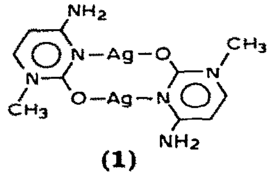
Coordination Chemistry Reviews, 35 (1981) 253—257
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

7. SILVER

W. EWEN SMITH

Silver compounds have a wide range of geometries, are often of low symmetry, and may also be polymeric. It is not surprising, therefore, that the chemistry of silver reported in the last year is preoccupied with an understanding of the complex species found in the solid state and in solution rather than with oxidation-state changes or with reactivity, although there are some examples of the latter and a prodigious literature of applied examples related to the photographic industry.

Most complexes investigated in detail last year were silver(I) complexes with nitrogen and oxygen donor groups. The structure of the complex Ag(en)(ClO_4), formed from solutions of silver(I) perchlorate and 1,2-diaminoethane (en), reveals a linear coordination of the silver with the ligand acting as a bridge to form a long-chain polymer [1]. In solution, the species $[Ag_2(en)_2]^{2+}$ predominates at higher concentrations [2]. Silver readily forms eight-membered ring sytems, and the structure of the nitrate complex of methylcytosine — a DNA base — is a unit consisting of two bidentate ligands and two silver atoms to give such a ring (1) [3]. The units are stacked so that cross-linking occurs between them, and the silver coordination rises to 4. This also extends the known degree of coordination of the base, and may account for the strong affinity of silver for DNA.



(1)

The theme of rather complex silver coordination is also exemplified by the reaction of (1,8-naphthalenedicarboxylato)disilver(I), $(C_{12}H_6O_4)Ag_2$, with a variety of phosphines, to give the novel complexes $[(C_{12}H_6O_4)_2(LAg)_4]$ (where L = PPh_3, $P(4\text{-}MeC_6H_4)_3$, $\frac{1}{2}$dppm or $\frac{1}{2}$dppe). The PPh_3 product has been shown to contain a core of four silver atoms bridged in a complex manner by the carboxylate ligands; the phosphine groups are coordinated to the silver on the outside of the core [4]. With the multidentate ligand (2), the results are somewhat more predictable, with the tridentate coordination of (2) and a fourth site occupied by a phosphine [5]. However, when the

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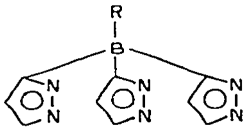
phosphine is bidentate, a bridged structure (3) is formed and (2) behaves as a bidentate ligand.



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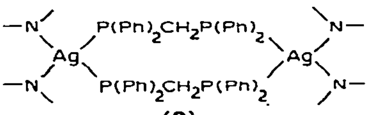


(3)

Quite a range of essentially preparative studies of silver complexes have been reported. Although complexes of silver with acetates and phosphines, arsines and stilbines are four-coordinate *pseudo*-tetrahedral [6], many complexes with larger ligands are polymeric 1 : 1 species, as is the case with 4-amino-5-mercapto-1,2,4-triazole [7], 4,4'-bipyridine [8] and 4-methylpyrazole [9]. The stability of silver thiourea complexes in solution is decreased on extensive substitution [10]. Solutions of 3 M sodium perchlorate containing imidazole (L) and silver produced $[AgL]^+$ and $[AgL_2]^+$ ions with excess imidazole, and the species Ag(OH)L formed at low imidazole concentrations [11].

Silver(I) is sufficiently soft to react with coordinated sulphur groups and will form a complex with, for example, $[(en)_2Co(SCH_2COOH)]$ without breaking the Co—S bond [12]. The adducts formed may be considered as potential intermediates in electron-transfer reactions.

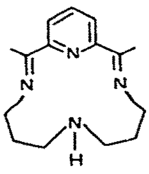
In the chemistry of silver with less complex ligands, a new silver compound $Ag^{II}(SO_3CF_3)_2$ has been characterised [13]. As well as being one of the few simple silver(II) compounds, it is also one of the few well-characterised transition-metal complexes of the $[SO_3CF_3]^-$ ion.

Mono- and disilicate metal complexes are common, trisilicate complexes are fewer and tetrasilicates are rare. One tetrasilicate characterised this year was $Ag_{10}Si_4O_{13}$ [14]. The compound $Co[Ag(SCN)_2]_2$ [15] and two forms of the compounds Ag_2WO_4, $Ag_2W_2O_7$ and $Ag_2W_4O_{13}$ have also been reported [16].

