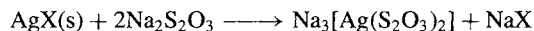


These steps are, in principle, reversible but in practice are not because the Ag is evidently liberated on a crystal dislocation, or defect, or at an impurity site such as may be provided by Ag_2S , all of which allow the electron to reduce its energy and so become "trapped". The function of the dye sensitizers is to extend the sensitivity of the emulsion across the whole visible spectrum, by absorbing light of characteristic frequency and providing a mechanism for transferring the energy to X^- in order to excite its electron. As more photons are incident on the grain, so more electrons migrate and discharge Ag atoms at the same point. A collection of just a few silver atoms on a grain (in especially sensitive cases a mere 4–6 atoms but, more usually, perhaps 10 times that number) constitutes a "speck", too small to be visible, but the concentration of grains possessing such specks varies across the film according to the varying intensity of the incident light thereby producing an invisible "latent image". The parallel formation of X atoms leads to the formation of X_2 which is absorbed by the gelatine.

(c) The "development" or intensification of the latent image is brought about by the action of a mild reducing agent whose function is to selectively reduce those grains which possess a speck of silver, while leaving unaffected all unexposed grains. To this end, such factors as temperature and concentration must be carefully controlled and the reduction stopped before any unexposed grains are affected. Hydroquinone, $1,6\text{-C}_6\text{H}_4(\text{OH})_2$ is a common "developer" and the reduction is a good example of a catalysed solid-state reaction. Its mechanism is imperfectly understood but the complete reduction to metal of a grain (say 10^{12} atoms of Ag), starting from a single speck (say 10 or 100 atoms of Ag), represents a remarkable intensification of the latent image of about 10^{11} or 10^{10} times, allowing vastly reduced exposure times; this is the real reason for the superiority of silver halides over all other photosensitive materials, though an intensive search for alternative systems still continues.

(d) After development, the image on the negative is "fixed" by dissolving away all

remaining silver salts to prevent their further reduction. This requires an appropriate complexing agent and sodium thiosulphate is the usual one since the reaction



goes essentially to completion and both products are water-soluble.

(e) A positive print is the reverse of the negative and is obtained by passing light through the negative and repeating the above steps using a printing paper instead of a transparent film.

28.3.5 Complexes^(15,16)

Oxidation states above +3 are attained only with difficulty and are confined mainly to AuF_5 , mentioned above, together with salts of the octahedral anion $[\text{AuF}_6]^-$, and to $\text{Cs}_2[\text{Cu}^{\text{IV}}\text{F}_6]$, prepared by fluorinating CsCuCl_3 at high temperature and pressure.

Oxidation state III (d^8)

Copper(III) is generally regarded as uncommon, being very easily reduced, but because of its possible involvement in biological electron transfer reactions (p. 1199) a number of Cu^{III} peptides have been prepared. The pale-green, paramagnetic (2 unpaired electrons), K_3CuF_6 , is obtained by the reaction of F_2 on $3\text{KCl} + \text{CuCl}$ and is readily reduced. This is the only high-spin Cu^{III} complex, the rest being low-spin, diamagnetic, and usually square planar, as is to be expected for a cation which, like Ni^{II} , has a d^8 configuration and is more highly charged. Examples are violet $[\text{CuBr}_2(\text{S}_2\text{CNBu}_2)]$, obtained by reacting $[\text{Cu}(\text{S}_2\text{CNBu}_2)]$ with Br_2

¹⁵ B. J. HATHAWAY, *Copper*, Chap. 53, pp. 533–774; R. J. LANCASHIRE, *Silver*, Chap. 54, pp. 775–859; R. J. PUDDEPHATT, *Gold*, Chap. 55, pp. 861–923 in *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon Press, Oxford, 1987.

¹⁶ For gold in oxidation states other than III, see H. SCHMIDBAUR and K. C. DASH, *Adv. Inorg. Chem.* **25**, 239–66 (1982).

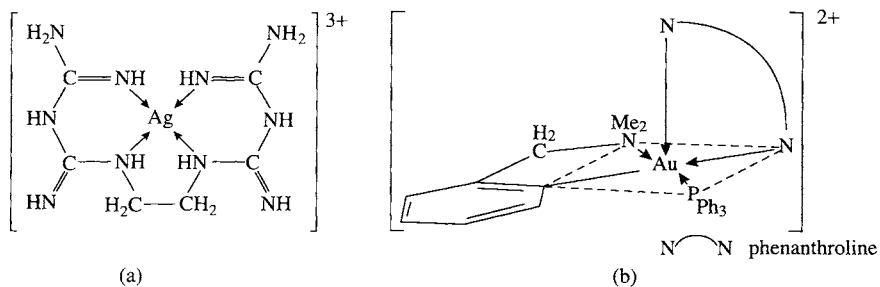
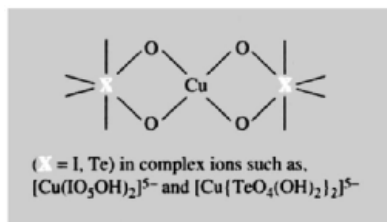


Figure 28.3 (a) Silver(III) ethylenedibiguanide complex ion; the counter anion can be HSO_4^- , ClO_4^- , NO_3^- or OH^- . (b) Gold(III) (dimethylamino)phenyl complex ion; the counter anion can be BF_4^- or ClO_4^- .

in CS_2 , and bluish MCuO_2 ($M = \text{alkali metal}$), obtained by heating CuO and MO_2 in oxygen. The oxidation of Cu^{II} by alkaline ClO^- in the presence of periodate or tellurate ions yields salts in which chelated ligands apparently produce square-planar coordinated copper:



Silver(III) is quite similar to copper(III) and analogous, though more stable, periodate and tellurate complexes can be produced by the oxidation of Ag^{I} with alkaline $\text{S}_2\text{O}_8^{2-}$. The diamagnetic, red ethylenedibiguanide complex (Fig. 28.3a) is also obtained by peroxodisulfate oxidation and is again quite stable to reduction. However, yellow, diamagnetic, square-planar fluoro-complexes such as $[\text{K}[\text{AgF}_4]]$, obtained by fluorinating $\text{AgNO}_3 + \text{KCl}$ at 300°C , are much less stable; they attack glass and fume in moist air.

For gold, by contrast, +3 is the element's best-known oxidation state and Au^{III} is often compared with the isoelectronic Pt^{II} (p. 1161). The usual route to gold(III) chemistry is by dissolving the metal in aqua regia, or the compound Au_2Cl_6 in conc HCl , after which evaporation yields yellow chloroauric acid, $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, from which numerous salts of the square-planar ion $[\text{AuCl}_4]^-$ can be obtained.

Other square-planar ions of the type $[\text{AuX}_4]^-$ can then be derived in which $X = \text{F}, \text{Br}, \text{I}, \text{CN}, \text{SCN}$ and NO_3 , the last of these being of interest as one of the few authenticated examples of the unidentate nitrate ion (cf. p. 1162). $[\text{Au}(\text{SCN})_4]^-$ contains S -bonded SCN^- but, as with Pt^{II} (p. 1162), this ligand also gives rise to linkage isomers, this time in the K^+ and $(\text{NEt}_4)^+$ salts of $[\text{Au}(\text{CN})_2(\text{SCN})_2]^-$ and $[\text{Au}(\text{CN})_2(\text{NCS})_2]^-$. Numerous cationic complexes have been prepared with amines, both unidentate (e.g. py, quinoline, as well as NH_3) and chelating (e.g. en, bipy, phen). $[\text{Au}(\text{C}_6\text{H}_4\text{-CH}_2\text{NMe}_2\text{-2})(\text{phen})(\text{PPh}_3)]^{2+}$ (Fig. 28.3b) is an example with the additional interest that its distorted square pyramidal structure⁽¹⁷⁾ provides a rare example of Au^{III} with a coordination number in excess of 4. Octahedral $[\text{Au}_2(\text{diars})_2]^+$ too has a "high" coordination number, though phosphine and arsine complexes are generally readily reduced to Au^{I} species. Reductions of Au^{III} to Au^{I} in aqueous solution by nucleophiles such as I^- , SCN^- and other S -donor ligands have been studied. Most take place by rapid ligand substitution followed by the rate determining electron transfer, though some reductions by I^- take place without substitution. With SCN^- the rates of substitution and electron transfer are finely balanced.⁽¹⁸⁾

¹⁷ J. VICENTE, M. T. CHICOTE, M. D. BERMUDEZ, P. G. JONES, C. FITTSCHEN and G. M. SHELDRIK, *J. Chem. Soc., Dalton Trans.*, 2361–6 (1986).

