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10. SILVER

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CONTENTS

INTRODUCTION

The chemistry of silver remains an active research area, with more emphasis on the production of new compounds and complexes than on redox behaviour. Moreover, there is a greater volume of work in peripheral areas such as the use of silver in organic catalysis, the incorporation of silver(I) ions as one of a range of univalent ions in a series of complexes, applied uses in photographic processes and in the development of devices such as photocells, and in studies of electrode and surface processes. The basic chemistry is reviewed in detail, with a more selective description of some aspects of the related fields. Perhaps the greatest change during the year has been the very rapid growth of interest in Surface Enhanced Raman Scattering (SERS) and this area is reviewed at the end of this article.

10.1 COMPLEXES OF SILVER

The extraction of silver(I) by crown ethers is possible, and this year a 1:1 complex of silver with dibenzo-18-crown-6-ether has been characterised [1]. More specific binding of silver, however, is required for many processes such as transport across a membrane, and this could be accomplished if complexes were synthesised which take account of the specific nature of silver bonding. For example, macrocycles with O_5N (1) [2] and N_3S_2 (2) [3] coordinating groups have been synthesised this year. In the latter case, the use of silver(I) as a template is valuable, since the equivalent copper(II) complex could not be made directly, but can be obtained by replacement of the silver(I). A copper(I)

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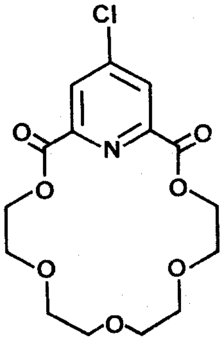

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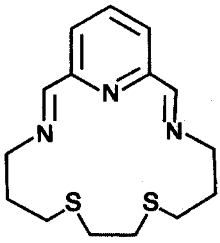
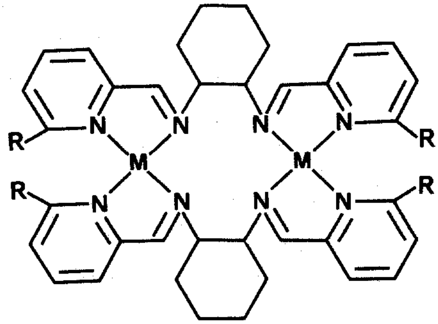


(2)

complex can be made subsequently by reduction of the copper(II) complex.

Other new complexes of silver(I) include complexes of the potentially tetradentate nitrogen ligands which act to form bridging complexes, as in (3) [4],



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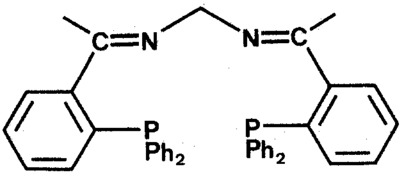

(4)

and a 1:1 silver Schiff base complex with phosphine complexing groups (4) [5]. Dimeric and tetrameric complexes of formamidines in which the ligand acts as a bridge between silver atoms [6] and complexes of alkynes [7] and cyclooctadiene [8] have been prepared. With cyclooctadiene, a silver complex, in which the silver can be regarded as cubically coordinated to the ends of the olefinic bonds in such a way that there are four shorter distances at tetrahedral angles, has been prepared [8]. The structure of bis(tetrasulphur tetraimide) silver(I) perchlorate involves nitrogen-metal coordination, and is analogous in structure to some organometallic compounds. The two S_4N_4 rings are tilted at an angle of 20° to each other and the silver ion is situated between them and displaced sideways from the centre to give a 'sandwich'-like structure [9].

Silver clusters are relatively easily formed either in matrices, as discussed later, or in isolable complexes. Dimeric complexes with derivatives of benzoic acid form the simplest example reported this year, namely, a dimer with a silver-silver bond [10]. The compounds L_3Ag_3 (L = Bis(δ-camphorquinone dioximato)M(II), M = Ni or Pd) are centred on a linear chain of three silver atoms in which silver-silver interactions are likely [11]. Bis(imidazole)silver(I) perchlorate crystals contain a silver cluster, with six linear bis(imidazole)silver(I) units arranged so that there is an equilateral triangle of three silver atoms, with the three other silver atoms lying radially along the two-fold axes of the triangle [12]. Complexes of penicillamine containing $\{Ag_8M_6\}$ (M = Ni or Pd) units have been synthesised [13], and complexes such as $(PPh_3)CoIrAg(RNCH_2N\text{-}4\text{-}C_6H_4Me)$ contain an iridium-silver bond [14].

