DALTON
FULL PAPER

Self-assembly of copper(I) and silver(I) complexes with square-grid and channel structures

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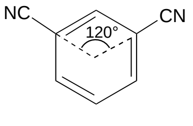
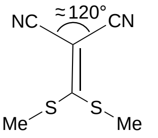
Copper(I) and silver(I) complexes of 2-[bis(methylsulfanyl)methylene]propanedinitrile (bmmp), $[Cu(bmmp)_2]ClO_4$ **1** and $[Ag(bmmp)_2]ClO_4$ **2**, have been prepared and their molecular structures determined by X-ray crystallography. The network topology of bmmp is found to depend on the metal-ion stereochemical preference. In **1** the copper(I) ion prefers a tetrahedral co-ordination geometry comprising four nitrogen atoms from four different bmmp molecules and each bmmp in turn bridges two copper(I) centres leading to a square-grid arrangement of alternating metal cations and organic ligands. In **2**, by contrast, the silver(I) ion involves an elongated octahedral environment with four N atoms forming a basal plane and two thioether S atoms occupying the axial positions; each bmmp acts as a non-chelating tridentate ligand bridging three metal centres, resulting in a three-dimensional channel structure. The influence of the metal-ion stereochemical preference on the co-ordination networks of bmmp is discussed.

The study of self-assembly of metal complexes continues to be of considerable current interest in the context of developing new solid-state polymeric materials with specific architectural and functional features.[1,2] In a recent account[3] we have demonstrated that in view of the rational design of such extended solids the strategy involves careful selection of the building blocks and control of the assembly and orientation of the individual molecules, in other words a combination of co-ordination bonds and non-covalent intermolecular interactions in a mutually compatible manner. Much study has been centered upon the use of multifunctional ligands. One of the simplest and most widely employed approaches is to use a bifunctional rod-like diatomic CN^- anion[4] and bidentate N,N′-donor linking groups such as diazapyrene,[5] pyrimidine,[6] dicyanodiphenylacetylene,[7] and pyridine-,[8] pyrazine-[9] and imidazole-based[10] ligands with a preference for binding metals at each end in a linear fashion, together with a metal center with preference for a polyhedral arrangement of ligands. The recent efforts in this field have even been extended to novel tri-[11] and tetra-dentate[12] ligands. Many research groups have already reached the goal of rational design of a number of multidimensional copper(I) and silver(I) polymeric co-ordination complexes with the individual frameworks varying significantly ranging from one-dimensional helical chains to two-dimensional hexagonal meshed layers, three-dimensional honeycomb structures containing hexagonal channels, interwoven diamondoid networks and infinite interpenetrating molecular ladders and bricks amongst other novel structures.[4–12]

Using 1,3-dicyanobenzene as a non-chelating, bent bridging ligand we have successfully obtained a copper(I) co-ordination polymer with a square cationic lattice in which acetone molecules and PF_6^- anions are incorporated in the cavity.[13] 2-[Bis(methylsulfanyl)methylene]propanedinitrile (bmmp) is analogous to 1,3-dicyanobenzene in terms of the conformation of the two cyano groups in the molecule. On the other hand, bmmp posses two additional methyl thioether co-ordination sites with high symmetry and unusual topology. Thus, it is particularly suitable as a non-chelating multidentate ligand since the rigidity of the molecular conformation prevents it from adopting a chelation configuration and forces the two bidentate groups apart. This paper presents our detailed studies on the co-ordination behaviour of bmmp with copper(I) and silver(I) ions, and it is shown that the stereochemical preference expressed by the metal ion is maintained, leading to the assembly of two different networks.



1,3-dicyanobenzene



bmmp

Experimental

All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. Organic solvents were of reagent grade, dried by published procedures, distilled under Ar and vacuum degassed before use. All chemicals were from Wako Pure Chemical Co., Japan, and used without further purification. The ^1H NMR spectra were recorded on a JEOL FX-200 FT spectrometer, and chemical shifts are given in ppm relative to tetramethylsilane as an internal reference. The infrared spectra of the compounds were measured as KBr discs on a JASCO 8000 FT spectrometer. **CAUTION**: perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared and handled with great care.