¹⁸ S. ELMROTH, L. H. SKIBSTED and L. I. ELDING, *Inorg. Chem.* **28**, 2703–10 (1989).

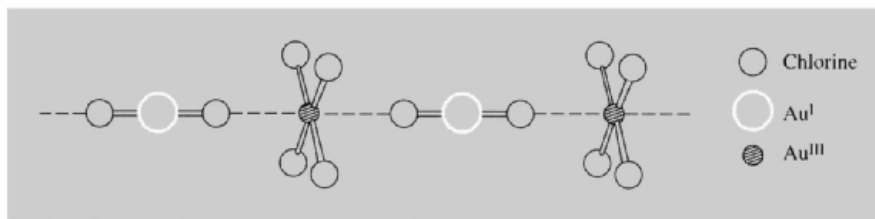
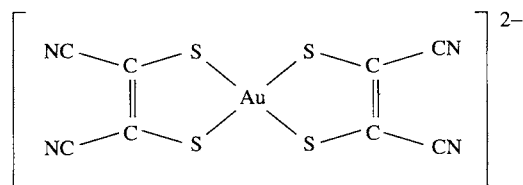


Figure 28.4 The anions of the chlorocomplex of stoichiometry, CsAuCl_3 , showing linearly coordinated Au^{I} and $(4 + 2)$ tetragonally distorted, octahedral Au^{III} , i.e. $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{Cl}_4]$.

In forming the fluoro complex $[\text{AuF}_4]^-$ mentioned above, and indeed in forming the simple fluoride AuF_3 , Au^{III} differs from the isoelectronic Pt^{II} since the corresponding $[\text{PtF}_4]^{2-}$ and PtF_2 are unknown.

Oxidation state II (d^9)

The importance of this oxidation state diminishes with increase in atomic number in the group, and most of the compounds ostensibly of Au^{II} are actually mixed valency $\text{Au}^{\text{I}}/\text{Au}^{\text{III}}$ compounds. Examples include the sulfate $\text{Au}^{\text{I}}\text{Au}^{\text{III}}(\text{SO}_4)_2$ and the chlorocomplex, $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{Cl}_4]$, the anions of the latter being arranged so as to give linearly coordinated Au^{I} and tetragonally distorted, octahedral Au^{III} (Fig. 28.4). The analogous mixed-metal complex, $\text{Cs}_2\text{AgAuCl}_6$, has the same structure with Ag^{I} instead of Au^{I} . One of the few authenticated examples of Au^{II} is the maleonitriledithiolato complex



which has a magnetic moment at room temperature of 1.85 BM. Even here, however, esr evidence indicates appreciable delocalization of the unpaired electron on to the ligands and, in solution, the complex is readily oxidized to Au^{III} .

Compounds of Ag^{II} are more familiar and are, in general, square planar and paramagnetic ($\mu_e \sim$

1.7–2.2 BM); this is as expected for an ion which is isoelectronic with Cu^{II} (see below), particularly in view of the greater crystal field splitting associated with 4d (as opposed to 3d) electrons. The $\text{Ag}^{\text{II}}(\text{aq})$ ion has a transitory existence when Ag^{I} salts are oxidized by ozone in a strongly acid solution, but it is an appreciably stronger oxidizing agent than MnO_4^- [$E^\circ(\text{Ag}^{2+}/\text{Ag}^+) = +1.980 \text{ V}$ in 4M HClO_4 ; $E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) = 1.507 \text{ V}$] and oxidizes water even when strongly acidic.[†] Of the acidic solutions the most stable is that in phosphoric acid, no doubt because of complex formation, and even NO_3^- and ClO_4^- ions appear to coordinate in solution since the colours of these solutions depend on their concentrations. A variety of complexes, particularly with heterocyclic amines, has been obtained by oxidation of Ag^{I} salts with $[\text{S}_2\text{O}_8]^{2-}$ in aqueous solution in the presence of the ligand. They include $[\text{Ag}(\text{py})_4]^{2+}$ and $[\text{Ag}(\text{bipy})_2]^{2+}$ and are comparatively stable providing the counter-anion is a non-reducing ion such as NO_3^- , ClO_4^- or $\text{S}_2\text{O}_8^{2-}$. Other complexes include some with N -, O -donor ligands such as pyridine carboxylates, and also the violet $\text{Ba}[\text{AgF}_4]$.

However, in this oxidation state it is copper which provides by far the most familiar and extensive chemistry. Simple salts are formed with most anions, except CN^- and I^- , which instead form covalent Cu^{I} compounds which are insoluble in water. The salts are predominantly water-soluble, the blue colour of their solutions

[†] Solutions of this type have potential use in the destruction of a variety of waste organic materials by electrochemical oxidation — see D. F. STEELE, *Chem. in Brit.* 27, 915–8 (1991).

arising from the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion, and they frequently crystallize as hydrates. The aqueous solutions are prone to slight hydrolysis and, unless stabilized by a small amount of acid, are liable to deposit basic salts. Basic carbonates occur in nature (p. 1174), basic sulfates and chlorides are produced by atmospheric corrosion of copper, and basic acetates (verdigris) find use as pigments.

The best-known simple salt is the sulfate pentahydrate ("blue vitriol"), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which is widely used in electroplating processes, as a fungicide (in Bordeaux mixture) to protect crops such as potatoes, and as an algicide in water purification. It is also the starting material in the production of most other copper compounds. It is significant, as will be seen presently, that in the crystalline salt 4 of the water molecules form a square plane around the Cu^{II} and 2, more remote, oxygen atoms from SO_4^{2-} ions complete an elongated octahedron. The fifth water is hydrogen-bonded between one of the coordinated waters and sulfate ions (p. 626). On being warmed, the pentahydrate loses water to give first the trihydrate, then the monohydrate; above about 200°C the virtually white anhydrous sulfate is obtained and this then forms CuO by loss of SO_3 above about 700°C . Amongst the few salts of Cu^{II} which crystallize with 6 molecules of water and contain the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion are the perchlorate, the nitrate (but the trihydrate is more easily produced) and Tutton salts.[†]

Attempts to prepare the anhydrous nitrate by dehydration always fail because of decomposition to a basic nitrate or to the oxide, and it was previously thought that $\text{Cu}(\text{NO}_3)_2$ could not exist. In fact it can be obtained by dissolving copper metal in a solution of N_2O_4 in ethyl acetate to produce $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$, and then driving off the N_2O_4 by heating this at $85\text{--}100^\circ\text{C}$. The observation by C. C. Addison

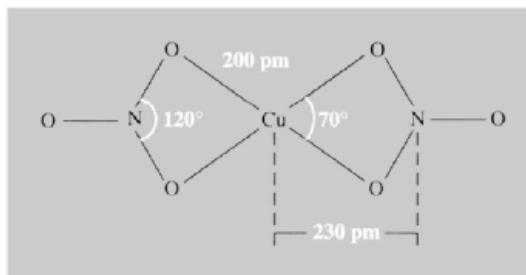


Figure 28.5 The $\text{Cu}(\text{NO}_3)_2$ molecule in the vapour phase (dimensions are approximate).

and B. J. Hathaway in 1958⁽¹⁹⁾ that the blue $\text{Cu}(\text{NO}_3)_2$ could be sublimed (at $150\text{--}200^\circ\text{C}$ under vacuum) and must therefore involve covalently bonded NO_3^- , was completely counter to current views on the bonding of nitrates and initiated a spate of work on the coordination chemistry of the ion (p. 469). Solid $\text{Cu}(\text{NO}_3)_2$ actually exists in two forms, both of which involve chains of copper atoms bridged by NO_3 groups, but its vapour is monomeric (Fig. 28.5).