10.2 MISCELLANEOUS

A number of unusual studies involving silver have been reported this year. Some hard biological materials are nucleated *in vivo* in small phospholipid vesicles, and the ability to vary the nature and size of the vesicle makes this an attractive method of controlling and studying crystal growth *in vitro*. The growth and characterisation of silver oxide in phosphatidylcholine vesicles has been described [15]. Milling is essential in many industrial processes and it is well known that, as well as a reduction in particle size, these mills can produce chemical reactions. For example, mechanical treatment of silver(I) oxalate with copper(II) causes the copper ions to dissolve in the silver(I) oxalate and form a dilute solution of copper(II) which can be detected by EPR [16]: more prolonged treatment of silver(I) oxalate produces a decomposition reaction analgous to that of thermal decomposition and which is accelerated by copper(II) [17]. In spite of the commercial significance of the milling process, few systems of this type have been fully investigated.

Various high-temperature techniques have been used this year. Cyclotetrathiatriazenium chloride reacts at a hot silver surface to produce S_2N_2, Ag_2S and AgCl as major products. This could be a useful route to S_2N_2 and, hence, to $(SN)_x$ polymers [18]. Silver(I) molybdate(VI) can be prepared using a nitrate melt as solvent [19]. A purified filament of silver has been used to generate gas-phase silver species such as $[Ag(NH_3)_x]$ (x = 3, 4 or 5): they were identified by mass spectrometry [20].

Matrix isolation techniques have been used to produce novel silver-containing compounds such as $[Ag(C_2H_4)]$ [21] and $[Ag(C_2H_4)_2]$ [22]. The latter is claimed to contain ligands which are conventionally π-bonded to silver. The absorption and emission spectra of silver atoms in argon, krypton and xenon matrices has been fully described [23] and the binary compounds AgMn, AgMo and AgCu have been tentatively identified [24]. These latter species have the same composition as immiscible or partially miscible alloy phases and, as such, they highlight a little-explored area, namely, the relationship between bonding in small molecules and clusters and that in metals and alloys. Theory would predict that discrete electronic wave functions rather than bands will be produced in small-sized metal particles and, consequently, small silver(II) particles should be paramagnetic. Changes in the EPR spectrum of silver(II) caused by the formation of such small particles in an argon matrix confirm this prediction and this experiment is one of the few direct experimental demonstrations of quantum-size effects [25].

Several studies have helped to characterise the bonding in silver compounds The complex $[(MePh_2P)_3Ag(H_3BCO_2C_2H_5)]$ contains a single M-H bond in the solid state but there is evidence of both single and double M-H bonds in solution [26]. $(R_3P)AgX$ compounds are usually polymeric, but $[\{(Me_3C)_3P\}Ag(ClO_4)]$ is a linear two-coordinate species [27] and the bulky phosphine, trimesytylphosphine, forms the first known 1:2 cationic adduct, $[Ag(PR_3)_2]^+$, of this type of silver compound [28]. Poly(pyrazolyl)borate ligands from complexes of the type $\{AgL\}_n$ [29] and the complex $[Ag_3PO(NCN)_3]$ has been characterised by ^{31}P NMR spectroscopy [30]. Coordinated sulphur in the form $[(en)_2Co(SH_2CO_2)]^{2+}$ will react with silver(I) to form a silver-sulphur bond and modify the bonding in the cobalt coordination sphere [31]. This compound is suggested as a model for inner-sphere electron-transfer processes.

