a single atom of copper [185–187]. A proposed mechanism is oxidation of the alcohol by Cu(III) which is reduced to Cu(I), and then reoxidised to Cu(III) by molecular oxygen. A variety of other oxidations are performed by this enzyme, and these workers [187] have suggested that copper(III) may be present as the 'active' species in other copper enzymes. Alternative explanations not involving Cu(III) have been proposed [188]. Copper(III) has also been implicated in the autoxidation of ascorbic acid catalysed by copper(II) [189], and in the specific oxidation of copper-coordinated oligopeptides [190]. While the involvement of oxidising Cu(III) centres in metalloenzymes has seemed increasingly reasonable as the extent of Cu(III) coordination chemistry has grown, the presence of an ESR-silent (d^8 probably planar) ion remains difficult to prove. Typical of the problems is the nature of the copper in cytochrome *c* oxidase, one possibility being that one (of the two) copper atoms is Cu(III). However, while X-ray absorption edge spectra of the oxidised oxidase clearly identify one copper as Cu(I), an unequivocal distinction between Cu(II) and Cu(III) formulations for the second was not possible [191].

C. COPPER(IV) CHEMISTRY

This very rare oxidation state is established in only one environment, in the hexafluoroanion $[CuF_6]^{2-}$. It has been suggested [30] that some Cu(IV) may be present in $BaCuO_{2.63}$ made from $BaCuO_2$ and oxygen at 500°C/400 atm, but this requires confirmation. It seems unlikely that Cu(IV) coordination complexes will be obtainable.

The $[CuF_6]^{2-}$ ion has been prepared as K, Rb and Cs salts by high pressure fluorination [2,192–194]. The structures are an orthorhombic distortion of the K_2PtCl_6 type, but different preparations yield materials with varying lattice parameters, an indication of the extreme instability of the products. The presence of Cu(IV) is confirmed by magnetic measurements ($\mu_{eff} \sim 1.5$ [193] or 1.7 [194] BM Cs salt), and by the ESR spectrum [193] characteristic of $t_{2g}^6 e_g^1$. Surprisingly it appears that Cs_2CuF_6 has also been obtained in a flow preparation at 1 atm pressure [195].

D. SILVER(II) CHEMISTRY

The ability of heterocyclic nitrogen donors to stabilise silver(II) has been known for many years, and more recently examples with other N-donors such as tetraazamacrocycles have been prepared. The only simple silver(II) compound appears to be the fluoride AgF_2, and a range of related fluorocomplexes have been characterised.

As d^9 species, silver(II) compounds are expected to be paramagnetic and in practice with the notable exception of AgF_2, the compounds are mostly magnetically dilute with μ_{eff} consistent with one unpaired electron. Many examples of planar four coordination are known, and a smaller number of six-coordinate complexes. The latter are expected to be distorted from regular octahedral coordination as a consequence of the Jahn–Teller effect ($t_{2g}^6 e_g^3$), although only a few detailed studies have been reported. A comparison with the very complicated stereochemistry of copper(II) suggests that detailed structural investigations of silver(II) are likely to be rewarding, although clearly the much more limited range of ligand types and the greater ligand field splittings will restrict the range of stereochemistries found.

(i) Fluorides and oxides

The only binary halide is AgF_2 although Ag^{2+} ions in alkali chloride lattices can be produced by X-ray irradiation of silver-doped alkali halides, and have been studied by ESR spectroscopy [196]. Silver(II) fluoride can be prepared by fluorination of silver powder, or a silver(I) halide by F_2 or ClF_3 at elevated temperatures [197–201] or by passing fluorine into a solution of AgF in anhydrous hydrogen fluoride [202]. The pure product is difficult to obtain and this is the main reason for the various colours ascribed to the compound—black, grey-black, brown or brown-black. The pure material is in fact dark blue [203], and turns brown on contact with moisture. A yellow 'AgF_2' [204] has not been confirmed.

The structure of AgF_2 has also been disputed [205–209], but is now established to consist of a distorted octahedral environment about the silver with orthorhombic symmetry [PbCa(O)]. The axial elongation is greater than in CuF_2. There are four short Ag–F bonds in a planar arrangement [2.07 Å], with two longer Ag–F axial [2.85 Å] [206,207], the in-plane AgF_4 units share corners to form puckered layers, and whereas in AgF_2 these layers are displaced alternately related by a glide plane, in CuF_2 the layers lie directly over one another related by a translation [210]. Under 60 kBar of argon AgF_2 converts into a new form which is a variant of the fluorite structure [211]. The ^{19}F NMR of AgF_2 has also been reported [212].

Silver difluoride is not magnetically dilute, and exhibits antiferromagnetic behaviour with a Neel temperature of 163 K, and a magnetic moment of ~ 2.0 BM at room temperature. Detailed variable temperature magnetic and neutron diffraction studies have been carried out [206,213,214].

AgF_2 is thermally stable and at 700°C the dissociation pressure of F_2 is < 0.1 atm [198], but it is violently hydrolysed by water [197]. It fluorinates many inorganic materials, and has been extensively used in the fluorinations of organic materials although neither use will be discussed here [215,216].

A variety of fluoroargentates(II) are known. The brown $MAgF_3$ (M = K, Rb, Cs) are formed [203] by heating MF and AgF_2 under argon. The potassium salt is orthorhombic, the others tetragonal versions of the perovskite structure, and like AgF_2 they are antiferromagnetic (Tc = 80 K ($KAgF_3$), 50 K ($CsAgF_3$)) at low temperatures, while at higher temperatures the magnetic moments ~ 1.0 BM are essentially temperature independent [203,217]. The $[NO]AgF_3$ analogue has recently been obtained from AgF_3 and NOF [218]. An $AgF_2 \cdot AsF_5$ adduct has been reported [218b].

Blue M_2AgF_4 complexes (M = K, Rb, Cs) are obtained by heating appropriate proportions of MF and AgF_2 in a gold tube under argon [203,219]. The powder patterns of the K and Rb salts have not been indexed, but Cs_2AgF_4 has the K_2NiF_4 structure [219]. Except at low temperatures the compounds obey the Curie–Weiss law with μ_{eff} ~ 1.5–1.7 BM. Fluorination of Ag_2SO_4/MY_2 ($MY_2 = BaCO_3$, $Sr(NO_3)_2$, $CaCO_3$ etc.) mixtures produces blue-violet $MAgF_4$ (M = Ba, Sr, Hg) or brown-violet $M'AgF_4$ (M′ = Ca, Cd) [220,221]. All have the tetragonal $K[BrF_4]$ structure [221] with Ag–F ~ 2.05 Å. They have the expected magnetic moments (μ_{eff} 1.8–2.0 BM) and obey the Curie–Weiss law [217,221]. Ba_2AgF_6 prepared from $Ag_2SO_4 + 4BaCO_3$ fluorinated at 500°C is also known [217].

Silver(II) hexafluorometallates(IV) $Ag[MF_6]$ (M = Ti, Ge, Sn, Pb, Rh, Pd, Pt, Zr, Hf, Mn) have been obtained by fluorination of appropriate mixtures of Ag_2SO_4 and metal halides or oxides, and vary in colour with M [222–224]. The SnF_6^{2-}, PbF_6^{2-} and PdF_6^{2-} ions are magnetically dilute, but there is strong $Ag^{2+} \leftrightarrow Ag^{2+}$ magnetic exchange in the $AgHfF_6$ and $AgZrF_6$ compounds. Modified pyrochlores $M^IAgM^{III}F_6$ [M^I = K, Rb, Cs; M^{III} = Tl, In, Ga, Al, Sc, Fe, Co] are known with a variety of colours ranging from dark green to dark blue, some of which vary with temperature [225,226]. The magnetic moments are ~ 1.1–1.3 BM and the susceptibilities do not follow the Curie–Weiss law. Single crystals of several examples were prepared and the structures determined [225]. The Ag^{2+} is in a distorted octahedral environment; Ag–F = 2.04–2.06 (×2) and 2.29–2.31 (×4) Å.

The Ag^{2+} ion is expected to produce distorted environments as a consequence of the Jahn–Teller effect (d^9). Two detailed studies of the electronic spectra and electron spin resonance spectra of various fluoroargentates(II) and of $AgMF_6$ have been published [227,228]. Typical diffuse reflectance

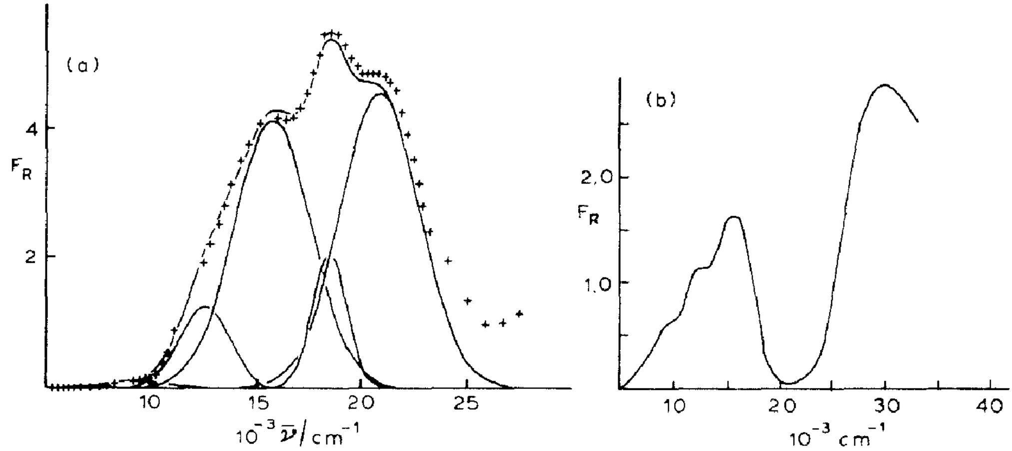


Fig. 17. Diffuse reflectance spectra of Ba[AgF_4] and Ag[PbF_6] from ref. 227.

spectra for Ag(II) in a planar environment [$BaAgF_4$], and in a distorted octahedral one [$AgPbF_6$] are shown in Fig. 17. It was also proposed that in $M^{I}_{2}AgF_4$ (M = Cs, Rb) the tetragonal distortion of the octahedra is much greater than in $AgMF_6$. The agreement between the two studies is good in view of the difficulties of handling these very moisture-sensitive materials, and the assignments confirm that in comparison with the Cu^{2+} analogues the ligand field splittings are ~ 50% greater and the electron delocalisation more extensive in the Ag(II) systems.

The oxidation of silver(I) salts to black higher oxides of silver has been known for many years, and many formulae have been proposed for the products including silver(I) peroxide Ag_2O_2, silver(II) oxide AgO, and various others—Ag_2O_3, Ag_3O_4, Ag_4O_5. Barbieri [229,230] showed that the peroxide formulation was unlikely as no reactions characteristic of peroxides were given by Ag_2O_2 (AgO). Slowly it became clear that the reports were confused both by the failure of some workers to realize that slow oxygen loss had often invalidated analytical data, and that many of the products made in acid solution contained incorporated anions, e.g. $Ag_7O_8NO_3$ obtained from $AgNO_3$. Further studies led to the formulation of AgO as the mixed valence $Ag^{I}Ag^{III}O_2$ (see p. 97), and it seems that no good evidence for a solid silver(II) oxide has been produced, although equally there seems no obvious reason why it should not exist if a suitable synthetic route can be found. Spectroscopic evidence for a gas phase AgO molecule is available [231].

Equally surprising is the almost complete absence of oxoargentate(II) anions. The only possible candidates appear to be the red incompletely characterised $KAgO_x$ ($x = 1.4$–1.6) and $RbAgO_y$ ($y \sim 1.0$–1.5) produced by heating MAg^IO in oxygen [232,233]. The products are paramagnetic [$KAgO_x$, $\mu = 1.1–1.3$ BM] but the structures and even the synthesis of pure samples have not been established. Since Ag(III) oxides are diamagnetic (q.v.) the paramagnetism possibly indicates Ag(II) is present.