Syntheses

$[Cu(bmmp)_2]ClO_4$ 1. Copper(II) perchlorate hexahydrate (37.1 mg, 0.10 mmol) and copper plates (3 × 3 × 1 mm, five pieces) were stirred in acetone (5 cm^3) under an ethylene atmosphere for 1 h, and to the resulting colourless solution was added an acetone solution (5 cm^3) containing bmmp (34 mg, 0.20 mmol) under argon. The yellow mixture was stirred, and the filtrate transferred to a 10 mm diameter glass tube and layered with *n*-pentane (2 cm^3) as a diffusion solvent. After standing for 2 weeks at 5 °C light yellow, analytically pure [Cu(bmmp)$_2$]ClO$_4$ was obtained. Yield: 48% based on copper. IR (KBr, cm^{-1}): 2212 [ν(C–N)] and 1140 [ν(ClO$_4^-$)]. ^{1}H NMR [(CD$_3$)$_2$CO, 200 MHz]: δ 2.856 (H of SCH$_3$) (Found: C, 28.80; H, 2.46; N, 11.21. Calc. for $C_{12}H_{12}CuClN_4O_4S_4$: C, 28.63; H, 2.40; N, 11.13%).

[Ag(bmmp)$_2$]ClO$_4$ 2. The preparation was carried out in vessels from which light was excluded. Silver(I) perchlorate (20.7 mg, 0.10 mmol) was dissolved in benzene (5 cm^3) and a benzene solution (5 cm^3) containing bmmp (34 mg, 0.20 mmol) was added. The mixture was stirred for 30 min and the colourless filtrate transferred to a 10 mm diameter glass tube and layered with *n*-pentane (2 cm^3) as a diffusion solvent. After standing for 1 week at ambient temperature colourless cubic crystals of [Ag(bmmp)$_2$]ClO$_4$ were isolated. Yield: 40% based on silver. IR (KBr, cm^{-1}): 2212 [ν(C–N)] and 1138 [ν(ClO$_4^-$)]. ^{1}H NMR [(CD$_3$)$_2$CO, 200 MHz]: δ 2.857 (H of SCH$_3$) (Found: C, 26.41; H, 2.24; N, 10.21. Calc. for $C_{12}H_{12}AgClN_4O_4S_4$: C, 26.31; H, 2.21; N, 10.23%).

Crystallography

The X-ray diffraction analyses for complexes **1** and **2** were performed at room temperature on a Rigaku AFC-7R four-circle diffractometer equipped with a 12 kW rotating-anode molybdenum X-ray source [$\lambda(K_\alpha) = 0.71\,069$ Å]. A suitable single crystal was mounted on a glass fiber coated with paraffin to avoid decomposition in the air. Unit-cell parameters were obtained from a least-squares analysis of the setting angles of 25 high-angle reflections. Space groups were selected on the basis of systematic absences and intensity statistics. Intensity data were collected by using standard scan techniques (ω–2θ) to a maximum 2θ value of 55.0°. The weak reflections [$F < 10.0\sigma(F)$] were rescanned (maximum of three scans) and the counts accumulated to ensure good counting statistics. The intensities of three representative reflections were measured after every 150. Over the course of data collection the standards increased by 0.4% for **1** and declined by 1.3% for **2**. A linear correction factor was applied to account for this.

The diffracted intensities were corrected for Lorentz-polarization and background effects. An empirical absorption correction using the program DIFABS[14a] was applied, which resulted in transmission factors ranging from 0.86 to 1.00, (**1**) and 0.84 to 1.09, (**2**) respectively. The structures were solved by a combination of direct methods and Fourier-difference methods and refined by full-matrix least squares. The heavy atoms were located from an *E* map calculated by the program MITHRIL.[14b] The remaining non-hydrogen atoms were found by direct-methods phase-refinement techniques (DIRDIF).[15] The counter anion ClO$_4^-$ in **2** was found to have high terminal motions. The positions of all the hydrogen atoms were determined from difference electron-density maps and included, but not refined. The final refinements were performed on data having $I > 3\sigma(I)$ and included anisotropic thermal parameters for all non-hydrogen atoms. Reliability factors are defined as $R = \Sigma(|F_o - F_c)|/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[16] All crystallographic computations were performed on a VAX computer by using the program system TEXSAN.[17] Details of the X-ray experiments and crystal data are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

CCDC reference number 186/867.

See http://www.rsc.org/suppdata/dt/1998/1121/ for crystallographic files in .cif format.