The most common coordination numbers of copper(II) are 4, 5 and 6, but regular geometries are rare and the distinction between square-planar and tetragonally distorted octahedral coordination is generally not easily made. The reason for this is ascribed to the Jahn–Teller effect (p. 1021) arising from the unequal occupation of the e_g pair of orbitals (d_{z^2} and $d_{x^2-y^2}$) when a d^9 ion is subjected to an octahedral crystal field. Occasionally, as in solid KAlCuF_6 for instance, this results in a compression of the octahedron, i.e. “2 + 4” coordination (2 short and 4 long bonds).⁽²⁰⁾ The usual result, however, is an elongation of the octahedron, i.e. “4 + 2” coordination (4 short and 2 long bonds), as is expected if the metal’s d_{z^2} orbital is filled and its $d_{x^2-y^2}$ half-filled. In its most extreme form this is equivalent to the complete loss of the axial ligands leaving a square-planar complex.

[†] Tutton salts are the double sulfates $\text{M}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ which all contain $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and belong to the more general class of double sulfates of M^{I} and M^{II} cations which are known as schönites after the naturally occurring $\text{K}^{\text{I}}/\text{Mg}^{\text{II}}$ compound.

¹⁹ C. C. ADDISON and B. J. HATHAWAY, *J. Chem. Soc.* 1958, 3099–106.

²⁰ M. ATANASOV, M. A. HITCHMAN, R. HOPPE, K. S. MURRAY, B. MOUBARAKI, D. REINEN and H. STRATEMEIER, *Inorg. Chem.* **32**, 3397–401 (1993).

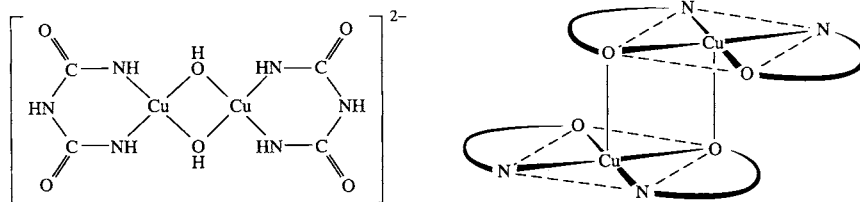


Figure 28.6 (a) Binuclear complex formed in biuret test (b) Schematic representation of square-pyramidal coordination of Cu^{II} in dimeric Schiff base complexes.

The effect of configurational mixing of higher-lying s orbitals into the ligand field d -orbital basis set is also likely to favour elongation rather than contraction.⁽²¹⁾

Elongation has the further consequence that the fifth and sixth stepwise stability constants (p. 908) are invariably much smaller than the first 4 for Cu^{II} complexes. This is clearly illustrated by the preparation of the amines. Tetraamines are easily isolated by adding ammonia to aqueous solutions of Cu^{II} until the initial precipitate of $\text{Cu}(\text{OH})_2$ redissolves, and then adding ethanol to the deep blue solution,[†] when $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot x\text{H}_2\text{O}$ slowly precipitates. Recrystallization of tetraamines from 0.880 ammonia yields violet-blue pentaamines, but the fifth NH_3 is easily lost; hexaamines can only be obtained from liquid ammonia and must be stored in an atmosphere of ammonia. Pyridine and other monoamines are similar in behaviour to ammonia. Likewise, chelating N -donor ligands such as en, bipy and phen show a reluctance to form tris complexes (though these can be obtained if a high concentration of ligand is used) and a number of 5-coordinate complexes such as $[\text{Cu}(\text{bipy})_2\text{I}]^+$ with a trigonal bipyramidal structure are known. The structure of $[\text{Cu}(\text{bipy})_3]^{2+}$ in its perchlorate has been described⁽²²⁾ as square pyramidal (4 short bonds, av. 202.6 pm, and 1 long, 222.3 pm) but, since the sixth N atom only 246.9 pm from

the Cu, distorted octahedral is perhaps a better description. The macrocyclic N -donor, phthalocyanine, forms a square-planar complex and substituted derivatives are used to produce a range of blue to green pigments which are thermally stable to over 500°C , and are widely used in inks, paints and plastics.

In alkaline solution biuret, $\text{HN}(\text{CONH}_2)_2$ reacts with copper(II) sulfate to give a characteristic violet colour due to the formation of the complexes $[\text{Cu}_2(\mu\text{-OH})_2(\text{NHCONHCONH})_4]^{2-}$ (Fig. 28.6a) and $[\text{Cu}(\text{NHCONHCONH})_2]^{2-}$. This is the basis of the “biuret test” in which an excess of NaOH solution is added to the unknown material together with a little CuSO_4 soln: a violet colour indicates the presence of a protein or other compound containing a peptide linkage.

Copper(II) also forms stable complexes with O -donor ligands. In addition to the hexaaquo ion, the square planar β -diketonates such as $[\text{Cu}(\text{acac})_2]$ (which can be precipitated from aqueous solution and recrystallized from non-aqueous solvents) are well known, and tartrate complexes are used in Fehling’s test (p. 1181).

Mixed O,N -donor ligands such as Schiff bases are of interest in that they provide examples not only of square-planar coordination but also, in the solid state, examples of square-pyramidal coordination by dimerization (Fig. 28.6(b)). A similar situation occurs in the bis-dimethylglyoximate complex, which dimerizes by sharing oxygen atoms, though the 4 coplanar donor atoms are all nitrogen atoms. Copper(II) carboxylates⁽¹⁵⁾ are easily obtained by crystallization from aqueous solution or, in the case of the higher carboxylates, by precipitation with the appropriate acid from ethanolic solutions

²¹ M. GERLOCH, *Inorg. Chem.* **20**, 638–40 (1981).

[†] This solution will dissolve cellulose which can be reprecipitated by acidification, a fact used in one of the processes for producing rayon.

²² Z.-M. LIU, Z.-H. JIANG, D.-H. LIAO, G.-L. WANG, X.-K. YAO and H.-G. WANG, *Polyhedron* **10**, 101–2 (1991).

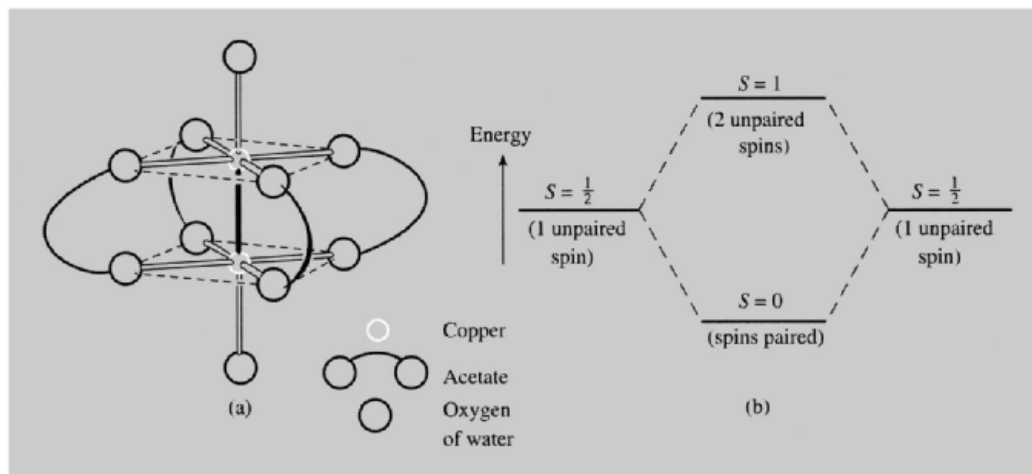


Figure 28.7 (a) Dinuclear structure of copper(II) acetate, and (b) spin singlet ($2S + 1 = 1$) and spin triplet ($2S + 1 = 3$) energy levels in dinuclear Cu^{II} carboxylates.

of the acetate. In the early 1950s it was found that the magnetic moment of green copper(II) acetate monohydrate is lower than the spin-only value (1.4 BM at room temperature as opposed to 1.73 BM) and that, contrary to the Curie law, its susceptibility reaches a maximum around 270 K but falls rapidly at lower temperatures. Furthermore, the compound has a dimeric structure in which 2 copper atoms are held together by 4 acetate bridges (Fig. 28.7a). Clearly the single unpaired electrons on the copper atoms interact, or “couple”, antiferromagnetically to produce a low-lying singlet (diamagnetic) and an excited but thermally accessible triplet (paramagnetic) level (Fig. 28.7b). The separation is therefore only a few kJ mol^{-1} (at room temperature, RT the thermal energy available to populate the higher level $\sim 2.5 \text{ kJ mol}^{-1}$) and as the temperature is reduced the population of the ground level increases and diamagnetism is eventually approached.