(ii) Group VIB donor ligands

Studies on Ag(II) in aqueous solution date from the classic work of Noyes et al. [234–236] on "argentic" ions (it would appear that Ag(III) was also present in some materials). Despite the formulation of AgO as $Ag^IAg^{III}O_2$ dissolution of the oxide in nitric acid, ozonisation of acid solutions of Ag(I) salts, or $S_2O_8^{2-}$, PbO_2 or F_2 oxidation of $AgNO_3$ lead to Ag(II) in solution [234–239]. More recently pulse radiolytic methods have been used to generate $Ag^{2+}aq$, $Ag(OH)^+$ and $Ag(OH)_2$ [39]. The nature of Ag(II) in solution and the kinetics and mechanisms of Ag(II) oxidations of a variety of inorganic and organic substrates have been reviewed very recently [240] and this article should be consulted for further details.

Isolated Ag(II) compounds with oxygen donor ligands are rare but include silver(II) fluorosulphate $Ag(SO_3F)_2$ a dark-brown powder obtained from prolonged reaction of silver powder and bis(fluorosulphuryl)peroxide, from AgF_2 and SO_3, or from silver(I) salts and $S_2O_6F_2$ [241,242]. The reaction of $S_2O_6F_2$ with Ag_2CO_3 or Ag_2O for shorter periods of time gives black $[Ag_2O(SO_3F)_2]$ [243]. It decomposes on heating to $AgSO_3F$ and $S_2O_6F_2$ and reacts with 2,2′-bipyridyl to give $[Ag(bipy)_2](SO_3F)_2$. The vibrational and electronic spectra suggest a square-planar environment for the silver in $Ag(SO_3F)_2$ but do not exclude a tetragonally distorted octahedral one, and magnetic studies show it follows the Curie–Weiss law ($\mu_{eff} = 1.92$ BM, $\theta + 20$) [242]. Sulphur trioxide and $CsAgF_4$ yield $Cs[Ag(SO_3F)_3]$ a green-brown moisture-sensitive solid, which is also magnetically dilute [$\mu = 1.92$ BM, $\theta \sim 4$] [244]. In contrast $K_2[Ag(SO_3F)_4]$ made from KSO_3F, Ag and $S_2O_6F_2$ and the mixed valence $Ag^I_2[Ag(SO_3F)_4]$ obtained from silver and $BrOSO_2F$ [242] are antiferromagnetic with Neel temperatures of 300 and 240 K respectively and room temperature (298 K) magnetic moments of 1.28 and 1.65 BM. $Ag^{II}[Pt^{IV}(SO_3F)_6]$ and Ag^{II} $SnSO_3F)_6]$ are also known [242]. Silver(II) trifluoromethanesulphonate $[Ag(O_3SCF_3)_2]$ has been prepared by exchange between $[Ag(SO_3F)_2]$ and HO_3SCF_3 [245]. It is a dark-brown solid with $\mu = 1.88$ BM, and probably of similar structure to the fluorosulphate. Although other Ag(II) oxoanions have not been isolated, there is good evidence that Ag(II) ions in solution coordinate anions readily including SO_4^{2-}, NO_3^- and PO_4^{3-} [240].

Numerous ESR studies of silver(II) dialkyldithiocarbamates have been undertaken but no pure samples of these complexes have been isolated. Addition of tetraalkylthiuram disulphide to solutions of $[Ag^I(R_2dtc)]$ results

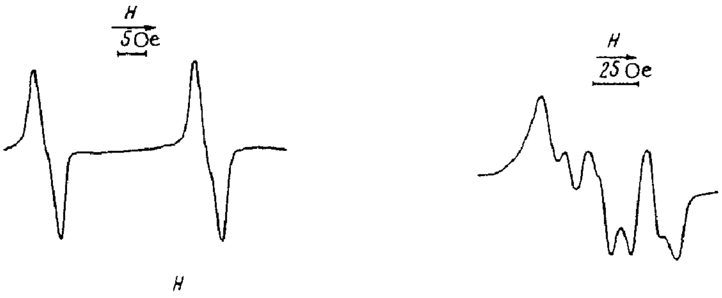


Fig. 18. ESR spectra of bis(hexamethylenedithiocarbamato)silver(II) as benzene solution (298 K) and chloroform glass (77 K) from ref. 247.

in a blue colouration [246] which ESR measurements confirmed to be due to a silver(II) complex. The ESR spectrum at room temperature showed a doublet which on expansion revealed the hyperfine splittings of both ^{107}Ag and ^{109}Ag ($g = 2.019$ and $a = 2.7 \times 10^{-3}$ cm^{-1}). The ESR spectrum of hexamethylenedithiocarbamate as a chloroform glass showed a more complex structure (Fig. 18) [247]. Single crystal ESR spectra of $[Ag(R_2dtc)_2]$ diluted in $[Zn(R_2dtc)_2]$ have been studied [248]. At low $[Ag(R_2dtc)_2]$ concentrations all the $[Ag(R_2dtc)_2]$ occurs in the form of $Ag(R_2dtc)_2$–$Zn(dtc)_2$ pairs giving rise to $S = \frac{1}{2}$ spectra. At higher Ag : Zn ratios some $Ag(dtc)_2$–$Ag(dtc)_2$ pairs are formed giving rise to an $S = 1$ spectrum, namely a triplet. The effect on the ESR spectra of $[Ag^{II}(dtc)_2]$ of adding organic bases, pyridine, 2-, 3- and 4-picolines and triethylamine has been studied [249]. Extra lines are seen in the spectra which are thought to arise from a 1 : 1 adduct. ESR parameters are reported. Polarised optical absorption studies of $[Ag(Et_2dtc)_2]$ crystallised in a lattice of $Zn(Et_2dtc)_2$ have been reported. Two (x, y) polarised bands at 16,000 and 22,100 cm^{-1} were observed and assigned to $^2A_2 \rightarrow {}^2B_1$ and $^2A_2 \rightarrow {}^2B_2$ transitions respectively giving an xz, yz separation of approximately 6100 cm^{-1} in good agreement with previous results. Molecular orbital coefficients were calculated from these data. Yamamoto and Ozeki [251] were able to analyse trace amounts of silver by forming the silver(II) dithiocarbamate and extracting into an organic solvent such as CS_2, benzene, carbon tetrachloride and others. In CS_2 a strong ESR signal is seen with a sensitivity of 0.1 ppb. Analysis was also possible by colorimetric methods by observing a band at 620 nm though this was less sensitive. Copper(II) and mercury(II) ions interfered with the process. There is ESR evidence for the existence of $[Ag(mnt)_2]^{2-}$ [99]. Two lines are seen in the spectrum arising from the two isotopes of silver. For $[Ag(mnt)_2]^{2-}$ in acetonitrile $g = 2.019$ and $a = 31.4$ gauss.

Silver(II) selenocarbamates have also been shown to exist by ESR spectroscopy. Studies in chloroform solution [252] of a powdered mixture of

$[Pd(dsc)_2]$ and $[Ag(dsc)_2]$ [252] and of single crystals with either $[Pd(dsc)_2]$ [253] or $[Ni(dsc)_2]$ [254,255] as diluents have been reported. The g-values have been found to be close to that for the free electron and it is thought that this arises from spin–orbit interaction of the selenium atoms and the strong π-covalency of the d^9 metal to selenium bond. It has been noted in this connection that the covalency of the silver(II) to ligand bond increases for different donor atom sets in the order $AgN_4 < AgS_4 < AgSe_4$ [256] and a corresponding shift of the g-values towards that of the free electron is also seen. Detailed molecular orbital calculations have been carried out [254,255] and comparisons made with copper(II) diselenocarbamates. As with the dithiocarbamate complexes none of these species has been isolated as a pure solid.

(iii) Group VB donor ligands

The chemistry of Ag(II) with group VB donors is limited to nitrogen ligands; there are no reported complexes with phosphines or arsines [257]. Copper(II) similarly fails to complex with the majority of heavier group VB ligands being readily reduced to Cu(I), although a few copper(II) complexes with hybrid arsine–amines and arsino-carboxylic acids have been reported [257]. No reports of Ag(II) analogues with these hybrids have appeared.

The chemistry of Ag(II) with heterocyclic and macrocyclic amine ligands was well reviewed by Po [4] in 1976, who presented extensive tabulations of magnetic, ESR and electronic spectral data of the known complexes. The present article will deal mainly with data published since Po's article, and will not comprehensively cover earlier work, although continuity and comparisons with the other sub-sections require description of some of the earlier work.

Silver(II) complexes of ammonia or di-primary amines have not been isolated, although the formation constant for the $Me_2C(CH_2NH_2)_2$ complex in solution has been reported [258]. Ag(II) amino-acid complexes are intermediates in the oxidation of glycine and related amino acids by pulse radiolytically generated Ag^{2+} [259]. The ESR spectrum of $AgClO_4$/MeCN glass at 77 K after irradiation with ^{60}Co γ rays has been interpreted in terms of a planar $[Ag(MeCN)_4]^{2+}$ ion [260], and white crystals $[Ag^{II}(MeCN)_4][Mo^{V}F_6]_2$ have been produced by oxidation of silver powder with MoF_6 in the presence of MeCN [261].

Heterocyclic N-donors such as pyridine derivatives or 2,2′-bipyridyl readily form Ag(II) complexes which range in colour from dark-red to yellow, and have ESR spectra [4] and magnetic moments [$\mu_{eff} = 1.7–2.1$ BM] consistent with magnetically dilute d^9 systems in which the orbital component is largely or completely quenched. The compounds are strongly oxidising [240]. The synthetic method most commonly used is persulphate oxidation of an $AgNO_3$ solution containing the appropriate ligand, which normally results in precipitation of the poorly soluble $[AgL_x]S_2O_8$, from which analogues with various other anions can be obtained by exchange. Anodic oxidation of a silver(I) solution containing excess ligand has also been widely used. $[Ag(2,2'\text{-bipyridyl})_2]X_2$ ($X = SO_3F$, CF_3SO_3) have been prepared [242,245] directly from AgX_2 and the ligand, but the absence of other AgX_2 materials, and the corrosive nature of the starting materials severely limits this route. Walton and Murtha [262–264] have studied a variety of these complexes by photoelectron spectroscopy, and found that the Ag $3d_{3/2}$ and $3d_{5/2}$ binding energies differ little between Ag(I) and Ag(II) complexes, generally being slightly *less* for the Ag(II) compounds, and thus do not provide a clear indication of oxidation state. In contrast the binding energies of Ag(III) complexes are appreciably greater. Secondary ion mass spectroscopy of Ag(II) complexes only show Ag(I) fragmentations due to reductive processes [265].

The $[Ag(py)_4]S_2O_8$ originally prepared by Barbieri [266] has been re-examined several times and anlogues prepared with a range of other anions [264,267,268], and has been much studied by ESR spectroscopy [268]. There is no evidence for association of more than four pyridines/Ag even in neat pyridine solution, and while in frozen nitric acid solution $[Ag(py)_2(NO_3)_2]$ was suggested to be formed [269], this has not been confirmed by a more recent study [268]. The data on substituted pyridine complexes are also conflicting in some cases. Thus Wasson [270] reported $[AgL'_4]S_2O_8$ [L′ = 3-Mepy, 4-Mepy] were readily obtained by $S_2O_8^{2-}$ oxidation of $AgNO_3$ solution + L′, but failed to make the 2-Mepy analogue. Smith and Walton [267] prepared 3-Clpy, and 3-Ipy analogues, but reported that with 2-Mepy at low temperature a Ag(I) complex was produced while at higher temperatures the ligand was oxidised to pyridine-2-carboxylic acid. Other pyridines including 3-HOpy, 4-Phpy, 2-MeOpy and 4-Mepy failed to give Ag(II) complexes. However, $[Ag(4\text{-Mepy})_4]S_2O_8$ was confirmed by Evans et al. [268]. In contrast to the pyridine complexes which are magnetically dilute, pyrazine produces the polymeric $[Ag(pyrazine)_2]S_2O_8$ which is antiferromagnetic [271].