Table 1 Crystal refinement data for complexes **1** and **2**

	1	**2**
Formula	$C_{12}H_{12}ClCuN_4O_4S_4$	$C_{12}H_{12}AgClN_4O_4S_4$
M	503.49	547.82
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pnna*
a/Å	7.704(1)	12.038(4)
b/Å	16.410(2)	22.323(5)
c/Å	7.6300(9)	7.665(4)
α/°	91.28(1)	
β/°	90.60(1)	
γ/°	96.25(1)	
U/Å^3	958.6(2)	2059(1)
Z	2	4
D_c/g cm^{-3}	1.744	1.766
Crystal size/mm	0.20 × 0.30 × 0.30	0.20 × 0.20 × 0.20
F(000)	508.0	1088.0
μ(Mo-Kα)/cm^{-1}	17.40	15.35
Scan speed/° min^{-1}	8.0	16.0
Scan width/°	1.73 + 0.30 tan θ	1.10 + 0.30 tan θ
No. reflections measured	4709	2725
No. observations [$I > 3.00\sigma(I)$]	3153	1191
No. parameters	235	109
R	0.050	0.070
R′	0.071	0.097
Goodness of fit	2.71	3.44
Largest difference peak and hole/e Å^{-3}	0.74, −0.62	1.02, −0.77

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

Complex **1**			
Cu–N(1)	1.989(5)	Cu–N(2)	2.003(4)
Cu–N(3)	1.977(5)	Cu–N(4)	2.000(5)
N(1)–Cu–N(2)	108.1(2)	N(1)–Cu–N(3)	108.8(2)
N(1)–Cu–N(4)	113.6(2)	N(2)–Cu–N(3)	112.2(2)
N(2)–Cu–N(4)	107.8(2)	N(3)–Cu–N(4)	106.5(2)
Complex **2**			
Ag–N(1)	2.39(1)	Ag(1)–N(2)	2.38(1)
Ag–S(2)	2.875(4)		
N(1)–Ag–N(1′)	91.6(7)	N(1)–Ag–N(2)	91.2(5)
N(1)–Ag–N(2′)	175.1(5)	N(2)–Ag–N(2′)	86.3(8)

Results and Discussion

Both complexes are easily prepared without elaborate synthetic procedures. In order to probe the influence of metal-ion stereochemical preference on the co-ordination network of bmmp, the study was carried out with the monovalent copper(I) and silver(I) salts having the same perchlorate counter anion. While silver(I) perchlorate is commercially available, copper(I) perchlorate was prepared by reduction of copper(II) perchlorate in acetone. Similar reactions to that described in the synthesis of **1** but performed in other solvents such as tetrahydrofuran and acetonitrile lead to a mixture of precipitate and tiny single crystals unsuitable for X-ray analysis. The infrared spectra of **1** and **2** exhibit bands that can be readily assigned to the ClO$_4^-$ anions and the strong non-split broad band at *ca.* 1140 cm^{-1} meets the criteria for non-co-ordination.[18] Both complexes exhibit strong ν(CN) absorptions at 2212 cm^{-1} and a ^{1}H NMR chemical shift of CH$_3$ at δ 2.86, as expected for the presence of bmmp.

Two-dimensional square-grid complex with Cu^I

Reaction of bmmp with the copper(I) perchlorate in acetone afforded light yellow crystals, [Cu(bmmp)$_2$]ClO$_4$ **1**, the elemental analyses of which were consistent with a 1 : 2 metal : ligand stoichiometry. The X-ray structural analysis of **1** confirmed the product to be a two-dimensional polymer. The copper atom is four-co-ordinated by the nitrogen atoms of four different bmmp molecules, with the Cu–N distances lying in the