Similar behaviour is found in many other carboxylates of Cu^{II} as well as their adducts in which axial water is replaced by other O - or N -donor ligands. In spite of a continuous flow of work on these compounds there is still no general agreement as to the actual mechanism of the interaction nor on possible correlations of its magnitude with relevant

properties of the carboxylate and axial ligands.⁽²³⁾ The simplest interpretation is to assume that the singlet and triplet levels arise from a single interaction between the unpaired spins of the copper atoms and, with B. N. Figgis and R. L. Martin,⁽²⁴⁾ that this takes the form of “face-to-face” or δ overlap of the copper $d_{x^2-y^2}$ orbitals. However, σ overlap of d_{z^2} orbitals, or even a “superexchange” interaction transmitted via the π orbitals of the bridging carboxylates, are also feasible. It seems generally true that the magnetic interaction is greater for alkylcarboxylates than arylcarboxylates and for N -donor rather than O -donor axial ligands. More extensive correlations are unfortunately difficult to deduce from published results because of the existence of polymeric or other isomeric forms beside the dinuclear, and because of the possible presence of mononuclear impurities.

Mononuclear carboxylates such as $\text{Ca}[\text{Cu}(\text{O}_2\text{-CMe})_4]$ and $[\text{Cu}(\text{bet})_4](\text{NO}_3)_2$, (bet = $\text{N}^+\text{Me}_3\text{-CH}_2\text{COO}^-$) are also known.⁽²⁵⁾ In these

²³ M. KATO and Y. MUTO, *Coord. Chem. Revs.* **92**, 45–83 (1988).

²⁴ B. N. FIGGIS and R. L. MARTIN, *J. Chem. Soc.* 1956, 3837–46 (cf. quadruple bond in Cr(II) acetate (pp. 1032–4)).

²⁵ X.-M. CHEN and T. C. W. MAK, *Polyhedron* **10**, 273–6 (1991).

compounds each carboxylate ligand has one O close to the Cu (192–197 pm) and one much further away (277–307 pm) producing a distorted dodecahedral structure.

Other copper(II) complexes of stereochemical interests are the halogenocuprate(II) anions which can be crystallized from mixed solutions of the appropriate halides. The structures of the solids are markedly dependent on the counter cation. The compounds MCuCl_3 ($\text{M} = \text{Li}, \text{K}, \text{NH}_4$) contain red, planar $[\text{Cu}_2\text{Cl}_6]^{2-}$ ions, and CsCuCl_3 has a polymeric structure in which chains of CuCl_6 octahedra (4 + 2 coordination) share opposite faces.⁽²⁶⁾ With larger counter cations such as $[\text{PPh}_4]^+$, discrete $[\text{Cu}_2\text{Cl}_6]^{2-}$ ions are found which are distinctly non-planar, the coordination about each Cu being intermediate between square planar and tetrahedral.⁽²⁷⁾ The $[\text{CuCl}_5]^-$ salts present an even greater variety which includes 5-coordinate trigonal bipyramidal and square-pyramidal coordination, as well as $[\text{dienH}_3][\text{CuCl}_4]\text{Cl}$ which contains a square-planar anion and exhibits a curious mixture of ferro- and antiferro-magnetic properties. But it is the salts of $[\text{CuX}_4]^{2-}$ which have received most attention⁽²⁸⁾: e.g. depending on the cation, $[\text{CuCl}_4]^{2-}$ displays structures ranging from square planar to almost tetrahedral (p. 913). The former is usually green and the latter orange in colour. $(\text{NH}_4)_2[\text{CuCl}_4]$ is an oft-quoted example of planar geometry, but 2 long Cu–Cl distances of 279 pm (compared to 4 Cu–Cl distances of 230 pm) make 4 + 2 coordination a more reasonable description. In the $[\text{EtNH}_3]^+$ salt the longer Cu–Cl distances increase still further to 298 pm, but the clearest example of square-planar $[\text{CuCl}_4]^{2-}$ is the methadone salt in which the fifth and sixth Cl atoms are more than 600 pm from the Cu^{II} . At the other extreme, $\text{Cs}[\text{CuX}_4]$ ($\text{X} = \text{Cl}, \text{Br}$) and $[\text{NMe}_4]_2[\text{CuCl}_4]$ approach a

tetrahedral geometry and it appears that this geometry is retained in aqueous solution since the electronic spectra in the two phases are the same. For $[\text{CuCl}_4]^{2-}$ the Cu–Cl distance is close to 223 pm and the somewhat flattened (Jahn–Teller distorted) tetrahedron has four Cl–Cu–Cl angles in the range 100–103° and the other two enlarged to 124° and 130°. The angular distortions in $[\text{CuBr}_4]^{2-}$ are almost identical: 4 at 100–102° and the others at 126° and 130°.

Electronic spectra and magnetic properties of copper(II) ^(15,29)

Because the d^9 configuration can be thought of as an inversion of d^1 , relatively simple spectra might be expected, and it is indeed true that the great majority of Cu^{II} compounds are blue or green because of a single broad absorption band in the region 11 000–16 000 cm^{-1} . However, as already noted, the d^9 ion is characterized by large distortions from octahedral symmetry and the band is unsymmetrical, being the result of a number of transitions which are by no means easy to assign unambiguously. The free-ion 2D ground term is expected to split in a crystal field in the same way as the 5D term of the d^4 ion (p. 1032) and a similar interpretation of the spectra is likewise expected. Unfortunately this is now more difficult because of the greater overlapping of bands which occurs in the case of Cu^{II} .

The T ground term of the tetrahedrally coordinated ion implies an orbital contribution to the magnetic moment, and therefore a value in excess of $\mu_{\text{spin-only}}$ (1.73 BM). But the E ground term of the octahedrally coordinated ion is also expected to yield a moment $[\mu_e = \mu_{\text{spin-only}}(1 - 2\lambda/10Dq)]$ in excess of 1.73 BM, because of “mixing” of the excited T term into the ground term, and the high value of λ (-850 cm^{-1}) makes the effect significant. In practice, moments of magnetically dilute compounds are in the range 1.9–2.2 BM, with compounds whose geometry approaches octahedral having moments

²⁶ W. J. A. MAASKANT, *Struct. & Bond.* **83**, 55–87 (1995).

²⁷ L. P. BATTAGLIA, A. B. CORRADI, U. GEISER, R. D. WILLETT, A. MOTORI, F. SANDROLINI, L. ANTOLINI, T. MANFREDINI, L. MENABUE and G. C. PELLACANI, *J. Chem. Soc., Dalton Trans.*, 265–71 (1988) and refs. therein.

²⁸ see for instance, C. L. BOUTCHARD, M. A. HITCHMAN, B. W. SKELTON and A. H. WHITE, *Aust. J. Chem.* **48**, 771–81 (1995).

²⁹ A. B. P. LEVER, *Inorganic Electronic Spectroscopy* 2nd edn., pp. 554–72, Elsevier, Amsterdam (1984).