The $[Ag(2,2'\text{-bipyridyl})_2]^{2+}$ is probably the most commonly prepared Ag(II) complex [268,272–276], and has been isolated with $S_2O_8^{2-}$, ClO_4^-, HSO_4^-, NO_3^-, ClO_3^-, $CF_3SO_3^-$ and SO_3F^- counter anions. The reported tris complexes $[Ag(2,2'\text{-bipy})_3]^{2+}$ [273] have been shown not to exist [268,277, 278], but $[Ag(2,2'\text{-bipy})_3]^{2+}$ is suggested [279] as an intermediate in the electrochemical studies of the Ag^+/Ag^{2+} system in propylene carbonate containing excess 2,2′-bipyridyl. The X-ray structure of $[Ag(2,2'\text{-bipy})_2](NO_3)_2 \cdot H_2O$ [280] has shown the presence of a distorted (~ 28°) from planar AgN_4 unit [Ag–N = 2.14, 2.15, 2.16, 2.18 Å], with weak axial interaction with two bridging nitrates (Fig. 19) to form a chain structure. In neutral

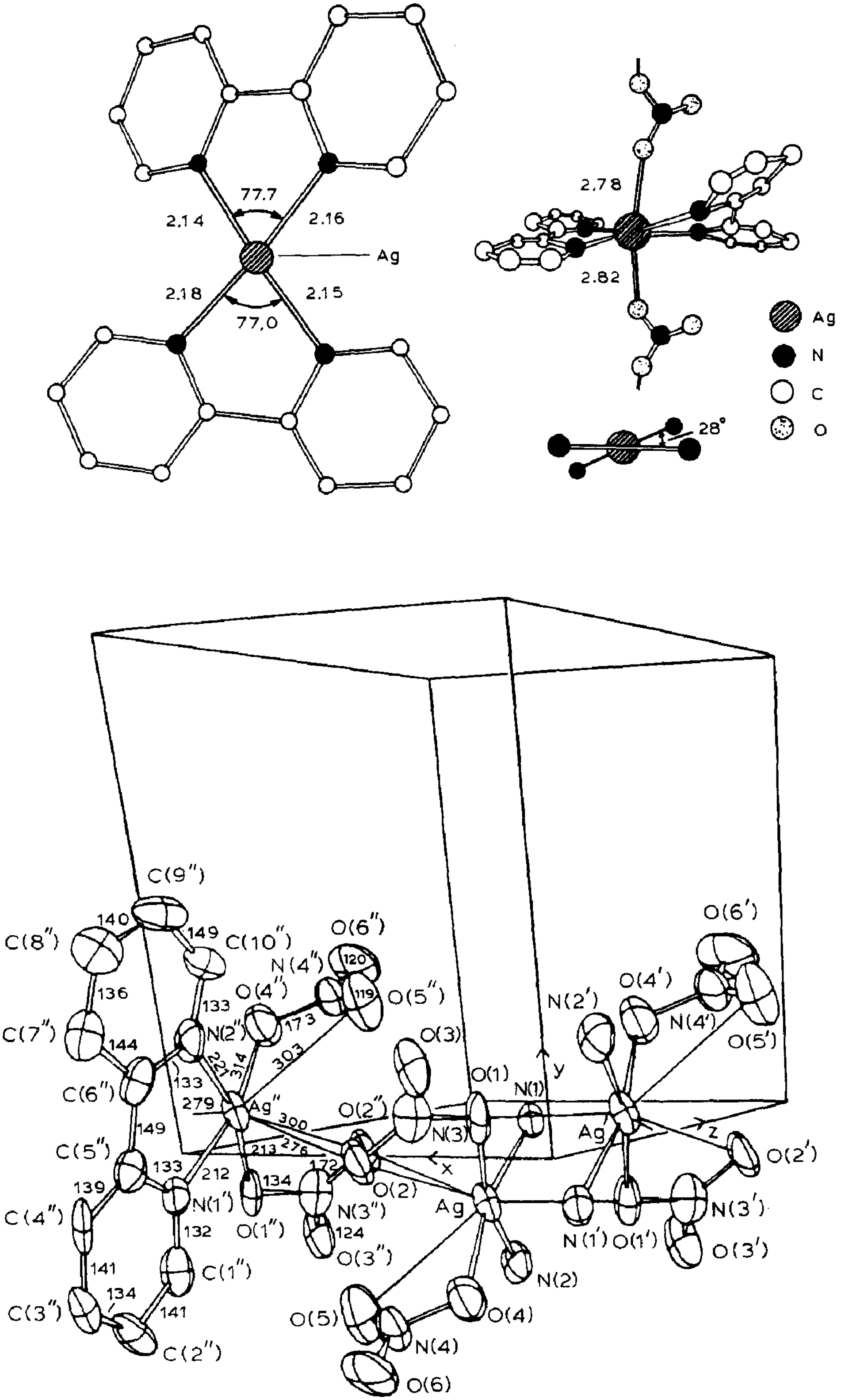


Fig. 19. Structures of [Ag(2,2′-bipy)$_2$](NO$_3$)$_2$·H$_2$O and [Ag(2,2′-bipy)(NO$_3$)$_2$] from refs. 280 and 281.

solution $[Ag(2,2'\text{-bipy})_2]^{2+}$ is present [268,276], but in HNO_3 $[Ag(2,2'\text{-bipyridyl})(NO_3)_2]$ is produced [268,274,276], and this has also been structurally characterised [281]. It has a distorted square-planar structure with a chelating bipyridyl ligand and two *cis* monodentate NO_3 groups (Ag–N = 2.124(16), 2.207(16) Å, Ag–O = 2.148(15), 2.136(15)), with long axial contacts (2.75, 2.76 Å) to two further NO_3 groups (Fig. 19).

o-Phenanthroline complexes $[Ag(phen)_2]Y_2$ [Y = NO_3, ClO_4, ClO_3, $\frac{1}{2}S_2O_8$] are generally similar to the 2,2′-bipyridyl analogues but are less soluble [268,282,283] and in nitric acid solution $[Ag(phen)(NO_3)]$ is formed. With the tridentate 2,2′,2″-terpyridyl, the 1:1 complexes $[Ag(terpy)Y_2]$ (Y = ClO_4, NO_2, $\frac{1}{2}S_2O_8$) are easily prepared [273,284] and are probably four coordinate $[N_3O]$. Dark-brown $[Ag(terpy)_2]S_2O_8 \cdot 3H_2O$ was obtained [263] from $AgNO_3$, $K_2S_2O_8$ and excess terpy, and based upon the PES spectrum, and the electronic spectrum which show absorptions at much lower energy than $[Ag(terpy)Y_2]$, is believed to be six coordinate. Confirmation by an X-ray study of six-coordinate Ag(II) bound to neutral ligands only is desirable.

The second class of nitrogen donor ligands to complex readily with Ag(II) are the pyridinecarboxylic acids. The favoured synthetic route is oxidation of the preformed Ag(I) complex, or of a mixture of $AgNO_3$ and the pyridinecarboxylic acid in solution with persulphate, although electrolytic oxidation has also been used [262,285–290]. The $Ag^I/S_2O_8^{2-}$ oxidation of 2Me-py to $2\text{-}C_5H_4NCO_2H$ has been noted above [264].

Three pyridinemonocarboxylic acids are known (Fig. 20), and all form bright orange-red or orange-brown 2:1 complexes with Ag(II). The 2-pic complex is believed to be planar with the structure shown in Fig. 21, because it is isomorphous with the Cu(II) analogue which has this structure [287]. This structure is also supported by the IR spectrum [283], and the complex is magnetically dilute ($\mu_{eff} = 1.83$ BM, $\theta = 10$ K). The structures of the nicotinic and isonicotinic acid complexes are less clear; the IR spectra are consistent with bonding through both N and CO_2^-, and since the geometry of the ligands precludes chelation, ligand bridged polymeric structures are indicated, although in the absence of single crystal X-ray data, the detailed geometry is uncertain [284,291]. The isonicotinic acid complex is magnetically dilute, but $[Ag(nic)_2]$ is antiferromagnetic, with a maximum susceptibility at 80 K, and the detailed behaviour fits the Ising type model [285].

Five pyridinedicarboxylic acids are known (Fig. 20), and these give deep-red Ag(II) complexes $[AgL_2]$ [262,267,285,290,292–297]. Generally the magnetic moments are slightly low ($\mu_{eff} = 1.6$–1.81 BM). The single crystal X-ray study of $[Ag(QuinH)_2 \cdot 2H_2O$ reveals the expected planar structure (Fig. 22) [295] with the QuinH chelated to the silver via the N and the $2\text{-}CO_2^-$ group (Ag–N = 2.12(1) Å, Ag–O = 2.13(1) Å), with weak interaction

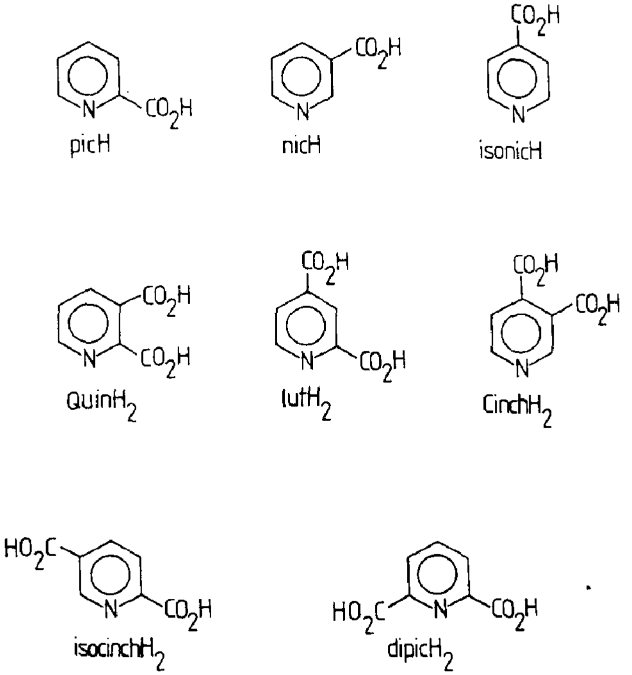


Fig. 20. Pyridinecarboxylic acids.

between the C=O of the 3-CO_2H group and silver atoms in adjacent molecules completing very distorted tetragonal octahedral coordination, Ag...OCOH = 2.98 Å. The complexes of isocinchomeronic, lutidinic, and cinchomeronic acids have been less studied, and although their properties point to the presence of planar AgN_2O_2 coordination, the structures are not known for certain. For the 3,4-substituted pyridine (cinchomeronic acid) a polymeric structure is likely, but those with a 2-CO_2H group are able to chelate like picolinic acid (Fig. 21) [262,285,297].

The silver(II) complex of dipicolinic acid is distinctly different. The material has been reported as mono-, di-, and tetrahydrates [285,293,294,297],

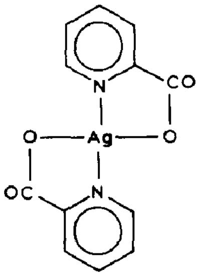


Fig. 21. Proposed structure of [Ag(2-pic)$_2$].