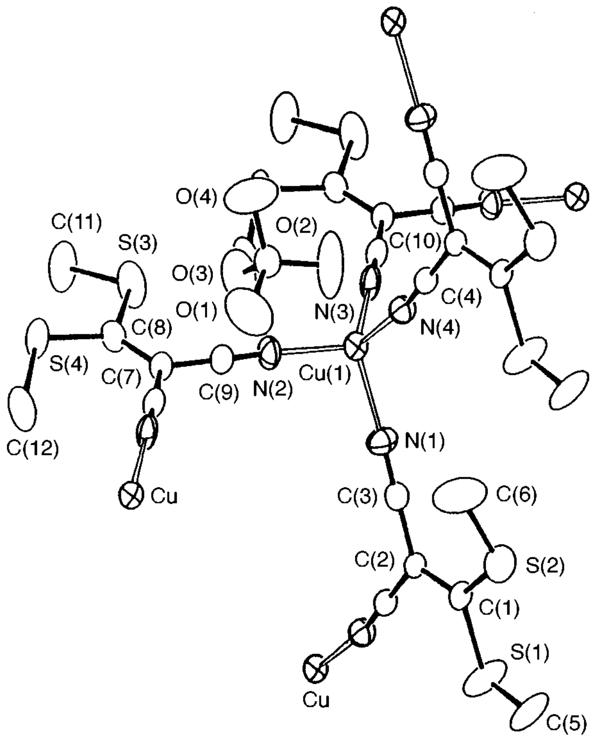


Fig. 1 Portion of the polymeric structure of [Cu(bmmp)$_2$]ClO$_4$ with the atom numbering scheme

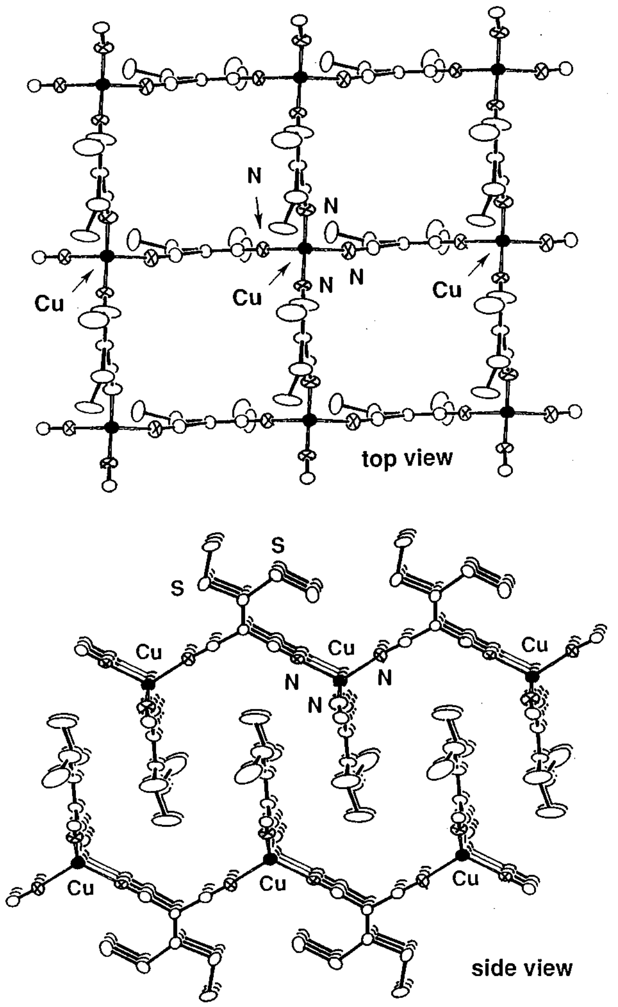


Fig. 2 Two views of the structure of [Cu(bmmp)$_2$]ClO$_4$ showing the square-grid network; ClO$_4^-$ anions omitted for clarity

range 1.977–2.003 Å, Fig. 1. The co-ordination geometry at the copper atom is probably best described as slightly distorted tetrahedral with the N–Cu–N angles varying from 106.5 to 113.6°. Each of the bmmp ligands in turn bridges two adjacent tetrahedral copper(I) centres with two nitrogen donors. This leads to two-dimensional cationic sheets consisting of alternating metal cations and organic ligands as shown in Fig. 2. The square grids formed are undulated with bridged copper cations 7.63 and 7.70 Å apart. The closest distance between copper centres in adjacent grids is 6.8 Å, there being no notable intercomplex interactions. The perchlorate ions are not co-ordinated, but located inside the grids through O · · · H(MeS group) interactions (2.52 and 2.64 Å).