The oxidation of glycine by silver(II) proceeds in two steps, complexation of carboxylate to silver and decarboxylation of the ligand [32]. The silver(I)-catalysed oxidation of glycine by peroxodisulphate in aqueous solution is assisted by copper(II), and it is suggested that the silver produces $[SO_4]^{\dot{-}}$, which reacts with glycine to give radicals which are trapped and oxidised by Cu^{2+} [33]. The reaction is very complex, however. For example, the silver(I)-catalysed decomposition of peroxodisulphate in aqueous solution produces dioxygen and, although the process can be suppressed with Ce^{3+}, the decomposition reaction is unaffected. Radical scavengers do reduce the rate of the decomposition reaction [34].

The rôle of silver in bonding to biologically important materials has been investigated. Silver ions inhibit enzyme activity even in some enzymes with no sulphydryl group and, in order to study the possible bonding types involved, some *N*-protected amino acid acomplexes of silver have been prepared in which the amino acids are reported to bond to the metal through the carboxylate group [35]. The crystal structure of bis(9-methylhypoxanthine)silver(I) perchlorate monohydrate shows that the silver is bonded between the ligands through a nitrogen group and a hydrogen-bonded water molecule joins an oxygen of both ligands. Analogous bonding in DNA may explain why silver can bond to DNA without causing loss of its structure [36]. The simultaneous bonding of silver(I) and platinum(II) to the model DNA base, 1-methylthymine, produces a complex in which the silver is bonded to four oxygens, two from each ligand, and the platinum bonds between the arms of the ligand [37].

Physical measurements on silver complexes have also produced some information useful in assessing the nature of silver compounds. ENDOR spectroscopy measurements on silver(II) tetraphenylporphyrin indicate that the unpaired electron lies in a molecular orbital with only about 38% Ag 4d character [38]. The use of nitric acid to dissolve silver(II) complexes of heterocycles is unwise, since the species created in such solutions are different from those in the solid state. Nitrogen hyperfine spectra were obtained in this study by dilution of the silver in the corresponding cadmium salt [39]. The He-I photoelectron spectra of silver halides in the gas phase include the first reports of the spectra of silver bromide and iodide [40]. The lowest energy band observed in silver chloride was assigned to predominantly chloride p orbitals and a higher energy band to silver 4d orbitals on which ligand field and spin-orbit coupling can be seen [41]. ^{109}Ag NMR spectra of silver ion complexes in non-aqueous solvents produced weak signals and were used only qualitatively [42]. Magnetic and spectroscopic evidence suggests that $CsAg(SO_3F)_3$ is a true silver(II) compound, with the silver(II) ion in a square planar or tetragonally distorted octahedral environment [43].

Among new inorganic compounds of silver reported this year were $Ag_{10}Si_4O_{13}$, which contains a linear ion which can produce the tetrameric $[Si_4O_{12}]^{8-}$ ion [44], a chromate $AgBi(CrO_4)_2$ [45], the compounds $AgAl(HPO_4)_2$ [46], $AgMn(PO_3)_3$ [47], and BaAgP [48], the complex $AgSbCl_5N(SO_2Cl)_2$ [49] and the fluorides Ag_3MF_6 (M = Al, Ga, Sc, In or Tl) [50]. The compound AgTlTe consists of $\{AgTe_4\}$ tetrahedra which are linked to form channels in which thalium ions are located [51], and $Cu_xAg_{1-x}I$ crystals are layer lattices with faulted long period polytypes [52].

The usual stoicheiometries AgL and AgL' appear, as expected, in a number of studies, *e.g.* where L = trithioallophanic acid [53], 4-hydroxybenzo-2,1,3-thiadiazole [54], 4-amino-5-mercapto-3-trifluoromethyl-1,2,4-triazole [55] or 3-ethyl-4-benzylideneamino-5-mercapto-1,2,4-triazole [56] and L' = *syn*-thiophene-2-aldoxime [57]. Complexes of both types can be formed by some hydrazides of anisic, benzoic and isonicotinic acid [58]. In most cases these compounds would be expected to be linear. Derivatives of $[NL_x][Ag(SCN)_2]_2$ (x = 3,4 or 6) form both ionic and polymeric bridged complexes [59].

Other points which may be of interest include the production of $[Ag(IO_3)_2]^-$ and $[Ag(IO_2)]^-$ in molten nitrates [60] and a study of the oxidation of silver(I) dialkyldithiocarbamates to silver(II) by tetraalkylthiuram. This latter reaction proceeds through an intermediate complex containing tetraalkylthiuram [61].

10.3 SURFACE ENHANCED RAMAN SPECTROSCOPY

One aspect of solid-state silver chemistry which has experienced a very rapid growth over the past two years is Surface Enhanced Raman Spectroscopy (SERS). Prior to 1978, there were only about ten papers on this subject, and since then over one hundred have been published. The interest stems from the observation that pyridine absorbed on an electrochemically treated silver surface has a very much enhanced Raman spectrum [62]. The nature of the silver surface is critical and the magnitude of the effect varies with the electrode potential (Figure 1). Nevertheless, an enhancement of the Raman signal of up to 10^6 has been claimed in some experiments [63], so that vibrational studies of molecules adsorbed on silver surfaces become much more feasible.

The reason for the enhancement is not known, but it is widely believed that the effect of electrochemical etching on the silver surface is to produce a local periodic potential which interacts with the pyridine molecule to induce a much greater degree of polarisability than would be present in pyridine itself [64]. This argument may well be a necessary part of any explanation of SERS but, from a chemist's viewpoint, it is not a sufficient explanation.

During the last year, SERS effects have been reported with aromatic and aliphatic amines and *N*-containing heterocycles [63], alkenes [65], nucleic acids [66], cytochrome *c* and myoglobin [67] ions such as $[\mathrm{edta}]^{4-}$ and $[NO_3]^-$ [68], $[CN]^-$ and $[NCO]^-$ [69,70], $[CH_3COO]^-$ [71] and diazines [72]. Thus, the effect appears to apply to a wide range of materials, but the magnitude of the enhance- differs considerably. Further, we [72a] confirmed the effect using pyridine relatively easily, but many other materials were not nearly so successful and,so far, the technique is particularly appropriate for nitrogen-containing ligands. The electronic spectrum of pyridine absorbed at a silver surface has three bands in the visible and near infrared spectral region [73] and different laser lines produce different relative intensities in the SERS spectrum [74], suggesting that there is some resonance or related effect. The interaction of potential complexing groups with a silver surface is not straightforward. For example HCO_2H, HCNO and HCO_2Me do not absorb on clean silver, but do adsorb strongly with oxygen present [75], and $[SCN]^-$ is chemically bonded to silver since its vibrational spectrum varies with the $Ag/[SCN]^-$ ratio [76]. Consequently, it would seem that any explanation of SERS must take into account the chemical nature of the bonding between the absorbed species and the surface and must also consider that a resonance effect arising from absorption bands in the visible region caused by this bonding may be present.

The SERS technique has been extended by coating silver electrodes with thin oxide films and studying the effect of adsorbates of them [77]. Some other metals [78,79] also produce surface enhancement but silver is the preferred