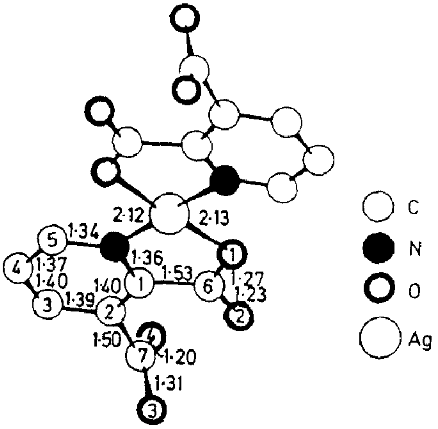


Fig. 22. Structure of $[Ag(QuinH)_2]\cdot 2\ H_2O$ from ref. 295.

which have similar diffuse reflectance spectra and are hence likely to contain the same silver environment. In solution the complex is green, the powders dark-brown, and the crystals green-black (tetrahydrate) or black (monohydrate). The presence of an electronic spectral absorption band at ca. 17,000 cm^{-1} (the other planar pyridine carboxylato complexes do not absorb below ca. 20,000 cm^{-1}) indicates six-coordination, and this has been confirmed by an X-ray study of the monohydrate, which moreover showed the two ligands to differ, and that the complex is best formulated $[Ag(dipic)(dipicH_2)]\cdot H_2O$ [294] (Fig. 23). The silver atom is bonded to one dianionic (dipic) ligand (Ag–N = 2.09(2) Å, Ag–O = 2.20(1) Å) and to one neutral ($dipicH_2$) ligand (Ag–N = 2.21(2) Å, Ag–O = 2.53(1) Å) with a considerably distorted environment about the Ag atom. The reason for the production of this

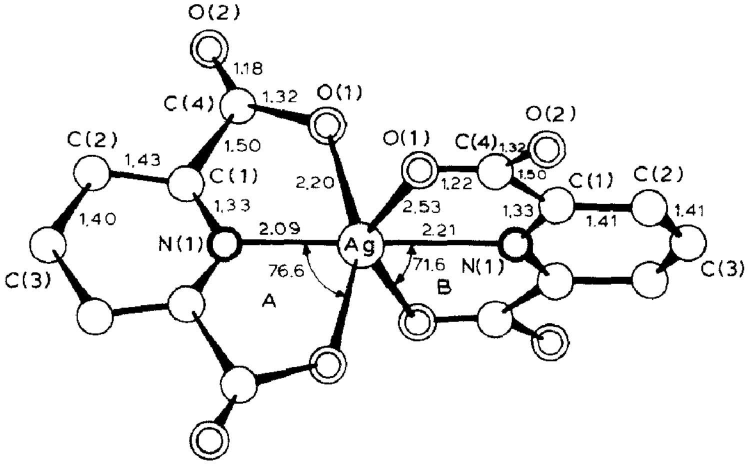


Fig. 23. Structure of $[Ag(dipic)(dipicH_2)]\cdot H_2O$ from ref. 294.

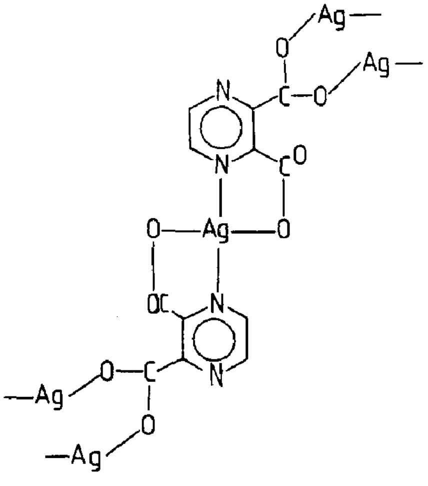


Fig. 24. Proposed structure of $[Ag^I_2Ag^{II}(pyr(CO_2)_2)_2]$.

structure rather than $[Ag(dipicH)_2]$ is unclear; possibly it involves the Jahn–Teller effect and the distorted environment (4 + 2) expected for the d^9 ion, the weak bonding of the $dipicH_2$ oxygens facilitating this.

Complexes with pyridinetricarboxylic acids (2,3,6-, 2,4,5-, 2,4,6-) have been briefly described [298]. They are surprisingly rather unstable orange (2,4,5-), green (2,3,6-) or black (2,4,6-) solids.

Pyrazine-2-carboxylic acid differs from pyrazine itself, in producing a magnetically dilute $[Ag(pyzCO_2)_2]$ ($\mu = 1.81$ BM) complex [271], probably with an analogous structure to the picolinic acid complex (Fig. 21). Pyrazine-2,3-dicarboxylic acid and aqueous $AgNO_3$ are oxidised by $(NH_4)_2S_2O_8$ to an orange-brown mixed valence material $[Ag^I_2Ag^{II}(pyz(CO_2)_2)_2]$ [262, 271,292] with the proposed structure (Fig. 24), but attempts to isolate a complex with pyrazine-3,4,5-tricarboxylic acid failed [271]. An orange $[Ag(isoquinoline\text{-}1\text{-}carboxylato)_2]$ has also been described [262].

A number of mixed ligand complexes containing pyridine carboxylato and neutral heterocyclic N-donors have been obtained [262,299,300] including $[Ag(dipic)(L)]xH_2O$ (L = 2,2′,2″-terpyridyl, 2,2′-bipyridyl, 1,10-phenanthroline), $[Ag(terpy)(L')]0.5\ S_2O_8$ (L′ = LutH, isochinchH, chinchH), and $[Ag(pic)_2L'']$ (L″ = isoquinoline, quinoline, 2 Me-quinoline). The complexes have normal magnetic moments, and the presence of low energy electronic spectral absorptions strongly suggests that the silver is six (or possibly five) coordinated.

The disproportionation of Cu(I) to Cu(II) and metallic Cu in the presence of certain nitrogen donor ligands has long been known, but the first example with Ag(I) was reported as recently as 1972. Kestner and Allred [301] found that the macrocycle Me_6aneN_4 (Fig. 9) reacted with $AgClO_4$ in dry acetonitrile to give $[Ag^{I}(Me_6aneN_4)]ClO_4$, but in water or water/methanol a silver mirror was produced and the yellow $[Ag(Me_6aneN_4)](ClO_4)_2$ ($\mu = 2.14$ BM) could be isolated from the solution. Barefield and Mocella [302] prepared $[AgL](ClO_4)_2$ complexes [L = L2, L13, L14, L17] by the same route as orange-yellow solids, which could be further oxidised to Ag(III) electrochemically or chemically. They are reasonably stable in solution in organic solvents or water. Recent studies [303,304] have shown that the $Ag^{I} \rightarrow Ag^{II} + Ag^{0}$ disproportionation depends upon the ring size of the macrocycle, thus while 14, 15 and 16 ring tetraaza macrocycles [L2, L4, L13, L14, L18] cause disproportionation, larger rings [L18 or L19] do not; indeed [L19] readily forms a Ag(I) complex. The smaller ring sizes lead to strong Ag–N interaction, which raises the antibonding 4*d* orbitals sufficiently so that removal of an electron is facilitated. The PES spectra of several Ag(II) macrocycles have been reported [303].

The essentially planar coordination in these complexes was confirmed by a single crystal X-ray study of the *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane complex $[Ag(L13)](NO_3)_2$ [305], in which the average Ag–N distance is 2.160(3) Å. There are weak $Ag–O(NO_2)$ contacts completing a very distorted six-coordination (Ag–O = 2.807(4) Å). A re-examination of the complex $[Ag(L2)](ClO_4)_2$ has shown that different structural forms can be isolated [306]. Slow crystallisation of the red-orange $[Ag(L2)](ClO_4)_2$ from dilute perchloric acid produces small amounts of yellow block crystals, and larger amounts of orange needles. The structure present in the yellow blocks is shown in Fig. 25; the silver sits on the crystallographic centre of symmetry (Ag–N = 2.158(2) Å). The needles contain ca. 25% of this form, and 75% of a second isomer (Fig. 26) with the Ag on the mirror plane bisecting the two six-membered rings (Ag–N = 2.192(11) Å (av)). The first form contains weak $Ag \cdots OClO_3$ interactions (2.788(2) Å), but the second does not. The first form is essentially the same as found in the *meso*-Me_6aneN_4 complex and is the thermodynamically stable form, while the second is the kinetically favoured form [306].

The electrochemical redox properties of $[AgL]^{2+}$ in solution (L = L2, L14, L17, L20] and $[Ag(LH_2)]^{4+}$ (L = 21) have been examined [307]. The behaviour is complex and both solvent and ligand dependent. The complexes of the ligands with secondary N atoms showed electrochemical redox behaviour corresponding to

$$Ag^{III}L \leftrightarrow Ag^{II}L \leftrightarrow Ag^{I}L \rightarrow Ag^{0} + L$$

but the tertiary-N ligands failed to stabilise Ag^{III}, while ligand (L21) not only yielded no stable Ag^{III} complex, but the reduction of $[Ag(LH_2)]^{4+}$ is a 2e process with no evidence for the formation of a stable Ag^{I} intermediate.

The other class of N-donor ligands which favour Ag(II) [and Ag(III)] over

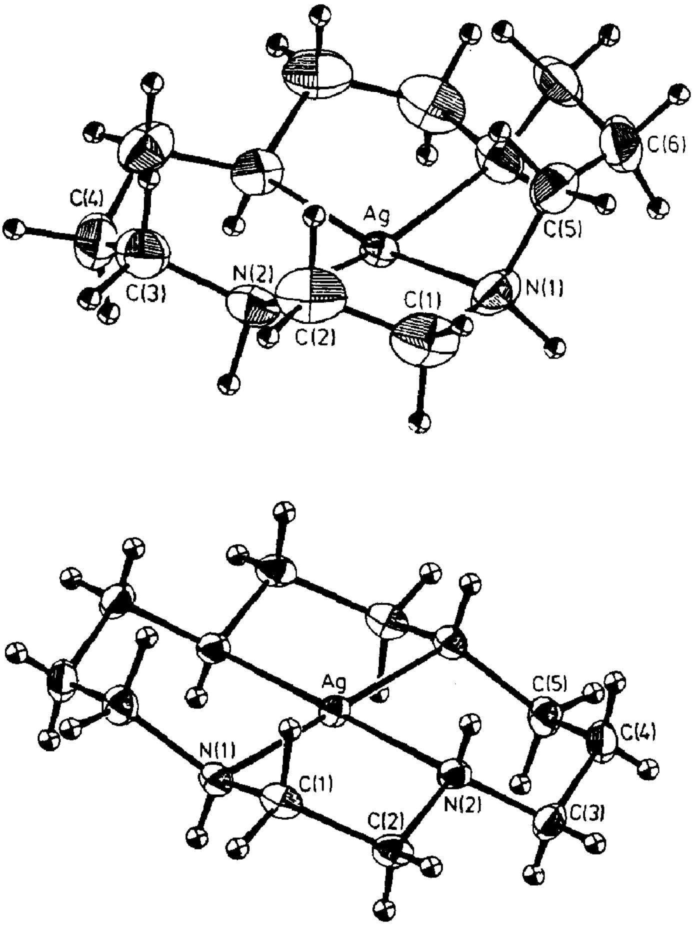


Fig. 25, and 26. Structures of the two isomers of $[Ag(L_2)](ClO_4)_2$ from ref. 306.

Ag(I) are porphyrins, which like macrocycles provide strong in-plane ligand fields which facilitate oxidation of the metal (Fig. 27). The Ag^{II}(porphyrins) have often been included in larger studies with various other M^{II} ions; the reported examples are in Table 9.