Three-dimensional channel complex with Ag^I

Treatment of bmmp with AgClO$_4$ in benzene at ambient temperature yielded air-sensitive white crystals of [Ag(bmmp)$_2$]-ClO$_4$ **2**. The molecular structure together with the atomic numbering scheme is given in Fig. 3(a). It contains an infinite three-dimensional cation and a non-interacting ClO$_4^-$ anion. In the cation all bmmp units are equivalent and attached to two silver centres on the CN groups with bond distances Ag–N(1) and Ag–N(2) being 2.39 and 2.38 Å, respectively. Each silver atom is co-ordinated by four bmmp donors in a slightly disordered square-planar arrangement with N(1)–Ag–N(1′) 91.6(7), N(1)–Ag–N(2) 91.2(5), N(2)–Ag–N(2′) 86.3 and N(1)–Ag–N(2′) 175.1(5)°. It should be pointed out that the silver atom lies on a two-fold axis and such square-planar co-ordination is not imposed by symmetry. Furthermore, the axial co-ordination sites of the silver ion are occupied by two S atoms from two symmetry-related methyl thioether groups of the fifth and the sixth bmmp molecules with Ag–S(2) 2.875(4) Å, to complete an approximate octahedral AgN$_4$S$_2$ core. Focusing on the basal plane, the one-dimensional chain consisting of bmmp-bridged (through two CN moieties) Ag atoms, which runs parallel to the *c* axis, can be regarded as a chain of *trans*-sharing octahedra. The adjacent two chains are connected by the third co-ordination site of bmmp, S(2), and the resulting layers stack along the *b* axis in ABAB sequence, similar to the packing of octahedra observed in the layers of CsI$_2$,[19] Fig. 3(b). This gives an infinite three-dimensional cationic network containing channels which incorporate the ClO$_4^-$ counter anions. Although the S(2) atom cannot be viewed as directly bonded to the metal ion, the Ag–S distance is short enough to suggest at least a weak co-ordinative interaction. A quick search on the Cambridge Data Base showed that there are few examples of compounds with long Ag–S bonds.[20] In ref. 20 the average Ag–S distance given was 2.817 Å. The silver ions are co-ordinated in a distorted octahedral arrangement by long-range, secondary Ag · · · S interactions. The longest Ag · · · S distance is 3.075(7) Å.

Co-ordination networks of bmmp

As the perchlorate anion is non-co-ordinating in both complexes **1** and **2**, it should be possible to pinpoint the specific co-ordination network of bmmp from materials obtained in which the metal ions are bonded only to bridging ligands. As mentioned in the introduction, bmmp possesses two cyano and two methyl thioether groups, each at an angle of *ca.* 120°. The diamondoid network with varying degrees of interpenetration is a common feature for linear rods or tetrahedral ligands bridging copper(I) and silver(I) complexes.[8,12] Unlike the rod-like ligands, the bmmp in the compound with copper(I) perchlorate, **1**, acts essentially as a bis(monodentate) N donor, with a 'Y' shape bridging between the two copper ions to satisfy the four-co-ordinate tetrahedral stereochemistry of the Cu^I, and leaves two thioether S atoms co-ordinatively free. This gives a two-dimensional square grid rather than a three-dimensional diamondoid network, Fig. 4. A similar network was observed in

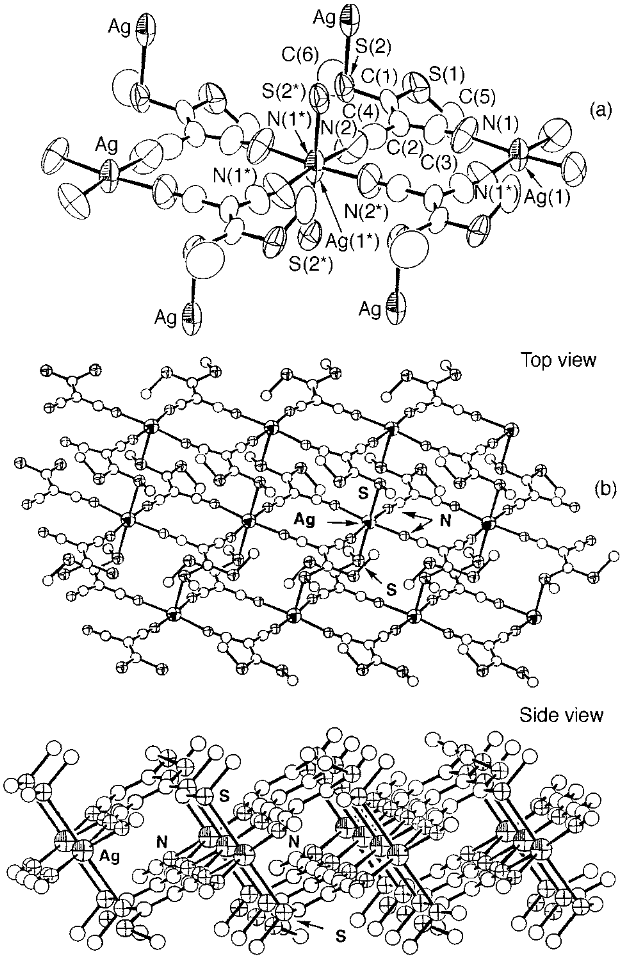


Fig. 3 Crystal structure of [Ag(bmmp)$_2$]ClO$_4$: (a) labelling scheme and (b) two views of the molecular packing showing the three-dimensional network; ClO$_4^-$ anions omitted for clarity

the 1,3-dicyanobenzene-bridged copper(I) complex as this ligand and bmmp possess two CN functional groups with analogous conformations.[13] The high selectivity of Ag^I for sulfur in complex **2** is expressed by the participation of one of the bmmp thioether groups in co-ordination. In this case, bmmp behaves as a tridentate ligand bridging three octahedral silver ions with one thioether S atom non-co-ordinating, leading to a three-dimensional edge-sharing octahedral network. This bonding mode is primarily associated with the metal ion having a ligand-field preference for an octahedral co-ordination geometry and its propensity for a soft sulfur atom. Similar results of varying the metal ion upon self-assembly of co-ordination compounds were obtained with 3,5-bis(2-pyridyl)pyrazole,[21] which acts as a bi-, tri- and tetra-dentate ligand with Cu^I, Ag^I and Cu^{II}, respectively, and bismbmp{bis[1-methyl-2-(6-methyl-2-pyridyl)benzimidazol-5-yl]methane},[22] which gives a double-helical structure with tetrahedral Cu^I and a triple-helical network with octahedral Co^{II}. The structure determination of the present two complexes confirms, at least in part, that bmmp is a potentially bi-, tri- and even tetra-dentate ligand, the co-ordination network depending essentially on the stereochemical preference of the metal ion, and can provide metal co-ordination polymers with diverse structures and unusual topology. Other studies in this area with different cations are in progress.

Acknowledgements

This work was partially supported by a Grant in Aid for Science Research No. 0845214 (to M. M.) and a Grant in Aid for Priority Area No. 08231267 (to M. M.) from the Ministry of Education, Science and Culture in Japan. The authors are also grateful to Kinki University for financial support (No. 9626).

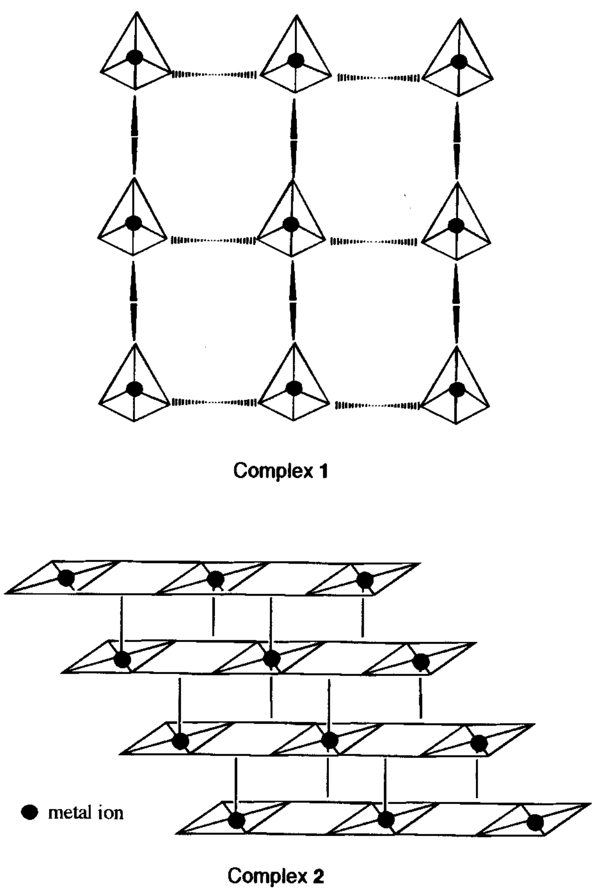


Fig. 4 Schematic presentation of different co-ordination networks observed in bmmp complexes of tetrahedral Cu^I and octahedral Ag^I

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Received 22nd *October* 1997; *Paper* 7/07617G