Returning to the theme of unusual coordination environments found in the chemistry of silver, in the complexes $(Ph_3P)_2Ag(BH_4)$ and $(Ph_3P)_3Ag(H_3BCO_2R)$ ($R = C_2H_5$ or H), the boron hydride is coordinated to the metal in a monodentate fashion. This is the least well characterised of the expected modes of borohydride coordination [17].

As is well known, silver can play an important part in many reaction processes, and is becoming more common as a reagent for organic synthesis. The silver ion is too large to fit into the hole in the macrocycle (4) and, consequently, when it was used in a template synthesis of this ligand, the 28-membered macrocycle (5) was formed [18]; it contained two four-coordinated silver ions. NO by itself is an ineffectual agent for *N*-nitrosation of amines, but an effective method of promoting the reaction is to react the amines as their silver complexes [19]. The reaction of silver(I) oxide with nitrogen oxide to produce silver nitrate proceeds through a silver nitrite intermediate; silver is produced in both stages [20]. The silver-catalysed oxidation of aspartic acid in aqueous solution is first order in $[S_2O_8]^{2-}$ and in Ag^+, and zero order in aspartic acid; the likely mechanism involves radical intermediates caused by hydrogen extraction from the amino acid [21].

Among the crystal structures which have appeared this year, perhaps the most unusual reveals a system of two 6-membered rings, (6), found in the complexes $M_2S_8\{Ag(PPh_3)\}_4$ (M = Mo or W) [22,23]. In (6), one phosphine is attached to each silver atom. The crystal structure of dimeric chlorobis(triphenylphosphine)silver(I) reveals, as expected, the presence of two bridging chloro groups [24]. The coordination numbers found for silver can vary considerably. Eight-coordination is found in $Ag_2Cl(NO_3)$ [25] and $Ag_2I(NO_3)$ [26], the former of which contains six almost planar oxygens with a chlorine above and below the plane; the latter has four oxygens and one iodine in a plane. Specific triangular coordination is found in tris(1-phenyl-3,5-dimethylpyrazole)silver(I) nitrate [27], and the silver is regarded as two- and three-coordinate in the structure of Ag_2BaGeS_4 [28]. In the compound $Rb_2AgAu_3I_8$, the silver environment is more ionic than that found for the gold [29].



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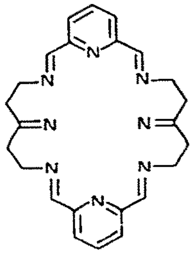

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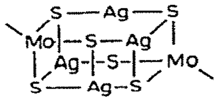

(6)

The environment of silver moieties in various media has been the subject of a number of detailed studies. X-ray solution studies of diammine and aqua silver(I) complexes in aqueous solution indicate that, in the former, two nitrogen—silver bonds of length 2.22 ± 0.02 Å exist and, in the latter, two silver—oxygen bonds of length 2.41 ± 0.02 Å are present [30]. The nature of the coordination of the two ammine groups to silver has also been probed by solid-state NMR studies of $[Ag(NH_3)_2][Ag(NO_2)_2]$ [31] and $AgSO_4 \cdot 4 NH_3$ [32]. Both indicate rapid reorientation of the ammine groups about the essentially linear species and, in the former case, a small deviation from linearity found originally by X-ray crystallography can again be detected.

The EPR spectra of an essentially square-planar site for Ag(II) in ethanenitrile after exposure to ^{60}Co γ-rays [33] and of $[AgBr_6]^{4-}$ units made by self-trapping of holes in crystals of $AgBr_{1-x}Cl_x$ [34] have been reported. Selective bimetallic photoaggregation of the rather disparate metals silver and chromium in an argon matrix can clearly be seen by the growth of new bands in the electronic spectrum of the matrix [35]. Studies of the structural role of silver ions in melts and glasses indicate that the glass Ag_2O/P_2O_5

is largely ionic at a mole ratio of 3 : 2, but contains polymers at other mole ratios [36]. Silver gives an endothermic heat of reaction in polymeric halide melts, due, probably, to it being too large to fit the polymeric structure [37].

Thus, the chemistry of silver this year is rather that of the effective characterisation of individual species and reactions, with little in the way of a more systematic understanding, or indeed of new concepts which might lead to such an understanding, being discernible.

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