The synthetic route generally used is reaction of the porphyrin with AgOAc in acetic acid, pyridine or $CHCl_3$ solutions. Extensive electronic spectroscopic studies show that most [Ag^{II}(porphyrin)] complexes exhibit two intense absorption bands above the Soret band which lies ca. < 450 nm. Detailed ESR spectra of most of these materials have been recorded, and are consistent with the expected planar N_4 environment. These studies also suggest that the Ag–N bonds are more highly covalent than the Cu–N bonds in copper(II) analogues. Several other porphyrin complexes, originally

TABLE 9

Ag(II) porphyrins [AgL] [a]

Compound	α	β	γ	δ	1	2	3	4	5	6	7	8	Refs.
$AgC_{44}H_{28}N_4$	Ph	Ph	Ph	Ph	H	H	H	H	H	H	H	H	313, 316–321,
	R–Ph	R–Ph	R–Ph	R–Ph	H	H	H	H	H	H	H	H	341
	(R = *p*-MeO, *p*-Me, *m*-Me, *p*-F, *p*-Cl, *p*-Br)												
$AgC_{36}H_{44}N_4$	H	H	H	H	Et	Et	Et	Et	Et	Et	Et	Et	313, 320, 322–324
$AgC_{32}H_{36}N_4$	H	H	H	H	Me	Et	Me	Et	Me	Et	Me	Et	325
$AgC_{32}H_{36}N_4$	H	H	H	H	Me	Et	Et	Me	Me	Et	Et	Me	326
$AgC_{36}H_{44}N_4$	H	H	H	H	Me	Pr	Pr	Me	Pr	Me	Me	Pr	327
$AgC_{48}H_{52}N_4O_{16}$	H	H	H	H	Me	$\underline{A}$	Me	$\underline{A}$	Me	$\underline{A}$	Me	$\underline{A}$	328
$AgC_{32}H_{32}N_4O_4$	H	H	H	H	Me	H	Me	H	Me	$\underline{B}$	$\underline{B}$	Me	326, 329, 330
$AgC_{36}H_{40}N_4O_4$	H	H	H	H	Me	Et	Me	Et	Me	$\underline{B}$	$\underline{B}$	Me	326, 327, 331, 332, 342
$AgC_{36}H_{36}N_4O_6$	H	H	H	H	Me	COMe	Me	COMe	Me	$\underline{B}$	$\underline{B}$	Me	326,330
$AgC_{34}H_{36}N_4O_6$	H	H	H	H	Me	$\underline{C}$	Me	$\underline{C}$	Me	$\underline{D}$	$\underline{D}$	Me	333
$AgC_{36}H_{40}N_4O_6$	H	H	H	H	Me	$\underline{C}$	Me	$\underline{C}$	Me	$\underline{B}$	$\underline{B}$	Me	334
$AgC_{38}H_{44}N_4O_6$	H	H	H	H	Me	$\underline{E}$	Me	$\underline{E}$	Me	$\underline{B}$	$\underline{B}$	Me	335
$AgC_{36}H_{40}N_4O_4$	Me	H	Me	H	Me	Et	Et	Me	Me	$\underline{D}$	$\underline{D}$	Me	335
$AgC_{44}H_{28}N_4O_{12}S_4$	PhS	PhS	PhS	PhS	H	H	H	H	H	H	H	H	336
$AgC_{48}H_{28}N_4O_8py$	$\underline{F}$	$\underline{F}$	$\underline{F}$	$\underline{F}$	H	H	H	H	H	H	H	H	337
$AgC_{44}H_{30}N_4$	Ph	Ph	Ph	Ph	H	H	H	H	H	H	2H	2H	321, 338
$AgC_{36}H_{36}N_4O_4$	H	H	H	H	Me	$\underline{G}$	Me	$\underline{G}$	Me	$\underline{B}$	$\underline{B}$	Me	334
$AgC_{36}H_{36}N_4O_8$	H	H	H	H	Me	$\underline{D}$	Me	$\underline{D}$	Me	$\underline{D}$	Me	$\underline{D}$	339
$AgC_{40}H_{44}N_4O_8$	H	H	H	H	Me	$\underline{B}$	$\underline{B}$	Me	Me	$\underline{B}$	$\underline{B}$	Me	340

[a] Underlined letters ($\underline{A}$–$\underline{G}$) refer to Fig. 27.

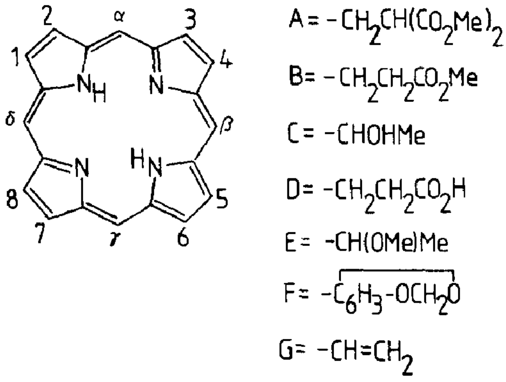


Fig. 27. Porphyrin ligands.

identified as Ag(I) complexes have been reformulated as Ag(II) [308]. The electrochemical reduction of silver(II) porphyrins results in generation of an unstable [Ag^I(porph)] which rapidly demetallates to form Ag^+ ions and the free porphyrin base [313]. The electronic structures of [Ag^{II}(porphyrin)] have been investigated by $X\alpha$-calculations [314]. Water-soluble Ag^{II}-porphyrins have been prepared mainly using modified tetraphenylporphyrin, the modifications involving p-$Me^+NC_5H_4-$, p-$Me_3^+NC_6H_4-$ or p-$O_3SC_6H_4$ groups replacing phenyl [309,310–312].

The Ag(II) complex of phthalocyanine has also been prepared and characterised [315].

(iv) Groups IIIB and IVB donor ligands

There are no isolated examples of organosilver(II) compounds, but Ag(II) has been widely used as an oxidant for organic substrates [240].

E. SILVER(III) CHEMISTRY

The chemistry of silver(III) is considerably more restricted than that of silver(II), and has received less recent attention than copper(III). Interest in silver(III) chemistry is nonetheless increasing and significant recent developments include the preparation and X-ray crystallographic characterisation of Ag_2O_3, and the synthesis (as yet unconfirmed) of AgF_3. Other examples of silver(III) include the long known $Ag^IAg^{III}O_2$ ("AgO") and the related silver oxo salts, fluoroanions and coordination complexes with nitrogen donor multidentates.

The common geometry of Ag(III) is square planar which is associated with diamagnetism; octahedral coordination is rare but is found in $M^I_3AgF_6$ which is paramagnetic, while diamagnetic tetragonal geometry (four strongly coordinated ligands in plane and weak coordination of two other axial ligands) has been found in a few cases.

(i) Fluorides and oxides

A red-brown material of composition AgF_3 has been prepared by oxidation of AgF_2 in anhydrous hydrogen fluoride by KrF_2 [218,342]. The product is stable at room temperature but decomposes to AgF_2 on heating and hydrolyses in air to AgF and AgO. The X-ray powder pattern indicates low symmetry but has not been indexed.

Variable temperature magnetic studies show the Curie–Weiss law is obeyed, but the low value of μ_{eff} (1.15 ± 0.05 BM) is unexpected. The authors suggest two explanations; either $Ag^{II}[Ag^{IV}F_6]$ which has d^9 and d^7 ions and would approximate to one unpaired electron/Ag, or two silver(III) environments only half of which give rise to paramagnetism (i.e. equal numbers of planar diamagnetic and six-coordinate paramagnetic Ag(III) environments). It is worth noting that $CsPd^{II}F_3$ contains equal numbers of four- and six-coordinate Pd(II) environments [193]. Further studies are required and perhaps only a single crystal X-ray will resolve the problem.

Two types of fluoroargentate(III) anion are known, $[AgF_4]^-$ and $[AgF_6]^{3-}$. The yellow, diamagnetic extremely moisture-sensitive compounds $M[AgF_4]$ (M = Na, K, Rb, Cs) are readily prepared by fluorination of 1 : 1 mixtures of MCl and $AgNO_3$ [343–345]. As expected the structures are of the tetragonal $K[BrF_4]$ type [345,346]. Unstable $NO[AgF_4]$ has recently been reported [218]. Fluorination of $BaCl_2 + AgNO_3$ mixture gives a mixture of BaF_2 and AgF_2, but $BaAgPO_4$ produces yellow $BaAgF_5$ [344]. The octahedral red-purple $Cs_2K[AgF_6]$ a paramagnetic ($\mu = 2.6$ BM) cubic elpasolite, appears to be the only example known of a silver analogue of $[CuF_6]^{3-}$, as even $Cs_2Rb[AgF_6]$ has not been obtained [2,3,47]. The diffuse reflectance spectrum of $[AgF_6]^{3-}$ has been reported and assigned [16] (Fig. 28), but that of $[AgF_4]^-$ does not appear to have been examined.

The early literature on higher oxides is confused and often contradictory although a number of claims were made for the preparation of Ag_2O_3 usually by electrochemical oxidation of $AgNO_3$ solution or by ozonisation of $AgNO_3$ or $AgClO_4$ solution under controlled conditions [348–351]. The instability of the products prevented complete characterisation, and while it is likely that in the more highly oxidised products the majority of the silver was present as Ag(III), their nature remains unclear. Very recently Jansen [352] obtained crystalline Ag_2O_3 by electrolysis of aqueous $AgPF_6$ at 0 °C between Pt electrodes. The black crystals lose oxygen at room temperature, but are stable at low temperature. The X-ray structure shows that Ag_2O_3 is very similar to Au_2O_3, containing planar AgO_4 groups linked into a three-dimensional network in which three of the oxygens are 3-coordinate (Ag–O = 2.03 Å (av)) and one is 2-coordinate (1.98 Å).

As mentioned above (p. 38) AgO is a mixed valence $Ag^IAg^{III}O_2$ and it

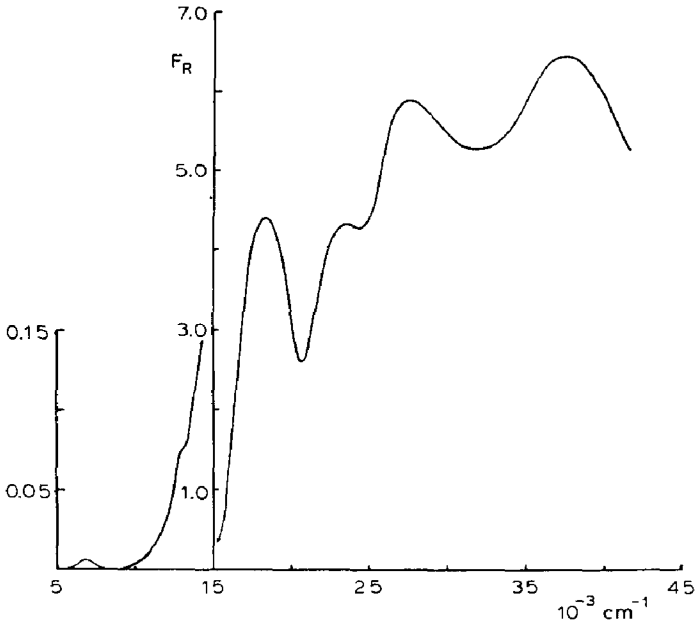


Fig. 28. Diffuse reflectance spectrum of $KCs_2[AgF_6]$ from ref. 16.

and the "argentic" oxosalts e.g. Ag_7O_8X are discussed here. The literature on "AgO" * is extensive, and in parts confused and contradictory in detail. The development of the silver oxide battery has resulted in extensive studies of the electrochemical synthesis of AgO, and of the properties of Ag/ Ag_2O/AgO on electrode surfaces, many of these reports being in the Patent literature. Most of the earlier work has been reviewed [5,353–355]. Oxides Ag_4O_5 and Ag_4O_3 have been reported [350,356], but have not been confirmed [10,11]. Oxidation of silver(I) salts in basic aqueous solution with ozone, $S_2O_8^{2-}$, or electrochemically afford AgO [348–350,357–359]. In acid solution "argentic" oxosalts are formed but these are converted into AgO by boiling in water or base [350,357,358]. AgO is diamagnetic [350,360–362].

The structure of AgO was initially reported to be monoclinic, the same as CuO [364–366] and hence the presence of Ag^{2+} was inferred. Further complications were introduced when some authors confused the powder patterns of argentic oxysalts with AgO, and this is the probable origin of reports (e.g. refs. 358,365) of a second (cubic) structural form of AgO. The conflict between the diamagnetism and the apparent presence of d^9 Ag(II) was initially explained in terms of strong coupling between the odd electrons

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* The "AgO" formulation has often been used for black silver oxides without supporting analytical or other data being given (especially true of a considerable amount of the Patent reports), and the purity and even identity of these products is impossible to establish.