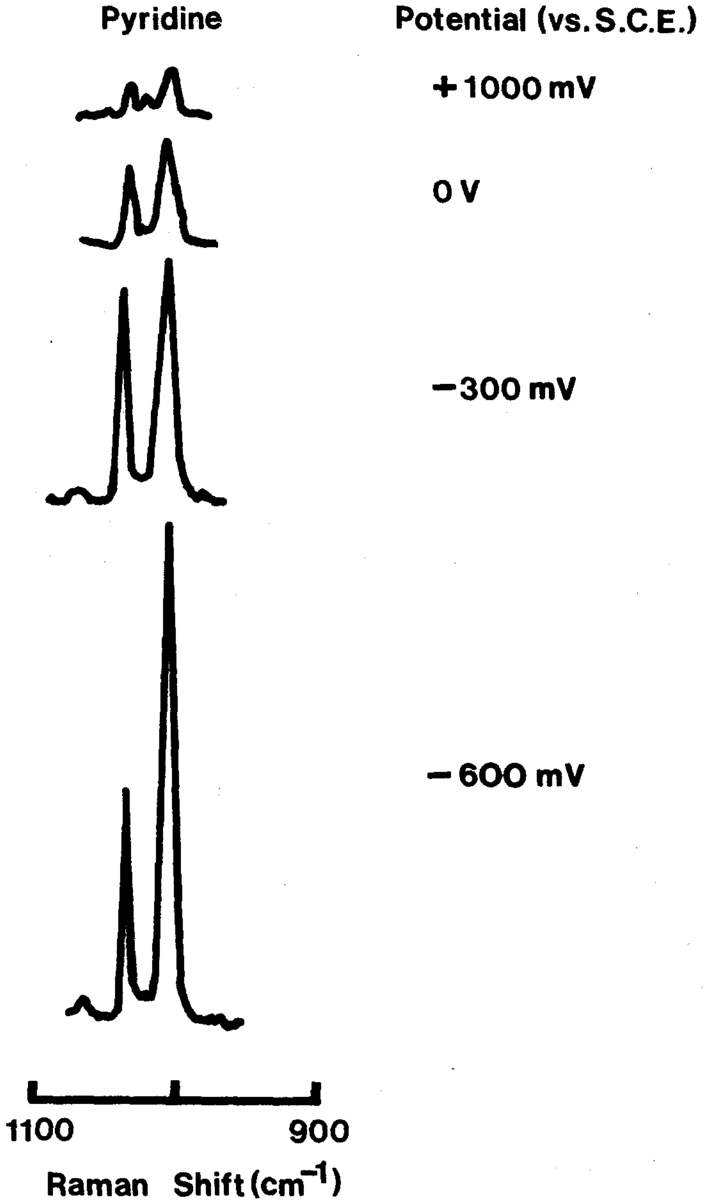

Fig. 1: SERS effect from the ring breathing modes of pyridine adsorbed at a silver electrode. The bulk solution contained 0.1 *M* pyridine in a 0.1 *M* KCl electrolyte. Potentials are stated relative to a standard calomel electrode; -600 mV is the potential of maximum enhancement. A 514.5 nm exciting line and 2.5 cm^{-1} slit width was used. The spectra are similar to those reported by Fleischmann *et al.* [62]. (Data courtesy of J. Nimmo, University of Strathclyde.)

choice. Reports of an enhanced Raman effect from adsorbates on silver colloid particles [80,81] suggest that the electrochemical method of producing the enhancement is not unique. The method itself is being improved and a surface-enhanced effect from cyanide, measured by picosecond Raman gain spectroscopy, is much more sensitive than conventional SERS [82]. It seems likely that this field will continue to be active during the next few years, and it is to be hoped that an improved understanding of the nature of the adsorption process will be achieved.

10.4 SOLID-STATE CHEMISTRY

Silver salts can be sensitised to light by the adsorption of dyes on the surfaces of the crystals. The orientation of the dyes is important and with 1,1'-diethyl-2,2'-cyanine, the degree of orientation depends on the face exposed and varies from 0 to 100% [83]. Mechanisms of sensitisation involving electron injection and energy transfer in the dye have been discussed [84] and an EPR signal induced by light is believed to be due to a positive hole created in the dye [85].

Some silver compounds are fast-ion conductors. β-Ag_2S is an electronic, as well as a fast-ion, conductor between 177 and 593 °C. This compound and α-AgI have similar anionic networks but, whereas the silver ions in AgI are ordered and conduct by a cooperative process, the silver ions are disordered in Ag_2S with significant Ag-Ag interactions [86]. The complex iodides KAg_4I_5 and $RbAg_4I_3$ are also fast-ion conductors and methods of preparation and spectral data have been reported this year [87,88]. $Tl_6Ag_2I_6$ contains both $[I_4]^{2-}$ and $[I_3]^-$ units [89].

Other matters of interest include a reversible electric-field-induced phase transition in Ag[TCNQ] films [90] which is accompanied by an abrupt increase in conductivity. The excited state of $[Ru(bipy)_3]^{2+}$ has been used to reduce solvated silver(I) [91], and the reactivity of amines to photo-electrochemical oxidation at a silver oxide electrode decreases from primary to tertiary amines [92]. $Cu_{1-y}AgI_2S_{1-x}Se_{2x}$ systems are direct band semiconductors which may be useful in solar-cell development [93].

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