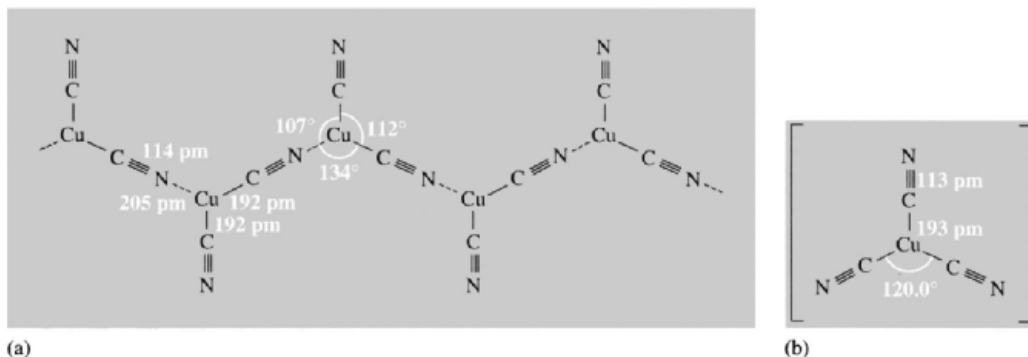


Figure 28.8 (a) Chain of Cu^{I} atoms linked by CN bridges to form the helical anion $[\text{Cu}(\text{CN})_2]_{\infty}^{-}$ in $\text{KCu}(\text{CN})_2$, and (b) one of the two types of $[\text{Cu}(\text{CN})_3]^{2-}$ ions in $\text{Na}_2[\text{Cu}(\text{CN})_3] \cdot 3\text{H}_2\text{O}$ — the other set have Cu–C 195 pm and C–N 116 pm.

at the lower end, and those with geometries approaching tetrahedral having moments at the higher end, but their measurements cannot be used diagnostically with safety unless supported by other evidence.

Oxidation state I (d^{10})

All M^{I} cations of this triad are diamagnetic and, unless coordinated to easily polarized ligands, colourless too. In aqueous solution the Cu^{I} ion is very unstable with respect to disproportionation ($2\text{Cu}^{\text{I}} \rightleftharpoons \text{Cu}^{\text{II}} + \text{Cu}(\text{s})$) largely because of the high heat of hydration of the divalent ion as already mentioned. At 25°C, K ($= [\text{Cu}^{\text{II}}][\text{Cu}^{\text{I}}]^{-2}$) is large, $(5.38 \pm 0.37) \times 10^5 \text{ l mol}^{-1}$, and standard reduction potentials have been calculated⁽³⁰⁾ to be:

$$E^{\circ}(\text{Cu}^{\text{+}}/\text{Cu}) = +0.5072 \text{ V}$$

$$\text{and } E^{\circ}(\text{Cu}^{2+}/\text{Cu}^{\text{+}}) = +0.1682 \text{ V}$$

Nevertheless, Cu^{I} can be stabilized either in compounds of very low solubility or by complexing with ligands having π -acceptor character. Its solutions in MeCN are stable and electrochemical oxidation of the metal in this solvent provides a convenient preparative route. The usual stereochemistry is tetrahedral as in

complexes such as $[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Cu}(\text{py})_4]^{\text{+}}$, and $[\text{Cu}(\text{L-L})_2]^{\text{+}}$ (e.g. L-L = bipy, phen), but lower coordination numbers are possible such as 2, in linear $[\text{CuCl}_2]^{-}$ formed when CuCl is dissolved in hydrochloric acid and 3, as in $\text{K}[\text{Cu}(\text{CN})_2]$, which in the solid contains trigonal, almost planar, $\text{Cu}(\text{CN})_3$ units linked in a polymeric chain (Fig. 28.8). The discrete planar anion $[\text{Cu}(\text{CN})_3]^{2-}$ is found in $\text{Na}_2[\text{Cu}(\text{CN})_3] \cdot 3\text{H}_2\text{O}$. In $2[\text{Cu}(\text{C}_{25}\text{H}_{28}\text{N}_2\text{S}_2)\text{Cl}]^{\text{+}}[\text{Cu}_2\text{Cl}_4]^{2-}$ the bulky cation, consisting of an N_2S_2 type macrocycle and a chloride ion coordinated to Cu^{II} , stabilizes the Cu^{I} anion in an unusual, non-planar form⁽³¹⁾ (Fig. 28.9a).

Polymers and oligomers form an expanding class of Cu^{I} complexes which, Cu^{I} being a d^{10} ion, are unlikely to involve M–M bonding. A wide range of structures, which frequently give rise to characteristic charge-transfer spectra,⁽³²⁾ is found. Stoichiometries of CuXL_n ($n = 0.5, 1, 1.5$ and 2) are common and many different structures have been identified including “cubane”, open “step” (or “chair”) and “ladder” (Fig. 28.9b, c, d) depending on the nature of L and the particular halide involved as well as the stoichiometry.⁽³³⁾

³¹ L. ESCRICHE, N. LUCENA, J. CASABO, F. TEIXIDOR, R. KIV-
EKÄS and R. SILLAPÄÄ, *Polyhedron* **14**, 649–54 (1995).

³² M. MELNIK, L. MACASKOVA and C. E. HOLLOWAY, *Coord. Chem. Revs.* **126**, 71–92 (1993).

³³ B. SKELTON, A. F. WATERS and A. H. WHITE, *Aust. J. Chem.* **44**, 1207–15 (1991).

³⁰ L. CRAVATTA, D. FERRI and R. PALOMBARI, *J. Inorg. Nucl. Chem.* **42**, 593–8 (1980).

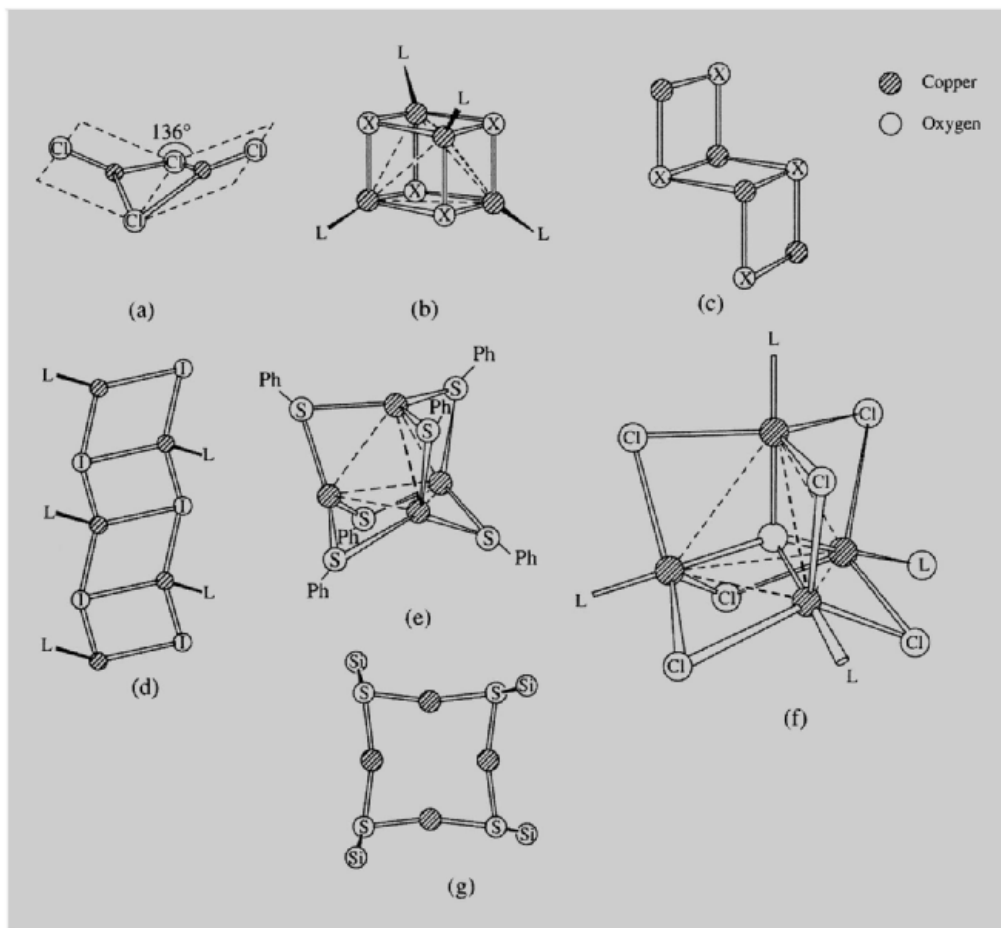


Figure 28.9 Some polymers and oligomers of Cu^{I} : (a) non-planar $[\text{Cu}_2\text{Cl}_4]^{2-}$. (b) "cubane" complexes $[\text{CuXL}]_4$; X = halide, L = phosphine or arsine. (c) "step" complexes $[\text{CuXL}]_4$; X = halide, L = phosphine or arsine. (d) extended "ladder" of $[\text{CuI}(\text{NC}_5\text{H}_4-2\text{-Me})]_x$. (e) $[\text{Cu}_4(\text{SPh})_6]^{2-}$. (f) $[\text{Cu}_4\text{OCl}_6\text{L}_4]$, L = OPPh_3 . (g) central portion of $[(\text{Bu}'\text{O})_3\text{SiSCu}]_4$.