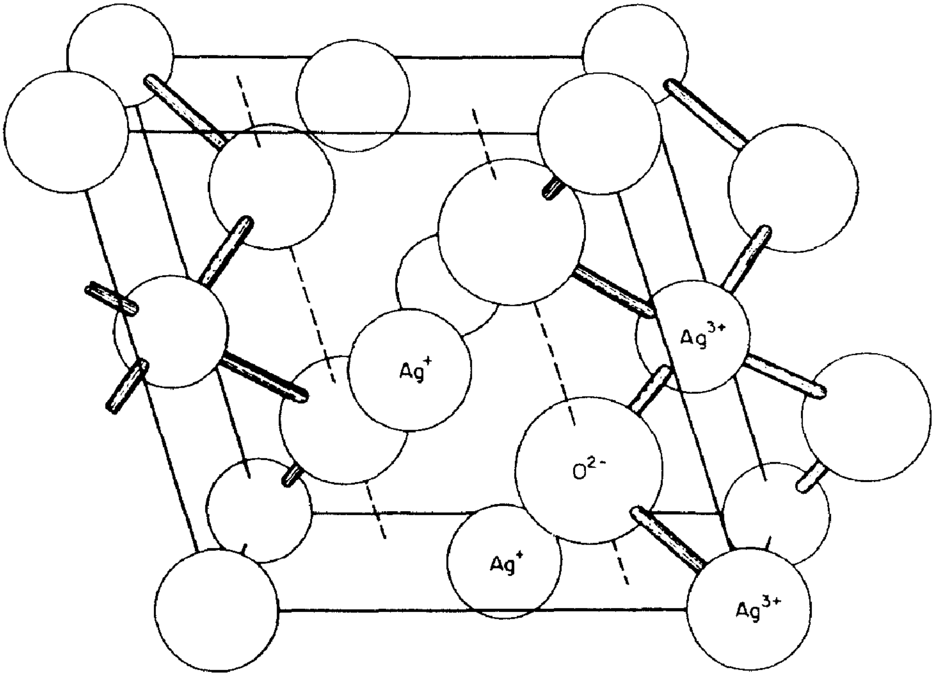


Fig. 29. Structure of AgO from ref. 366.

of neighbouring silver ions, but as pointed out by McMillan [366] the X-ray powder data could also be interpreted as consistent with equal numbers of Ag(I) and Ag(III) ions with Ag(I)–O ~ Ag(III)–O ~ 2.1 Å (the oxygen atom positions were poorly defined from X-ray powder data). Better powder data, and finally a neutron diffraction study which gave accurate oxygen positions [362] confirmed the $Ag^IAg^{III}O_2$ formulation with the structure (Fig. 29) with planar Ag^{III}–O_4 units (Ag–O = 2.01, 2.05 Å) and linear Ag^IO_2(Ag–O = 2.18 Å).

On heating AgO readily loses oxygen, and although it is not appreciably decomposed by hot water, it dissolves readily in acids to give Ag(II) species (p. 39). It also dissolves slightly in aqueous alkali, but the solutions are ESR-silent and probably Ag(I) and Ag(III) are present. Oxidations of organic materials by AgO has also received considerable attention [367].

Anodic oxidation of silver in acids or electrochemical or chemical oxidation of silver(I) salts in acid solution gives black 'argentic' oxosalts, which were often erroneously identified as a second form of AgO or as impure Ag_2O_3 (see above). Careful analytical work established the formulations as Ag_7O_8X [234,349,350,357,364,368], the most stable examples being with X = NO_3 or HF_2, although examples with X = F, ClO_4, BF_4 or HSO_4 have also been prepared [349,350,365,368–371]. X-ray powder data showed that all are cubic, and the detailed structure established for $Ag_7O_8NO_3$ by both

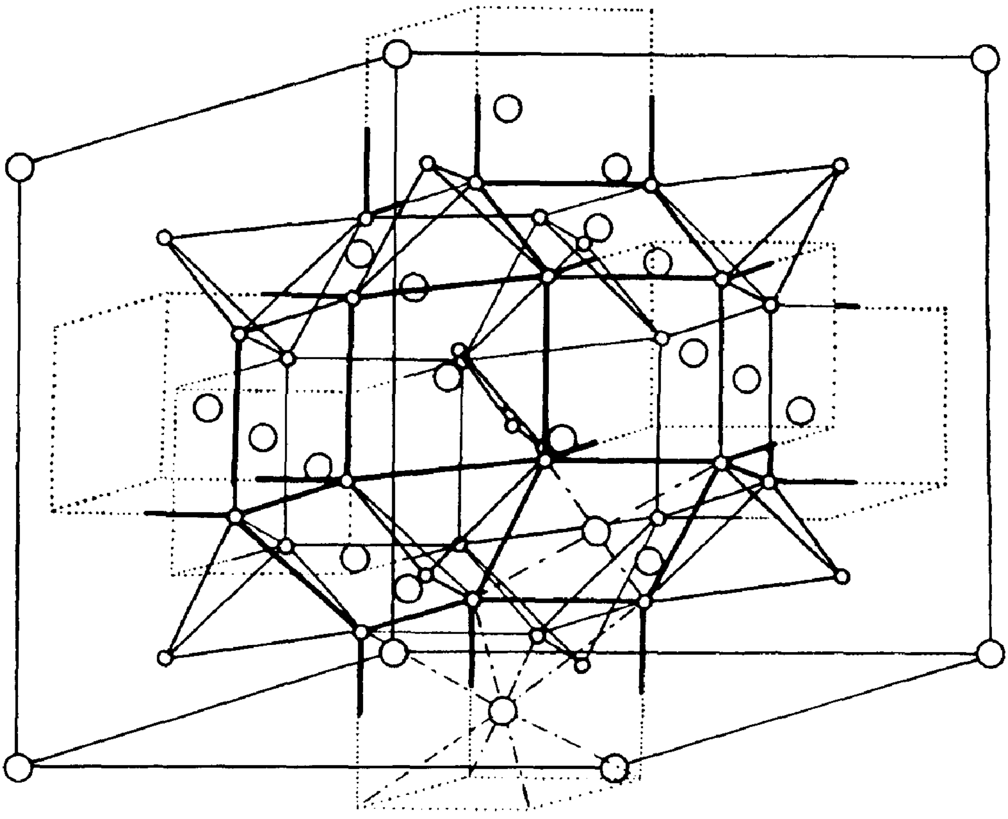


Fig. 30. Structure of $Ag_7O_8NO_3$ from ref. 373.

X-ray and neutron diffraction is probably present in all [17,371–375]. The structure (Fig. 30) is based upon a cubo-octadodecahedron, made up from six planar AgO_4 units (Ag–O = 2.05 Å), which are joined by face sharing, with smaller cubes between the units having the Ag(I) ions at the centres (Ag–O = 2.52 Å). The NO_3^- (or the other X group) lies within the large polyhedron and thus these materials could be described as clathrates. The compounds are diamagnetic (reports of weak paramagnetism appear to be due to impurities) and have metallic conductivity and reflectivity [371,373,375–377]. Assignment of oxidation states to the silver ions has been disputed, but the diamagnetism argues against any Ag(II) (as does the structure of AgO). The eight-coordinate silver ions are Ag(I) but if the AgO_4 units contain only Ag(III) the charge balance fails. Robin and Day [354] propose that the AgO_4 units combine to form Ag_6O_8 a mixed valence class III system with an average oxidation state of $2\frac{2}{3}$ for each silver atom. The Ag_7O_8X salts decompose on heating in a complex manner [378,379], evolve oxygen and form AgO and AgX in boiling water, and have similar oxidising properties to AgO.

(ii) Group VIB donor ligands

The simplest solution species containing silver(III) is $[Ag(OH)_4]^-$ which is the main constituent of the yellow solution produced by anodic oxidation of silver in 12 M aqueous KOH [380]. The anion has not been isolated in the solid state, but is well established in solution, most readily identified by its UV–visible spectrum which has a maximum at 271 nm. The alkaline solution decomposes to AgO and oxygen with a half life of ca. 100 min in 1.2 M NaOH, and ca. 30 min in 0.1 M NaOH [381]. The reaction of $[Ag(OH)_4]^-$ with periodate or tellurate leads to the corresponding Ag(III) complexes (below) [49,380]. It is likely that the transient Ag^{3+} species produced by pulse radiolysis of Ag^+ in neutral solution is $[Ag(OH)_4]^-$ [382]. Kirschenbaum and co-workers have carried out kinetic studies upon the substitution reactions of $[Ag(OH)_4]^-$ with a variety of substrates including periodate [49], tellurate [49], phosphate, borate, carbonate and arsenate [383], and its reduction by ethylenediamine [384], H_2O_2 [385], $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$ [386,387], MnO_4^{2-}, N_3^- [388], $S_2O_3^{2-}$ [389], AsO_2^- [390]. The reductions are 2-electron processes (inner-sphere) for N_3^-, $S_2O_3^-$, en and AsO_2^-, but involve Ag(II) intermediates in the cases of H_2O_2, the octacyano complexes, $[Fe(CN)_6]^{2-}$ and MnO_4^{2-} [386]. Unexpectedly pyrophosphate and $[Ag(OH)_4]^-$ produce a Ag(II) adduct in solution [383].

The other well-established oxygen donor complexes are the diperiodato- and ditellurato-argentates(III). The periodato complexes have been prepared by electrochemical oxidation of a silver anode in a KOH/KIO_4 solution, by $K_2S_2O_8$ oxidation of $Ag_2SO_4/KOH/KIO_4$ solutions, or by dissolution of AgO in alkaline KIO_3 solution [42,49,52,391–393]. Sodium salts have been prepared by exchange of the potassium analogues with aqueous NaOH [392,393]. The products have generally been formulated $M^I_7[Ag(IO_6)_2]nH_2O$ [M = some combination of K, Na, H^+]. The tellurato analogues $M^I_9[Ag(TeO_6)_2]nH_2O$ are made by generally similar routes starting with Ag_2SO_4 and TeO_2 or Na_2TeO_4 [42,49,392,393]. Both series are diamagnetic [43,47,392–394], and there are several reports of the electronic spectra [50–52,54,55,393] of which the most detailed are in refs. 50 and 55. As with the Cu(III) analogues (q.v.) the formulations above have recently been questioned [49,50,55], and on the basis of careful conductimetric, analytical and spectroscopic studies the formulations $M_5[Ag(IO_6H)_2]$ and $M_5[Ag(TeO_6H_2)_2]$ (water of hydration not specified) have been proposed. This is supported by an X-ray crystallographic study of $K_5[Ag(IO_6H)_2] \cdot 8H_2O$ [395] which revealed a structure (Fig. 31) with distorted square-planar coordination about the silver (Ag–O = 1.965(8)–1.993(7) Å) with the I–O(H) bonds axial w.r.t. the AgO_4 plane. Although these complexes are sometimes represented as five coordinate (the fifth ligand is water) in old reports, this is

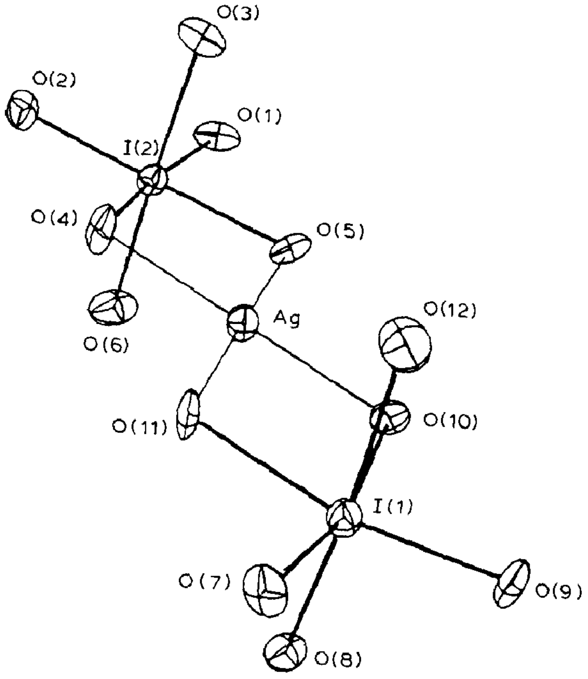
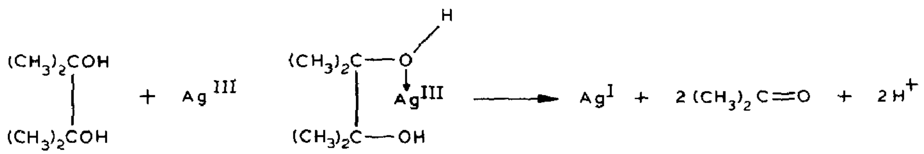


Fig. 31. Structure of $K_5[Ag(IO_6H)_2]\cdot 8H_2O$ from ref. 395.

in error. The complexes are strong oxidants, and representative examples of this aspect of their chemistry are the reactions with NO_2^- [396], $(COOH)_2$ [397], aldehydes [398], alcohols [59,399] and amines [400].