Iodocuprates(I) provide a series of polymeric anions made up of planar $\{\text{CuI}_3\}$ or tetrahedral $\{\text{CuI}_4\}$ units, culminating in $(\text{pyH})_{24}[\text{Cu}_{36}\text{I}_{56}]\text{I}_4$. The large anion in this consists of 36 $\{\text{CuI}_4\}$ tetrahedra joined by 2 or 3 edges, and may be visualized as a section of a c.c.p. lattice of iodides with Cu^{I} atoms occupying some of the tetrahedral interstices.⁽³⁴⁾

S-donor ligands also contribute to this stereochemical diversity, Cu_4 tetrahedra being found in

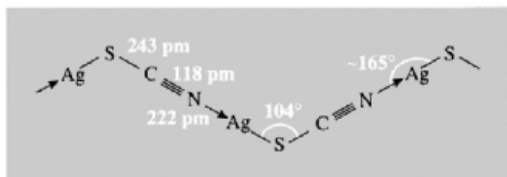
$[\text{Cu}_4(\text{SPh})_6]^{2-}$ and in $[\text{Cu}_4\text{OCl}_6(\text{OPPh}_3)_4]$, while $[(\text{Bu}'\text{O})_3\text{SiSCu}]_4$ provided⁽³⁵⁾ the first example of a square planar Cu_4S_4 ring (Fig. 28.9e, f, g).

The +1 state is by far the best-known oxidation state of silver and salts with most anions are formed. These reveal the reluctance of Ag^{I} to coordinate to oxygen for, with the exceptions of the nitrate, perchlorate and fluoride, most are insoluble in water. The last two of these salts are also among the very few Ag^{I} salts which form

³⁴ H. HARTL and J. FUCHS, *Angew. Chem. Int. Edn. Engl.* **25**, 569–70 (1986).

³⁵ B. BECKER, W. WOJNOWSKI, K. PETERS, E.-M. PETERS and H. G. VON SCHNERING, *Polyhedron* **9**, 1659–66 (1990).

hydrates and, paradoxically, their solubilities are actually noted for their astonishingly high values (respectively 5570 and 1800 g l⁻¹ at 25°C). The hydrated ion is present in aqueous solution and a coordination number of 4 has been established.⁽³⁶⁾ Unlike Cu^I, however, Ag^I forms 4-coordinate tetrahedral complexes less readily than 2-coordinate linear ones. A wide variety of the latter are formed with *N*-, *P*- and *S*-donor ligands, some of them of great practical importance. The familiar dissolution of AgCl in aqueous ammonia is due to the formation of [Ag(NH₃)₂]⁺; the formation of [Ag(S₂O₃)₂]³⁻ in photographic "fixing" has already been mentioned (p. 1187), and the cyanide extraction process depends upon the formation of [M(CN)₂]⁻ (M = Ag, Au) (contrast polymeric [Cu(CN)₂]⁻, Fig. 28.8). AgCN itself is a linear polymer, {Ag-C≡N→Ag-C≡N→} but AgSCN is non-linear mainly because the sp³ hybridization of the sulfur forces a zigzag structure; there is also slight non-linearity at the Ag^I atom.



Because of their inability to form linear complexes, chelating ligands tend instead to produce polymeric species, but compounds with coordination numbers higher than 2 can be produced, e.g. the almost tetrahedral diphosphine and diarsine complexes [Ag(L-L)₂]⁺ and the almost planar 5-coordinate [Ag(quinquepyridine)][PF₆].⁽³⁷⁾ Four-coordination is also found in tetrameric phosphine and arsine halides [AgXL]₄ which occur in "cubane" and "step" (or "chair") forms like their copper analogues (Fig. 28.9). Indeed, [AgI(PPh₃)₄] exists in both forms. As with Cu^I, sulfur and *S*-donor ligands yield many complexes

of high nuclearity. [Ag₄(SCH₂C₆H₄CH₂S)₃]²⁻ contains the same tetrahedral {M₄S₆} centre⁽³⁸⁾ found in [Cu₄(SPh)₆]²⁻ (Fig. 28.9e), while in the dark-red Na₂[Ag₆S₄] the metal atoms are disposed octahedrally.⁽³⁹⁾ The cyclohexanethiolato complex [Ag(SC₆H₁₁)₁₂] and (PPh₃)₄[AgSBU⁻]₁₄⁽⁴⁰⁾ consist respectively of 24- and 28-membered puckered rings of alternate Ag and S atoms.

Like Ag^I, Au^I also readily forms linear 2-coordinate complexes such as [AuX₂]⁻ (X = Cl, Br, I)⁽⁴¹⁾ and also the technologically important [Au(CN)₂]⁻. But it is much more susceptible to oxidation and to disproportionation into Au^{III} and Au⁰ which renders all its binary compounds, except AuCN, unstable to water. It is also more clearly a class b or "soft" metal with a preference for the heavier donor atoms P, As and S. Stable, linear complexes are obtained when tertiary phosphines reduce Au^{III} in ethanol,



The Cl ligand can be replaced by other halides and pseudo-halides by metathetical reactions. Trigonal planar coordination is found in phosphine complexes of the stoichiometry [AuL₂X] but 4-coordination, though possible, is less prevalent. Diarsine gives the almost tetrahedral complex [Au(diars)₂]⁺ but, for reasons which are not clear, the colourless complexes [AuL₄]⁺[BPh₄]⁻ with monodentate phosphines fail to achieve a regular tetrahedral geometry.

Complexes with dithiocarbamates involve linear S-Au-S coordination but are dimeric and the Au-Au distance of 276 pm compared with 288 pm in the metal and 250 pm in gaseous Au₂ is indicative of metal-metal bonding.[†]

³⁸ G. HENKEL, P. BETZ and B. KREBS, *Angew. Chem. Int. Edn. Engl.* **26**, 145-6 (1987).

³⁹ J. HUSTER, B. BONSMANN and W. BRONGER, *Z. anorg. allg. Chem.* **619**, 70-2 (1993).

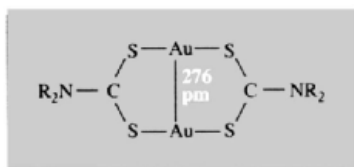
⁴⁰ I. DANCE, L. FITZPATRICK, M. SCUDDER and D. CRAIG, *J. Chem. Soc., Chem. Commun.*, 17-8 (1984).

⁴¹ P. BRAUNSTEIN, A. MÜLLER and H. BÖGGE, *Inorg. Chem.* **25**, 2104-6 (1986).

[†] The stability of the 6s orbital in gold already referred to (p. 1180), allows it to participate in M-M interactions. This

³⁶ J. TEXTER, J. S. HASTRELTER and J. L. HALL, *J. Phys. Chem.* **87**, 4690-3 (1983). See also *Acta Chem. Scand.* **A38**, 437-51 (1984).

³⁷ E. C. CONSTABLE, M. G. B. DREW, G. FORSYTH and M. D. WARD, *J. Chem. Soc., Chem. Commun.*, 1450-1 (1988).



In the thermal production of gold coatings on ceramics and glass, paints are used which comprise Au^{III} chloro-complexes and sulfur-containing resins dissolved in an organic solvent. It seems likely that polymeric species are responsible for rendering the gold soluble.