Silver(I) ions catalyse the oxidative cleavage of 2-methyl-2-hydroxy-3-butanone, pyruvic acid and various diols by $S_2O_8^{2-}$ [401,402]. The mechanism is thought to involve oxidation of the silver(I) to silver(III) by the peroxydisulphate followed by two competing pathways. The first is "complexation" of the substrate to the silver(III) ions via the alcohol oxygen and electron transfer.



$$\begin{matrix}(CH_3)_2COH\\ |\\ (CH_3)_2COH\end{matrix} + Ag^{III} \qquad \begin{matrix}(CH_3)_2C—O{-}H\\ |\quad\ \downarrow\\ |\quad\ Ag^{III}\\ (CH_3)_2C—OH\end{matrix} \longrightarrow Ag^{I} + 2\,(CH_3)_2C{=}O + 2H^+$$

The alternative involves reaction of silver(III) and silver(I) ions to give silver(II) ions which then react with the substrate via a radical pathway. Kinetic analysis suggests that the first pathway occurs at high [Ag^I] while the latter is favoured by low substrate concentrations. Also the ability of the substrate to interact with the silver ion is of significance. The more facile reaction of *cis*-diols over *trans*-diols suggests that a cyclic intermediate may be necessary.

The only known complexes of the heavier group VIB donor atoms are dithiocarbamate complexes reported by Bergendahl and Bergendahl [403]. In air a solution of $[Ag(n\text{-}Bu_2dtc)]$ and a half-molar equivalent of the corresponding thiuram disulphide resulted in a mixture of silver(III) and silver(II) dithiocarbamate complexes. With a one molar equivalent of the thiuram disulphide a dark red colouration appeared and faded gradually. The former complex was thought to be $[Ag^{III}(n\text{-}Bu_2dtc)_2]^+$ and the latter $[Ag^{III}(n\text{-}Bu_2dtc)_3]$. These have not been isolated. It is thought that the neutral complex undergoes an equilibrium

$$[Ag^{III}(n\text{-}Bu_2dtc)_3] \rightleftharpoons [Ag^{II}(n\text{-}Bu_2dtc)_2] + 0.5[n\text{-}Bu_2\text{-}NCS_2]_2$$

(iii) Group VB donor ligands

Macrocycles

Silver(III) complexes of tetraazamacrocyclic ligands L_2 and L_{13} were prepared by oxidation of the corresponding silver(II) complexes with $NOClO_4$ in acetonitrile [302]. An electrochemical preparation was successful for L_{13} but with L_2 decomposition of the product formed resulted in very low yields. The pale-yellow complexes were diamagnetic and did not show any low energy *d–d* bands in the electronic spectra. The silver(II) complexes are also oxidised by concentrated HNO_3 and the ^1H NMR was recorded in this medium. Addition of concentrated HCl to such solutions resulted in the formation of deep red-orange crystals thought to contain $[AgL_nCl_2]^+$ as a mixed nitrate perchlorate salt. Two electrochemical studies of various silver(II) macrocycles have been reported [307,404]. Clark and Harrowfield [307] attempted oxidations of silver(II) complexes of L_2, L_{13}, L_{17}, L_{20} and L_{21}. $[Ag(L_2)]^{2+}$ was oxidised and a large peak separation (>100 mV) observed. This was interpreted as consistent with a change in conformation on oxidation, such as inversion via deprotonation at a donor nitrogen. Of the two isomers of L_{13} one behaved as L_2 while the other showed peak separation of 59 mV, the value for a reversible process, indicating that in this case the silver(II) and silver(III) species have a common diastereoisomeric form. For silver(II) complexes of L_{17}, L_{20} and L_{21} oxidation did not result in the formation of silver(III) complexes with appreciable life times. Fabbrizzi and co-workers further investigated the electrochemistry of $[Ag^{II}(L_2)]^{2+}$ [404]; they found that the oxidation potential was pH dependent and varied linearly with temperature and also with $-\log[SO_4^{2-}]$. From this behaviour they concluded that two water molecules are coordinated in solution in the $[Ag^{III}(L_2)]^{3+}$ complex.

Porphyrins

Considerable interest has been shown in silver porphyrin complexes and a number of silver(III) systems have been studied. It was discovered [322] that octaethylporphinatosilver(II) undergoes oxidation at 0.44 V to form a corresponding silver(III) complex. Oxidation with $Fe^{III}(ClO_4)_3$ resulted in disappearance of the ESR spectrum. Diamagnetism was observed in the solid complex (Gouy method), analyses were satisfactory and the electronic spectrum reported with bands at 552 nm (25,200) and 526 nm (9800) which are typical for porphyrin complexes indicating that the metal and not the ligand has been oxidised. The XPS spectrum of octaethylporphinatosilver(III) has been compared with that of the silver(II) porphyrin [324]. A shift of 2.7 eV vs. Ag(II) octaethylporphyrin and of 3.1 eV vs. Ag(0) confirms the formulation of an Ag(III) oxidation state. This was also reflected in the change in the nitrogen shifts (~ 1.0 eV) which were consistent with the greater electron withdrawing power of Ag(III) over Ag(II). Morano and Po [405] have studied the oxidation kinetics of silver(II) octaethylporphyrin to the silver(III) complex by Fe^{3+} using stopped flow methods. It was found that if old solutions of the starting material were used then the rate of reaction was enhanced. This has been attributed to the catalytic effect of silver(II) ions arising from dissociation of the silver(II) porphyrin complex. It has also been shown that $[Ag^{II}(bipy)_2]^{2+}$ oxidises the silver(II) porphyrin complex very rapidly. A study of the electronic structures of $[Ag(III)(OEP)]^+$ and a comparison with the gold(III) analogue has been made [320] and the lack of luminescence of the silver(III) complex explained. The kinetics of the reaction between tetrakis(*p*-sulphonatophenyl)porphinatosilver(II), $[Ag^{II}$(TPPS)] and nitric acid were investigated [310]. The silver(II) complex exists as a dimer which can disproportionate to give Ag(III)(TPPS) and a silver(I) porphyrin. Ag(III)(TPPS) was slowly reduced by γ-irradiation to Ag(II)(TPPS) [406], but as the Ag^{II} complex is reduced so the rate of reduction of the Ag(III) complex is increased. Holzwarth et al. have studied the oxidation of Ag(II)(TPPS) with $[IrCl_6]^{2-}$ and $[Os(bipy)_3]^{3+}$ [407]. It was suggested that electron transfer occurs in the axial position of the complex, though a simple bridging mechanism was excluded. Monopositive cations enhanced the reaction rate. The redox chemistry of silver(II) tetrakis(*N*-methylpyridinium)porphyrin (TMpyP) has been studied [309]. The electrochemistry showed $Ag(II)(TMpyP)^{4+}$ to undergo a reversible one-electron oxidation (unlike many metalloporphyrins which yield ligand-oxidised materials) with $E = 0.84 \pm 0.02$ V vs. NHE. Coulometric experiments showed the oxidation to be a one-electron, metal-centred process. The electronic spectrum of the product was consistent with this, in that it did not show the typical spectrum of the radical cation seen where the ligand has been oxidised. Pulse radiolysis showed the rate of the reaction

$$\mathrm{Ag(II)(TMpyP)^{4+} + Br_2^{-\cdot} \rightarrow Ag^{III}(TMpyP)^{5+} + 2\ Br^-}$$

to be $(3.5 \pm 1.0) \times 10^8\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$. Chemical oxidation with persulphate or hypochlorite yielded the same product. Hambright et al. [312] have studied the reduction of $\mathrm{Ag^{III}(TPPS)}$ by $\mathrm{Fe^{II}(EDTA)^{2-}}$, $\mathrm{Fe(CN)_6^{4-}}$ and $\mathrm{Mo(CN)_8^{4-}}$ and have determined the $\mathrm{Ag^{II/III}}$ self-exchange constant to be $4 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$ from the Marcus relationship. Krishnamurthy and Sutter [311] have studied the monomer–dimer equilibrium of the silver(III) complex of tetrakis(*p*-(trimethylammonio)phenyl)porphyrin, $\mathrm{Ag^{III}(TAPP)^{5+}}$. The equilibrium varied with salt concentration and at > 0.15 M $\mathrm{NaNO_3}$ the equilibrium was shifted completely to the dimer. An equilibrium constant was calculated to be $K_\mathrm{D} = 1.2 \times 10^5\ \mathrm{M^{-1}}$. This is the first example of a silver(III) porphyrin aggregating in this manner.

Polypeptides

Trivalent silver(III) complexes of tri- and tetra-glycine ($\mathrm{G_3}$ and $\mathrm{G_4}$ respectively) have been prepared [408] by direct reaction of the ligand and $\mathrm{[Ag(OH)_4]^-}$ in aqueous alkali media in analogy with those copper(III) complexes prepared by Margerum [3]. These complexes were ESR silent and the electronic spectra showed bands at 245 and 315 nm which were not perturbed by addition of coordinating anions. The kinetics of formation were exceedingly complicated and are not fully understood, while decomposition resulted in silver(I) ions and oxidised peptides (with or without decarboxylation).

Biguanides

The silver(III) biguanide complexes were discovered by Ray and Chakravorty [409,410], who prepared $\mathrm{[Ag^{III}(enBigH)_2]X_3}$ (where $\mathrm{X} = \frac{1}{2}\mathrm{SO_4}$, $\mathrm{NO_3}$, $\mathrm{ClO_4}$ or OH). These diamagnetic complexes were stable at room temperature, the conductivities were commensurate with a 3 : 1 electrolyte and two equivalents of iodine per silver atom were liberated from a solution of acidified KI. Their preparations have been described [411] and their decomposition kinetics and aqueous hydrolyses have been investigated [412,413]. Banerjee and Basu have reported their ligand field spectra [414] and have attempted to interpret the *d–d* bands seen between 400 and 600 nm. Sen [415] prepared complexes of simple biguanide and of methyl biguanide and characterised them by elemental analyses and magnetic susceptibility measurements. The kinetics of formation of silver(III) ethylenebisbiguanide by peroxydisulphate oxidation of the silver(I) salt has been investigated [416] by following the appearance of the band at 370 nm in the product. It was concluded that oxidation occurred in one electron steps via the silver(II) complex. A polarographic study of silver(III) ethylenedibiguanide nitrate revealed three reduction waves [417] corresponding to the processes Ag(III)

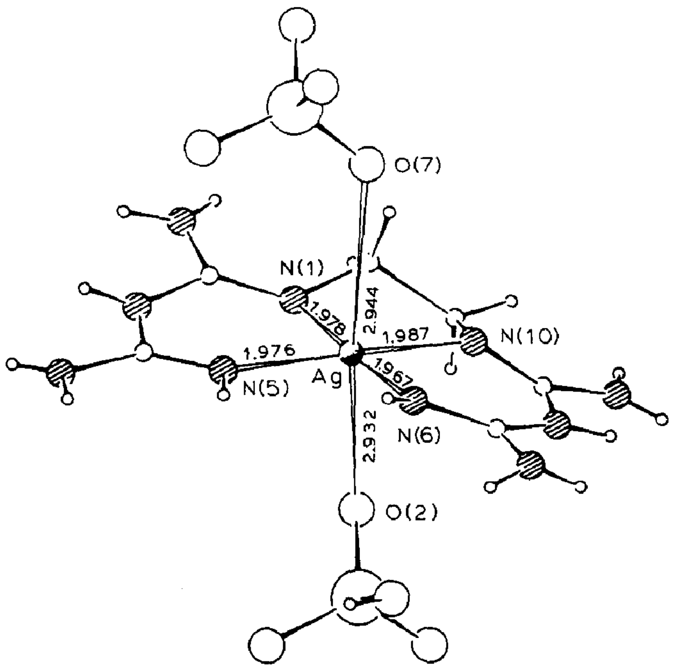


Fig. 32. Structure of $[\mathrm{Ag^{III}en(bigH)_2}]\mathrm{SO_4HSO_4}$ from ref. 422.

→ Ag(II), Ag(II) → Ag(I) and Ag(I) → Ag(0). Silver(III) piperazine-biguanide complexes have been prepared [418] ($[\mathrm{Ag^{III}pipz(bigH)_2}]\mathrm{X_3}$ where $\mathrm{X = NO_3^-}$, $\mathrm{OH^-}$, $\frac{1}{2}\mathrm{SO_4^{2-}}$). XPS measurements on these complexes have confirmed the metal oxidation state [419]. Three crystal structure determinations of silver(III) biguanide complexes have been made [420–422]. These have all shown essentially the same structure with variations in coordinating properties of the different counter ions. $[\mathrm{Ag^{III}en(bigH)_2}](\mathrm{NO_3})_3$ and $[\mathrm{Ag^{III}en(bigH)_2}]\mathrm{SO_4 \cdot HSO_4}$ both showed axial coordination of two counter ions while $[\mathrm{Ag^{III}en(bigH)_2}](\mathrm{ClO_4})_3$ only showed axial coordination of one perchlorate ion. The coordination sphere is a distorted square plane with Ag–N bond lengths of between 1.96 and 2.03 Å. The structure of $[\mathrm{Ag^{III}en(bigH)_2}]\mathrm{SO_4HSO_4}$ is shown in Fig. 32.

Banerjee and Ghosh [423] have prepared a silver(III) complex of 2-guanidinobenzimidazole by adding $\mathrm{Ag_2SO_4}$ and potassium peroxodisulphate solutions to the ligand in 2 N sulphuric acid. This diamagnetic complex oxidised two equivalents of iodide per equivalent of complex and water is lost on heating. It was suggested that this was a six-coordinate complex with two water molecules coordinated axially. Silver(III) complexes of *N*′-amidinoisourea (au), *O*-methylamidinoisourea (amn) and *O*-ethylamidinoisourea (eau) have all been reported [424]. These were characterised by elemental analyses, thermal analyses, infrared and electronic spectroscopy.

They acted as 2-electron oxidising agents towards ferrous sulphate or acidified KI solutions and were found to be diamagnetic. It is assumed that they are square planar in analogy with the closely related biguanide complexes. A silver(III) complex of biuret, $[Ag^{III}(biH_2)_2](NO_3)_3$ has been prepared by persulphate oxidation of a silver(I) complex followed by precipitation with sodium nitrate [425]. The complex was characterised by elemental analysis and infrared spectroscopy and assignment of an N-bonded ligand was made on this basis. The complex presumably has square-planar geometry.

Phosphines and arsines

The only silver(III) complexes of phosphines and arsines have been prepared by Warren and Bennett [159]. The complexes $[Ag(L-L)_2](ClO_4)_3$ (where L–L = diphos or diars) were obtained by treating $[Ag(L-L)_2]ClO_4$ in $HClO_4$ with concentrated HNO_3. The yellow solids showed electronic absorption at 322 nm (diphos complex) and 340 nm (diars complex) and were irreversibly reduced with potentials -0.03 and $+0.24$ V respectively versus $Ag/AgClO_4$ in CH_3CN. Bright yellow $[Ag(diphos)_2Cl]^{2+}$ and orange $[Ag(diphos)_2Cl_2]^+$ were prepared in acetonitrile solution, but were not isolated because of their instability.

F. SILVER(IV) OR (V) CHEMISTRY

Unstable fluoroanions which may contain Ag(IV) or Ag(V) have been described by the groups of Hoppe [2,193,426] and Hagenmuller [427,428], although the extreme instability has prevented complete characterisation. Fluorination of $2CsF + AgF_2$ or $Cs_2[AgF_4]$ under high pressure (> 300 atm) and high temperatures ($> 400\,°C$) produces orange $Cs_2[AgF_6]$, which is light and moisture sensitive, and loses fluorine at room temperature. X-ray powder diffraction shows it to have the K_2PtCl_6 structure, but the magnetic properties are disputed, one group reporting paramagnetism ($\mu_{eff} \sim 1.36$ BM) and hence Ag(IV) (d^7), the other finding essentially diamagnetic products and arguing for a $Cs_2Ag^{III}_{0.5}Ag^{V}_{0.5}F_6$ constitution. However, since $Ag^{III}F_6^{3-}$ in $Cs_2K[AgF_6]$ is paramagnetic, the latter requires the distortion of the Ag^{III} environment to produce diamagnetism. Attempts to prepare $Rb_2[AgF_6]$ have failed.

Fluorination of $AgF_2/CsF/GaF_3$ mixture yields $Cs_2Ag_{0.5}Ga_{0.5}F_6$ also an orange solid, diamagnetic and with the K_2PtCl_6 structure [428]. This appears to be a genuine Ag(V) complex, although attempts to prepare $Cs[AgF_6]$ have so far failed.

G. GOLD CHEMISTRY, SOME COMPARISONS

The detailed chemistry of gold falls outside the scope of this article, but some comparison with high valent copper and silver is of interest. There are two main oxidation states of gold, d^{10} Au(I) and d^8 Au(III), and there is a rapidly growing chemistry of gold cluster compounds [429]. Other oxidation states are rare, and have been reviewed by Dash and Schmidbauer [430].

The scarcity of Au(II) is rationalised at least in part by the ionisation potentials (Table 2) which show that formation of Au^{2+} is more endothermic than either Ag^{2+} or Cu^{2+}, while Au^{3+} is easier to produce than either Cu^{3+} or Ag^{3+}. The greater ligand field splitting in gold, raise the antibonding *d*-orbitals to higher energy making removal of electrons easier. Although numerous Au(II) complexes have been claimed [9,430], most have proved to be mixed valence Au^{I}–Au^{III} materials upon detailed investigation, e.g. $AuCl_2$ contains linear $Au^{I}Cl_2$ and planar $Au^{III}Cl_4$ units in a chair-like Au_4Cl_8 (Fig. 33) [431], and $CsAuCl_3$ is structurally $Cs_2[Au^{I}Cl_2][Au^{III}Cl_4]$ [432]. Among the few genuine mononuclear Au(II) complexes are the phthalocyanine [433] and the carborane $[Au\text{-}(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2]^{2-}$ [164], while there is ESR evidence for Au(II)-dithiocarbamates in solution, although like the Ag(II) analogues no solids have been isolated [403]. The maleonitriledithiolate $[Bu_4N]_2[Au(mnt)_2]$ has been isolated but detailed ESR studies suggest a gold(III)–radical ligand description is more realistic [434,435]. Binuclear Au(II) complexes with Au–Au bonds are formed by halogen oxidation of gold(I) ylids or gold(I)–bis(diphenylphosphino)methane complexes [436,437] (Fig. 34).

Gold(III) is always diamagnetic, and usually planar four coordinated, although five coordination (distorted square pyramidal) is found in $[Au(2,9\text{-}Me_2\text{-}1,10\text{-phenanthroline})X_3]$ [438] and tetragonal [412] coordination in $[Au(o\text{-}C_6H_4(AsMe_2)_2)_2I_2]I$ [439]. The only fluoroanion is $[AuF_4]^-$, al-

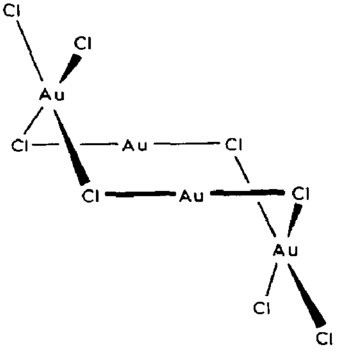


Fig. 33. Structure of Au_4Cl_8.

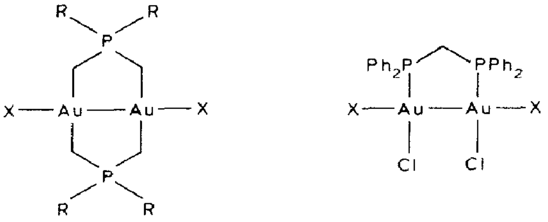


Fig. 34. Structures of two binuclear gold(II) complexes.

though the existence of $[AuF_6]^{3-}$ which would be paramagnetic has not been completely ruled out [193].

There appear to be no examples of Au(IV) d^7 established. The reaction of $[NO][AuF_6]$, NOF and F_2 produces a mixture of products including $[NO][AuF_4]$ and $[NO][AuF_6]$, and the presence of a third $\nu(NO)$ vibration was suggested to be due to $[NO]_2[Au^{IV}F_6]$. No Raman bands for the anion were observed, the authors suggesting that these were coincident with $[AuF_6]^-$ [440]. The evidence for Au(IV) is thus tenuous, but the recent characterisation of complexes of the isoelectronic Pt(III) [441] suggests a careful examination of electrochemical oxidation of Au(III) may be worthwhile.

Gold differs from its lighter analogues in that the 5+ oxidation state is clearly established in AuF_5 and $[AuF_6]^-$ [442–446]. The anion is known with a variety of cations including Cs, K, XeF_5^+, $Xe_2F_{11}^+$, KrF^+, O_2^+ and an X-ray of $[Xe_2F_{11}][AuF_6]$ confirms the octahedral structure of the anion [446]. Au(V) in these complexes has also been confirmed by ^{197}Au Mössbauer spectra [447].

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NOTE ADDED IN PROOF

This section extends coverage to include literature available to us up to September 1986.

B. COPPER(III) CHEMISTRY

Crystals of $KCs_2[CuF_6]$ have been obtained by annealing the powder [540°C/100 d], and from a single crystal X-ray study have been shown to have d(Cu–F) = 1.838 Å, 0.1 Å shorter than inferred from previous powder work [448]. Copper(III) has been suggested to be involved in the copper catalysed photodecomposition of H_2O_2 [449]. The X-ray structure of $[Bu_4N][Cu(tdt)_2]$ has been obtained, and further studies of its solution redox and spectroscopic properties have led to the proposal that it should be viewed as a Cu(II)-ligand radical complex [450].

Various deprotonated forms of the Cu(III) complex of tri-α-amino-isobutyryl amide have been observed; the tetradeprotonated form is significantly stabilised against photodecomposition [451].

D. SILVER(II) CHEMISTRY

The structure of Ag(II) *meso*-tetraphenylporphyrin has been reported [452]. The solution chemistry of various Ag(II) and Ag(III) porphyrins has been further studied [453–455].

E. SILVER(III) CHEMISTRY

Full details of the structure of Ag_2O_3 have appeared [456]. By anodic oxidation of silver fluoride or perchlorate solutions at lower potential, the Ag(II, III) oxide Ag_3O_4 was isolated [457]. X-ray studies show all the silver to be in planar oxygen environments. Ag^{II}–O = 2.03, Ag^{III}–O = 2.07 Å with the unit cell corresponding to $Ag^{II}{}_2Ag^{III}{}_4O_8$.

G. GOLD CHEMISTRY, SOME COMPARISONS

A review of the structural chemistry and Mössbauer spectra of gold compounds has been published very recently [458].

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