Gold cluster compounds⁽⁴²⁻⁴⁴⁾

Polymeric complexes of the types formed by copper and silver are not found for gold but instead a range of variously coloured cluster compounds, with gold in an average oxidation state <1 and involving M–M bonds, can be obtained by the general process of reducing a gold phosphine halide, usually with sodium borohydride. Yellow $[\text{Au}_6\{\text{P}(\text{C}_6\text{H}_4\text{-4-Me})_3\}_6]^{2+}$ consists of an octahedron of 6 gold atoms with a phosphine attached to each. Red $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$ can be regarded as a chair-like, centred hexagon of gold atoms with an eighth gold situated above the chair, each gold atom having a phosphine attached to it (Fig. 28.10a). Clusters are known in which further gold atoms are added to the chair in a more or less spherical manner (e.g. $[\text{Au}_{11}(\text{P}(\text{C}_6\text{H}_4\text{-4-F})_3)_7\text{I}_3]$ Fig. 28.10c in which the central gold has no attached ligand) and giving ultimately a centred icosahedron as found in the dark-red $[\text{Au}_{13}\text{Cl}_2(\text{PMe}_2\text{Ph})_{10}]^{3+}$ (Fig. 28.10d). Another series of clusters can be distinguished with flatter, ring or torus shapes as in the red-brown $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$ and

facilitates M–M bonding in compounds of Au^{I} , which would otherwise not be expected for d^{10} ions, and considerably enhances the strength of this bonding when the oxidation state of Au < 1 .

⁴² D. M. P. MINGOS pp. 189–97 in A. J. WELCH and S. K. CHAPMAN (eds.), *The Chemistry of the Copper and Zinc Triads*, R. S. C., Cambridge, 1993.

⁴³ B. K. TEO, H. ZHANG and X. SHI *ibid.* pp. 211–34.

⁴⁴ D. M. P. MINGOS and M. J. WATSON, *Adv. Inorg. Chem.* **39**, 327–99 (1992).

green $[\text{Au}_9\{\text{P}(\text{C}_6\text{H}_4\text{-4-Me})_3\}_8]^{3+}$ (Fig. 28.10b). This latter series is characterized by lower electron counts than the former, reflecting a lower involvement of p-orbitals in M–M bonding and therefore less tangential skeletal bonding (cf. p. 1170 for Pt). This accords with the observation that only clusters with an icosahedral structure (stabilized by both tangential *and* radial skeletal bonding) are stereochemically rigid on the nmr time scale at room temperature⁽⁴²⁾.

Heteronuclear clusters⁽⁴⁴⁾ incorporating a range of other transition metals can be produced by the general method of reacting AuPR_3 with a carbonyl anion of the appropriate metal. “Clusters of clusters” of Au–Ag have been synthesized with metal frameworks based on vertex sharing icosahedra, the basic unit being an Au-centred $\{\text{Au}_7\text{Ag}_6\}$ icosahedron⁽⁴³⁾. The largest of these is $[\text{Au}_{22}\text{Ag}_{24}(\text{PPh}_3)_{12}\text{Cl}_{10}]$ consisting of four $\{\text{Au}_7\text{Ag}_6\}$ icosahedra arranged tetrahedrally with six shared vertices. The spectacular, red-brown $[\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6]$ is prepared by reducing $\text{Au}(\text{PPh}_3)\text{Cl}$ with B_2H_6 and is probably best viewed as a cubo-octahedral fragment of close-packed Au atoms. From it, water soluble $[\text{Au}_{55}(\text{Ph}_2\text{PC}_6\text{H}_4\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O})_{12}\text{Cl}_6]$ can be obtained by ligand exchange.⁽⁴⁵⁾

28.3.6 Biochemistry of copper^(46,47)

Metallic copper and silver both have antibacterial properties[†] and Au^{I} thiol complexes have found increasing use in the treatment of rheumatoid arthritis, but only copper of this group has a biological role in sustaining life. It is widely distributed in the plant and animal worlds, and its redox chemistry is involved in a variety of

⁴⁵ G. SCHMID, N. KLEIN, L. KORSTE, U. KREIBIG and D. SCHÖNAUER, *Polyhedron* **7**, 605–8 (1988).

⁴⁶ K. D. KARLIN and Z. TYEKLAR (eds.), *Bioinorganic Chemistry of Copper*, Chapman & Hall, New York, 1993, 506 pp.

⁴⁷ pp. 187–214 of W. KAIM and B. SCHWEDERSKI, *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*, Wiley, Chichester, 1994.

[†] This was unknowingly utilized in ancient Persia where, by law, drinking water had to be stored in bright copper vessels.

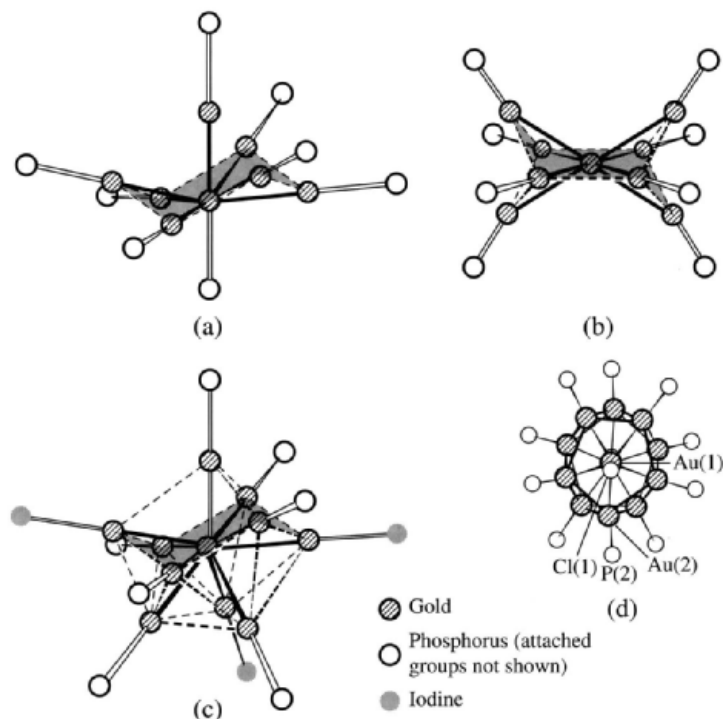


Figure 28.10 Some gold cluster compounds. Note that a chair-like centred hexagon of gold atoms persists throughout these structures and is shaded in (a), (b), and (c): (a) $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$, (b) $\text{Au}_9\{\text{P}(\text{C}_6\text{H}_4\text{-4-Me})_3\}_8]^{3+}$, (c) $\text{Au}_{11}\text{I}_3\{\text{P}(\text{C}_6\text{H}_4\text{-4-F})_3\}_7]$, and (d) $[\text{Au}_{13}\text{Cl}_2(\text{PMe}_2\text{Ph})_{10}]^{3+}$. In (d) the 12th icosahedral gold atom and the 13th (central) gold atom are obscured by Au(1).

oxidation processes. A human adult contains around 100 mg of copper, mostly attached to protein, an amount exceeded only by iron and zinc amongst transition metals, and requiring a daily intake of some 3–5 mg. Copper deficiency results in anaemia, and the congenital inability to excrete Cu, resulting in its accumulation, is Wilson's disease. The presence of copper, along with haem, in the electron transfer agent cytochrome c oxidase has already been mentioned (p. 1101).

Although complete structural details are rare, considerable progress has been made in understanding the mode of action of copper proteins, synthetic modelling being a major factor in this.⁽⁴⁸⁾ Biologically active copper centres can be divided into three main types:

Type 1: “blue” monomeric Cu with very distorted “3 + 1” coordination of 2N- and 2S-donors. This is apparently a compromise between the square planar 4N preferred by Cu^{II} and the tetrahedral 4S preferred by Cu^{I} , with a degree of flexibility facilitating a $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple. This type of centre is characterized by an intense blue colour because of a strong absorption at 600 nm arising from $S \rightarrow \text{Cu}^{\text{II}}$ charge transfer.

Type 2: “normal” monomeric Cu^{II} in an essentially square planar environment with additional, very weak, tetragonal interactions and exhibiting normal esr.

Type 3: a pair of Cu^{I} atoms about 360 pm apart and attached to protein through histidine residues; these effect O_2 transport by means of the reversible reaction $2\text{Cu}^{\text{I}} \xrightleftharpoons{\text{O}_2} \text{Cu}^{\text{II}}(\mu\text{-O}_2)\text{Cu}^{\text{II}}$. Whether the O_2 is bonded as a $\eta^1:\eta^1$ linear Cu–O–O–Cu bridge or $\eta^2:\eta^2$ (i.e. O–O

⁴⁸ N. KITAJIMA, *Adv. Inorg. Chem.* **39**, 1–77 (1992).

perpendicular to the Cu–Cu axis) is still uncertain. The copper are esr inactive: Cu^{I} because of its d^{10} configuration and Cu^{II} because strong antiferromagnetic interaction between the two atoms renders them diamagnetic.

A further class, *Type 4*, has been proposed. It is composed of three Cu^{II} atoms two of which are strongly coupled, being only ~ 340 pm apart. The third Cu atom completes an isosceles triangle, being 390–400 pm from each of the first two, and is “normal”.

In a large number of molluscs the oxygen-carrying pigment is not haemoglobin but a haemocyanin. These proteins, with molecular weights of the order of 10^6 , are composed of differing numbers of subunits each containing a pair of type 3 copper centres. A limited cooperativity (p 1100) is displayed but its mechanism is not yet clear. The “blue proteins”⁽⁴⁹⁾ laccase and ascorbic oxidase are found in a variety of plants where they are involved in the oxidation of phenols, amines and ascorbate by O_2 . They contain a type 1 copper, responsible for their colour and name, along with a type 4 trimer which together form a very distorted 4Cu tetrahedron. One-electron transfers by means of $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couples are involved but the mechanism by which O_2 is reduced is far from clear. Ceruloplasmin is also a blue protein which is found in all mammals: it participates in copper transport and storage as well as in oxidation processes. It is the deficiency of this protein which is responsible for Wilson’s disease.

Another oxidase, but non-blue, is galactose oxidase found in fungi where it catalyses the oxidation of $-\text{CH}_2\text{OH}$ in galactose to $-\text{CHO}$, simultaneously reducing O_2 to H_2O_2 . With a molecular weight of 68 000 and containing a single type 2 Cu, it was thought likely that a $\text{Cu}^{\text{III}}/\text{Cu}^{\text{I}}$ couple effected the 2-electron reduction of O_2 . However, spectroscopic evidence appears to refute this. The coordination of the Cu is square pyramidal with two histidine nitrogens, two tyrosine oxygens and an acetate oxygen. The currently favoured interpretation is that the more

tightly bound of the two tyrosines undergoes a 1-electron redox change which, together with a $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple, affords the required 2-electron transfer.

Cytochrome c oxidase contains two, or possibly three, copper atoms referred to as Cu_A and Cu_B since they do not fit into the usual classification. The former (possibly a dimer) is situated outside the mitochondrial membrane, whereas the latter is associated with an iron atom within the membrane. Both have electron transfer functions but details are as yet unclear.

28.3.7 Organometallic compounds⁽⁵⁰⁾

Neutral binary carbonyls are not formed by these metals at normal temperatures[†] but copper and gold each form an unstable carbonyl halide, $[\text{M}(\text{CO})\text{Cl}]$. These colourless compounds can be obtained by passing CO over MCl or, in the case of copper only (since the gold compound is very sensitive to moisture), by bubbling CO through a solution of CuCl in conc HCl or in aqueous NH_3 . The latter reactions can in fact be used for the quantitative estimation of the CO content of gases. A silver carbonyl $[\text{Ag}(\text{CO})][\text{B}(\text{OTeF}_5)_4]$ has also been prepared by mixing AgOTeF_5 and $\text{B}(\text{OTeF}_5)_3$ under $\text{CO}^{(51)}$ but the weakness of the Ag–C bond is indicated by the fact that the CO stretching frequency (2204 cm^{-1}) is the highest of any metal carbonyl. Complexes of the type $[\text{MLX}]$, which are often polymeric, can be obtained for Cu^{I} and Ag^{I} with many olefins (alkenes) and acetylenes (alkynes) either by anhydrous methods or in solution. They are generally rather labile, often decomposing when

⁵⁰ F. P. PRUCHNIK, *Organometallic Chemistry of the Transition Elements*, Plenum Press, New York, 1990, 757 pp.

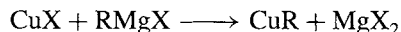
[†] Some have been synthesized by the condensation of Cu or Ag vapour and CO at temperatures of 6–15 K: e.g. $\text{M}(\text{CO})_3$, $\text{M}_2(\text{CO})_6$, $\text{M}(\text{CO})_2$ and $\text{M}(\text{CO})$. Thus $[\text{Ag}(\text{CO})_3]$ is green, planar and paramagnetic; above 25–30 K it apparently dimerizes, perhaps by formation of an Ag–Ag bond (see D. McINTOSH and G. A. OZIN, *J. Am. Chem. Soc.* **98**, 3167–75 (1976), and references therein).

⁵¹ P. K. HURLBURT, O. P. ANDERSON and S. H. STRAUSS, *J. Am. Chem. Soc.* **113**, 6277–8 (1991).

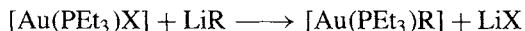
⁴⁹ A. G. SYKES, *Adv. Inorg. Chem.* **36**, 377–408 (1991).

isolated. The silver complexes have received most attention and the silver–olefin bonds are found to be thermodynamically weaker than, for instance, corresponding platinum–olefin bonds. Since the former bonds are also found to be somewhat unsymmetrical it seems likely that π bonding is weaker for the group 11 metals. Gold also forms olefin complexes, but not nearly so readily as silver and then only with high molecular weight olefins.

M–C σ bonds can be formed by each of the M^I metals. The simple alkyls and aryls of Ag^I are less stable than those of Cu^I, while those of Au^I have not been isolated. Copper alkyls and aryls⁽⁵²⁾ are prepared by the action of LiR or a Grignard reagent on a Cu^I halide:



CuMe is a yellow polymeric solid which explodes if allowed to dry in air, and CuPh, which is white and also polymeric, though more stable, is still sensitive to both air and water. Much greater stability is achieved by the σ -cyclopentadienyl complex [Cu(η^1 -C₅H₅)(PEt₃)] prepared by the reaction of C₅H₆, CuO and PEt₃ in petroleum ether; a similar Au^I compound, [Au(η^1 -C₅H₄Me)(PPh₃)], is also known. Au^I alkyls can be obtained like those of copper but only with an appropriate ligand present, e.g.:



The colourless solids are composed of linear monomers. A few anionic Au^I alkyls are known of which [N(PPh₃)₂]⁺[Au(acac)₂]⁻ might be mentioned.⁽⁵³⁾ In this it is the central C of the ligand, HC(COMe)₂ which is attached to the metal.

The alkyl derivatives of Au^{III} were discovered by W. J. Pope and C. S. Gibson in 1907; they include some of the most familiar and stable organo compounds of the group, and are notable for not requiring the stabilizing presence of π -bonding ligands. They are of three types:

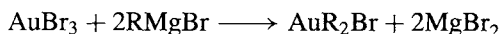
⁵² P. P. POWER, *Prog. Inorg. Chem.* **39**, 75–112 (1991).

⁵³ J. VICENTE, M.-T. CHICOTE, I. SAURA-LLAMAS and M.-C. LAGUNAS, *J. Chem. Soc., Chem. Commun.*, 915–6 (1992).

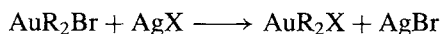
- AuR₃ (stable, when they occur at all, only in ether below –35°C);
- AuR₂X (much the most stable); X = anionic ligand especially Br;
- AuRX₂ (unstable, only dibromides characterized).

Corresponding aryl derivatives are rare and unstable. Thus, while AuMe₃ decomposes above –35°C but is stabilized in [AuMe₃(PPh₃)], AuPh₃ is unknown.

The dialkylgold(III) halides are generally prepared from the tribromide and a Grignard reagent:



Many other anions can then be introduced by metathetical reactions with the appropriate silver salt:



In all cases where the structure has been determined, the Au^{III} attains planar four-fold coordination and polymerizes as appropriate to achieve this. The halides for instance are dimeric but with the cyanide, which forms linear rather than bent bridges, tetramers are produced:

