Co-ordinative Versatility of 3,5-Bis(2-pyridyl)pyrazole in Silver and Copper Compounds†

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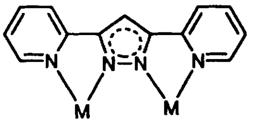
Two silver(I) and one copper(II) complex with 3,5-bis(2-pyridyl)pyrazole (Hbpypz) have been synthesized and their molecular structures determined by X-ray crystallography. In the dinuclear complex $[Ag_2(Hbpypz)_4][ClO_4]_2{\cdot}2Me_2CO$ there are two crystallographically independent monomeric units linked by intramolecular hydrogen bonds. In each unit Hbpypz only uses two of its four nitrogen atoms, acting as a typical bidentate chelate ligand. In the polymeric complex $\{[Ag(Hbpypz)]ClO_4\}_\infty$ each silver(I) ion is co-ordinated to three nitrogen atoms of two different Hbpypz molecules and each ligand in turn bridges two separate Ag atoms forming an infinite-chain structure of macrocations with non-interacting ClO_4^- anions. The tetranuclear complex $[Cu_4(bpypz)_4(ClO_4)_4]{\cdot}2H_2O$ consists of two weakly associated dimeric units coupled *via* intramolecular stacking between the pyridine and pyrazole rings with an average spacing of 3.50 Å, which gives rise to charge-transfer absorption bands in the near-UV region. The temperature dependence of the ESR spectrum and magnetic susceptibility indicates the presence of an antiferromagnetic interaction in the system. While Hbpypz is strictly planar in the copper(II) complex, a non-coplanar conformation is observed in both silver(I) complexes, indicative of the unique co-ordinative versatility of the pyrazole derivative.

Since the first comprehensive review of pyrazole-derived ligands appeared in 1972[1] the co-ordination chemistry of pyrazole and its derivatives has developed vigorously over the last two decades.[2–7] The pyrazole molecule can co-ordinate to metals in a monodentate mode through the N^2 atom or act in an exobidentate fashion when deprotonated, to bind two separate metals through both nitrogen atoms. In recent years there have been many studies of co-ordination compounds of biheteroaromatic ligands.[8] 3,5-Bis(2-pyridyl)pyrazole (Hbpypz), in which the pyrazole ring is attached to bulky nitrogen heterocycles at the 3,5 positions, belongs to this class of ligands and was first reported by Ball and Blake[9] in 1969. Surprisingly, it has received little attention until recently despite its attractive versatile properties in respect of the formation of multimetallic transition-metal complexes. Pons and his co-workers[4–7] have studied a series of Hbpypz complexes with the divalent metal ions Ni^{II}, Co^{II}, Zn^{II} and Cu^{II}. Structural data for the nickel(II)[6] and copper(II)[7] complexes have shown that this tetradentate nitrogen donor has a strong preference for formation of dinuclear complexes in which the ligand itself exhibits a strictly planar bridging mode with the axial co-ordination sites of the metal ions occupied by additional solvent molecules, **a**. Despite these findings, there are no reports of univalent metal complexes containing Hbpypz and of polynuclear complexes.

As part of a continuing study on the structures and properties of polymeric copper and silver complexes of aromatic ligands,[10,11] we report here two silver(I) and one copper(II) complex with Hbpypz. We present the first structural evidence for two other co-ordination modes **b** and **c** in a dinuclear and a polynuclear silver(I) complex, respectively. In addition, we provide another example of intramolecular aromatic ring stacking in the Cu^{II}–bpypz system to demonstrate that this type of ligand interaction is particularly unique in respect of coupling two dimers into a tetrameric structure.



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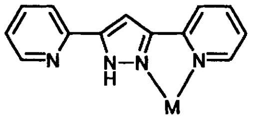
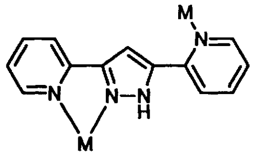


b



c

Results and Discussion

Synthesis and Spectroscopic Properties of the Complexes.— The reaction of Hbpypz and $AgClO_4$ in different solvents at various molar ratios surprisingly leads to the isolation of two totally different silver(I) products. Colourless brick crystals of the dinuclear complex $[Ag_2(Hbpypz)_4][ClO_4]_2{\cdot}2Me_2CO$ were prepared by slow diffusion of $AgClO_4$ with 2 molar equivalents of Hbpypz in pentane, while pale yellow plates of the polynuclear complex $\{[Ag(Hbpypz)]ClO_4\}_\infty$, were obtained by direct reaction of $AgClO_4$ with 1 molar equivalent of Hbpypz in MeOH. The IR frequencies observed at *ca.* 3220 and 3000 cm^{-1} for each complex correspond to the N–H and C–H stretching bands, respectively, and a strong non-split broad band at *ca.* 1140 cm^{-1} corresponds to the unco-ordinated ClO_4^- anion, leaving little doubt as to the identity of the ligand as neutral Hbpypz.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

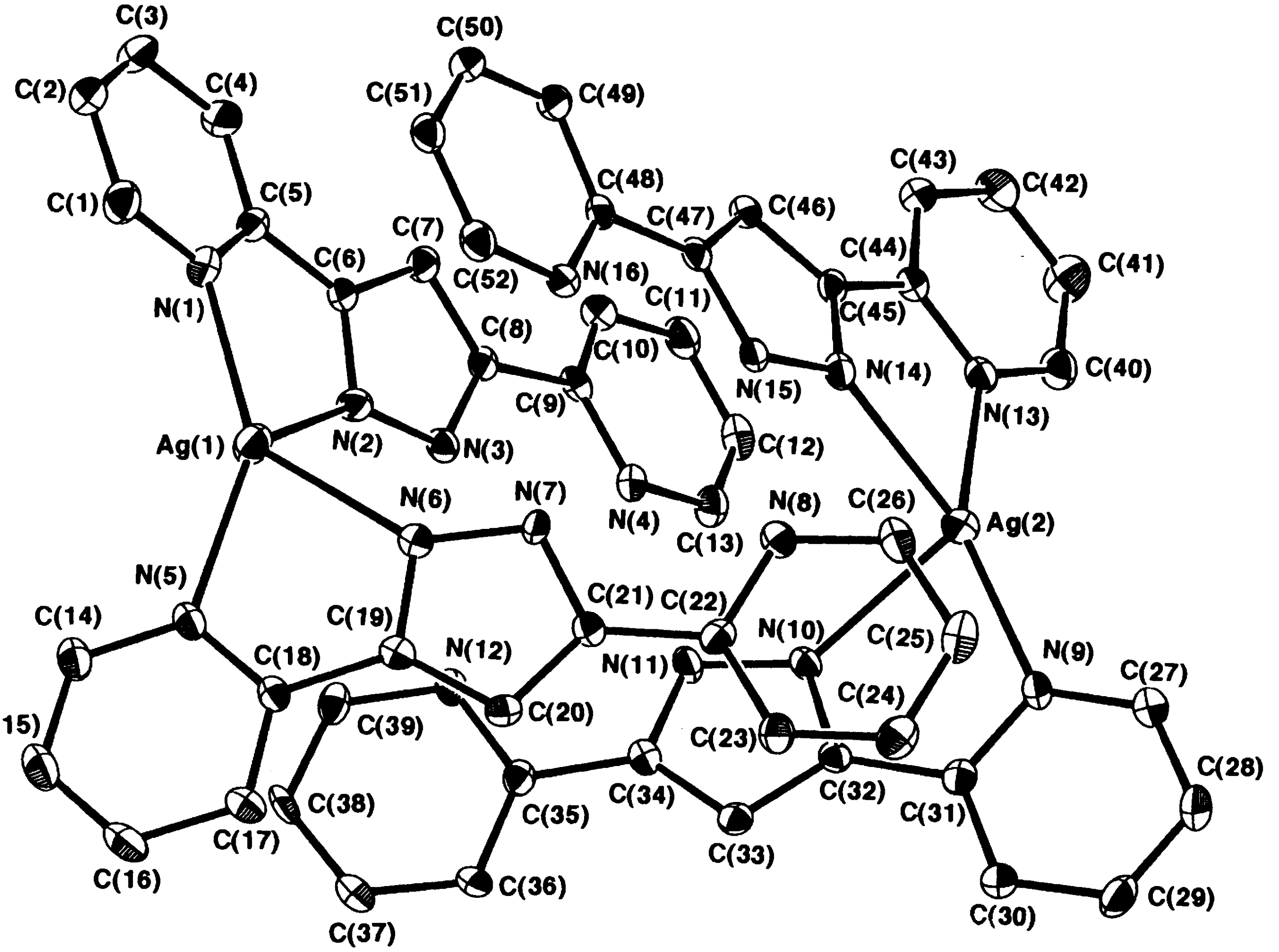


Fig. 1 An ORTEP[13] view of the molecular structure of complex **1**. Hydrogen-bond distances: N(3) ··· N(12) 2.87(1), N(4) ··· N(11) 2.86(2), N(7) ··· N(16) 2.87(1), N(8) ··· N(15) 2.87(1) Å. The thermal ellipsoids enclose 40% probability

The initial success we had with the synthesis of silver(I) complexes encouraged us to make similar copper(I) species. However, attempts to obtain a corresponding bi- or poly-nuclear complex have been unsuccessful. When the preparation is carried out directly by $[Cu(MeCN)_4]PF_6$ and Hbpypz in MeCN single yellow crystals of a copper(I) species are obtainable at −15 °C, but they undergo slow oxidation at their edges at room temperature, which prevents structure analysis. Starting with reduction of $Cu(ClO_4)_2 \cdot 6H_2O$ by copper metal sheets in an ethylene atmosphere followed by reaction with Hbpypz eventually gave the copper(II) species $[Cu_4(bpypz)_4(ClO_4)_4] \cdot 2H_2O$ **3** even under Ar. The IR spectrum shows the absence of the N–H stretching vibration of pure Hbpypz in the solid state at 3202 cm^{-1}. The splitting of the perchlorate v_3 band into three components at 1144, 1113 and 1086 cm^{-1} is indicative of co-ordinated ClO_4^-.[12] Thus, the ligand is present as its anion, consistent with the stoichiometry of the compound.

Crystal Structure of $[Ag_2(Hbpypz)_4][ClO_4]_2 \cdot 2Me_2CO$ **1**.—The molecular structure of complex **1** together with the atomic numbering scheme is given in Fig. 1. Interatomic distances and angles relevant to the silver co-ordination sphere are summarized in Table 1. The structure of the dimer consists of two crystallographically independent cationic units of $[Ag(Hbpypz)_2]^+$ linked by intramolecular hydrogen bonds, with an Ag(1) ··· Ag(2) separation of 8.66 Å. In each monomeric cation the Ag atom is co-ordinated to two Hbpypz molecules through one pyridine and one pyrazole nitrogen atom of each ligand in a highly distorted geometry. Thus, the ligand only uses two of the four nitrogen atoms, acting as a typical bidentate chelate and forming a five-membered Ag–N–C–C–N metallocycle. The dihedral angle between the two Hbpypz mean planes is 46.82° for Ag(1) and 45.19° for Ag(2). The Ag–N (pyrazole) bond distances are consistently longer than those of Ag–N (pyridine) by an average of 0.15 and 0.14 Å for Ag(1) and Ag(2), respectively. The atom Ag(1) deviates by only 0.14 Å from the least-squares plane defined by N(1)N(5)N(6) and the sum of the three bond angles around Ag(1) [N(1)–Ag(1)–N(5) 147.6(4), N(1)–Ag(1)–N(6) 139.2(4), N(5)–Ag(1)–N(6) 71.7(4)°] is 358.5°. These values and the extremely long distance of Ag(1)–N(2) [2.485(9) Å] suggest that the Ag(1) ion is in a trigonal-pyramidal environment formed by N(1), N(5) and N(6) as the base plane, with N(2) atom weakly co-ordinated in the axial position. The Ag(2) ion has a similar co-ordination sphere.

There is intramolecular hydrogen bonding within the dimeric structure between the free pyridine nitrogen atom of one monomeric unit and the NH of a pyrazole belonging to another monomeric moiety with N ··· N *ca.* 2.87 Å [N(3) ··· N(12) 2.87(1), N(4) ··· N(11) 2.86(2), N(7) ··· N(16) 2.87(1), N(8) ··· N(15) 2.87(1) Å]. As shown in Fig. 1, it is these four interconnected strong hydrogen bonds[14] that link the two monomers constituting a dimeric structure.

Crystal Structure of $\{[Ag(Hbpypz)]ClO_4\}_\infty$ **2**.—The single-crystal X-ray diffraction analysis reveals that complex **2** is composed of non-interacting ClO_4^- anions and $\{[Ag(Hbpypz)]^+\}_\infty$ macrocations. Fig. 2 indicates a portion of

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1**–**3**

Complex **1**			
Ag(1)–N(1)	2.25(1)	Ag(1)–N(2)	2.485(9)
Ag(1)–N(5)	2.281(9)	Ag(1)–N(6)	2.342(9)
Ag(2)–N(9)	2.26(1)	Ag(2)–N(10)	2.391(9)
Ag(2)–N(13)	2.265(9)	Ag(2)–N(14)	2.412(9)
N(1)–Ag(1)–N(2)	70.7(4)	N(1)–Ag(1)–N(5)	147.6(4)
N(1)–Ag(1)–N(6)	139.2(4)	N(2)–Ag(1)–N(5)	127.2(3)
N(2)–Ag(1)–N(6)	93.5(4)	N(5)–Ag(1)–N(6)	71.7(4)
N(9)–Ag(2)–N(10)	72.3(4)	N(9)–Ag(2)–N(13)	148.3(4)
N(9)–Ag(2)–N(14)	136.6(4)	N(10)–Ag(2)–N(13)	129.8(4)
N(10)–Ag(2)–N(14)	93.3(3)	N(13)–Ag(2)–N(14)	71.2(4)
Complex **2**			
Ag–N(1)	2.388(3)	Ag–N(2)	2.287(4)
Ag–N(4′)	2.213(3)		
N(1)–Ag–N(2)	71.6(1)	N(1)–Ag–N(4′)	138.0(1)
N(2)–Ag–N(4′)	143.4(1)		
Complex **3**			
Cu(1)–O(5)	2.357(5)	Cu(1)–N(1)	2.066(5)
Cu(1)–N(2)	1.937(5)	Cu(1)–N(7)	1.941(5)
Cu(1)–N(8)	2.077(5)	Cu(2)–O(4)	2.365(5)
Cu(2)–N(3)	1.943(4)	Cu(2)–N(4)	2.078(5)
Cu(2)–N(5)	2.086(5)	Cu(2)–N(6)	1.929(5)
O(5)–Cu(1)–N(1)	92.1(2)	O(5)–Cu(1)–N(2)	93.5(2)
O(5)–Cu(1)–N(7)	93.7(2)	O(5)–Cu(1)–N(8)	94.3(2)
N(1)–Cu(1)–N(2)	80.3(2)	N(1)–Cu(1)–N(7)	170.0(2)
N(1)–Cu(1)–N(8)	107.6(2)	N(2)–Cu(1)–N(7)	91.2(2)
N(2)–Cu(1)–N(8)	168.7(2)	N(7)–Cu(1)–N(8)	80.1(2)
O(4)–Cu(2)–N(3)	98.8(2)	O(4)–Cu(2)–N(4)	85.5(2)
O(4)–Cu(2)–N(5)	88.9(2)	O(4)–Cu(2)–N(6)	101.5(2)
N(3)–Cu(2)–N(4)	79.8(2)	N(3)–Cu(2)–N(5)	169.6(2)
N(3)–Cu(2)–N(6)	91.6(2)	N(4)–Cu(2)–N(5)	107.8(2)
N(4)–Cu(2)–N(6)	169.7(2)	N(5)–Cu(2)–N(6)	80.0(2)

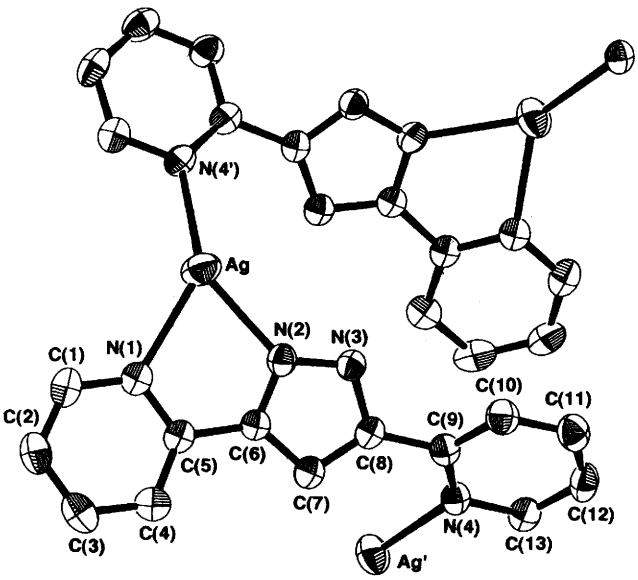


Fig. 2 An ORTEP view of portions of the macrocations $\{[Ag(Hbpypz)]^+\}_\infty$ in complex **2**. The thermal ellipsoids enclose 50% probability

the cation in which each silver(I) ion is co-ordinated to three nitrogen atoms from two different (but crystallographically equivalent) Hbpypz ligands and each Hbpypz molecule in turn co-ordinates to two separate Ag atoms. The total crystal structure is built up from these repeating units to give one-dimensional polymeric chains extended along the *b* axis. Fig. 3 shows the framework of the non-planar polymeric chain in which the silver atoms are arranged in a zigzag mode. The co-ordination around the metal ion is distorted trigonal planar and the Ag atom deviates by 0.31 Å from the plane defined by N(1)N(2)N(4′). The counter anion ClO_4^- is not co-ordinated as the closest contact between its oxygen atoms and the silver is 2.999(5) Å.

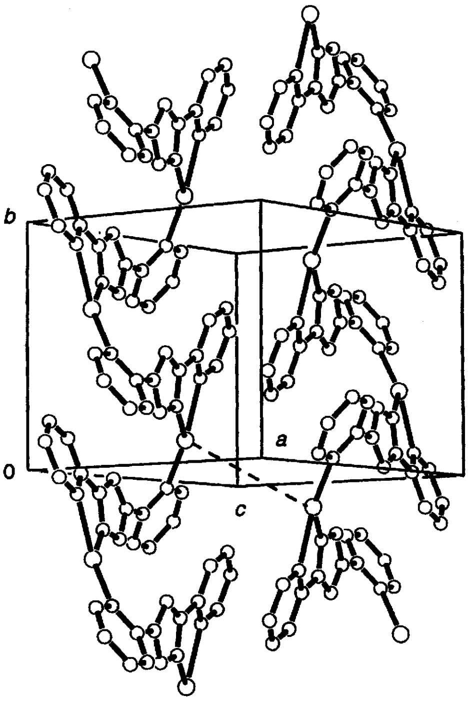


Fig. 3 Molecular packing diagram of the macrocation $\{[Ag(Hbpypz)]^+\}_\infty$ in complex **2**. The dashed line shows the contact between the nearest silver atoms, Ag ··· Ag 5.67 Å

Similar polymerization has been observed previously for silver(I) and copper(I) complexes of bis(2-pyridyl)ethylene (bpen).[15] Although all three compounds possess one-dimensional polymeric chain structures, the arrangements of the metal ions are different, being of rectangular wave-chain type for the copper and zigzag triangular mode for the silver. Furthermore, with bpen both Cu^I and Ag^I have a two-co-ordinate linear geometry, characteristic of d^{10} metals, while with Hbpypz in **2** the Ag atom exhibits a three-co-ordinate trigonal-planar stereochemistry. Compared with linear and tetrahedral silver(I) compounds, three-co-ordinate silver(I) complexes are much less extensive, especially polynuclear ones.[16] Polymeric silver(I) complexes containing the uninegative pyrazolate ion have been known since 1889 when the formation of an insoluble silver pyrazolate salt Ag(pz) was reported;[17] however, its structure has never been crystallographically established.

Crystal Structure of $[Cu_4(bpypz)_4(ClO_4)_4]\cdot 2H_2O$ **3**.—The molecular structure of complex **3** involves a dimeric structure with loose stacking interaction to give a tetramer in the unit cell. In the dimeric units $[Cu_2(bpypz)_2(ClO_4)_2]$ each copper atom is bound to two pyridine and two pyrazole nitrogen atoms on the basal plane and the fifth axial position is occupied by one oxygen atom of the perchlorate anion, forming a square-pyramidal environment. An overall view of the dimeric structure is shown in Fig. 4 and selected bond parameters are given in Table 1. Each bpypz displays a tetradentate dinucleating mode, bridging two metal centres with a Cu ··· Cu separation of 4.05 Å. The two dimeric fragments are mutually coupled *via* stacking of pyrazole ring of one dimer and a pyridine ring belonging to the other at approximately 3.50 Å. Fig. 5 illustrates four such tetramers packed in the unit cell.

The perchlorate oxygen–copper distances are 2.357(5) and 2.365(5) Å for Cu(1) and Cu(2), respectively, indicative of semi-co-ordination.[18] The Cu–N bond lengths are in the range 1.937(5)–2.077(5) Å for Cu(1) and 1.929(5)–2.086 Å for Cu(2). The copper ion and the four basal nitrogen atoms are coplanar and the copper atoms are only displaced by 0.01 Å out of the basal plane toward the axial oxygen.

The gross structural features of complex **3** are most readily compared with those of the previously reported nitrate $[Cu_4(bpypz)_4(H_2O)_4][NO_3]_4{\cdot}4H_2O$,[7] including the pattern of bond distances and angles of the bpypz, as well as its conformation. However, in the nitrate complex the fifth axial position of the Cu^{II} is occupied by a water molecule instead of the counter anion NO_3^-. In addition, the two fifth Cu–O bonds in **3** adopt a *trans* rather than *cis* conformation as observed in the nitrate.

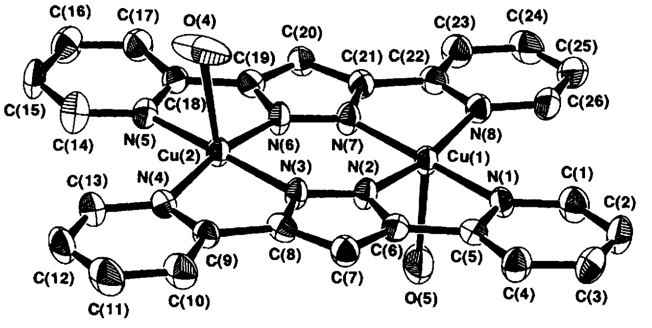
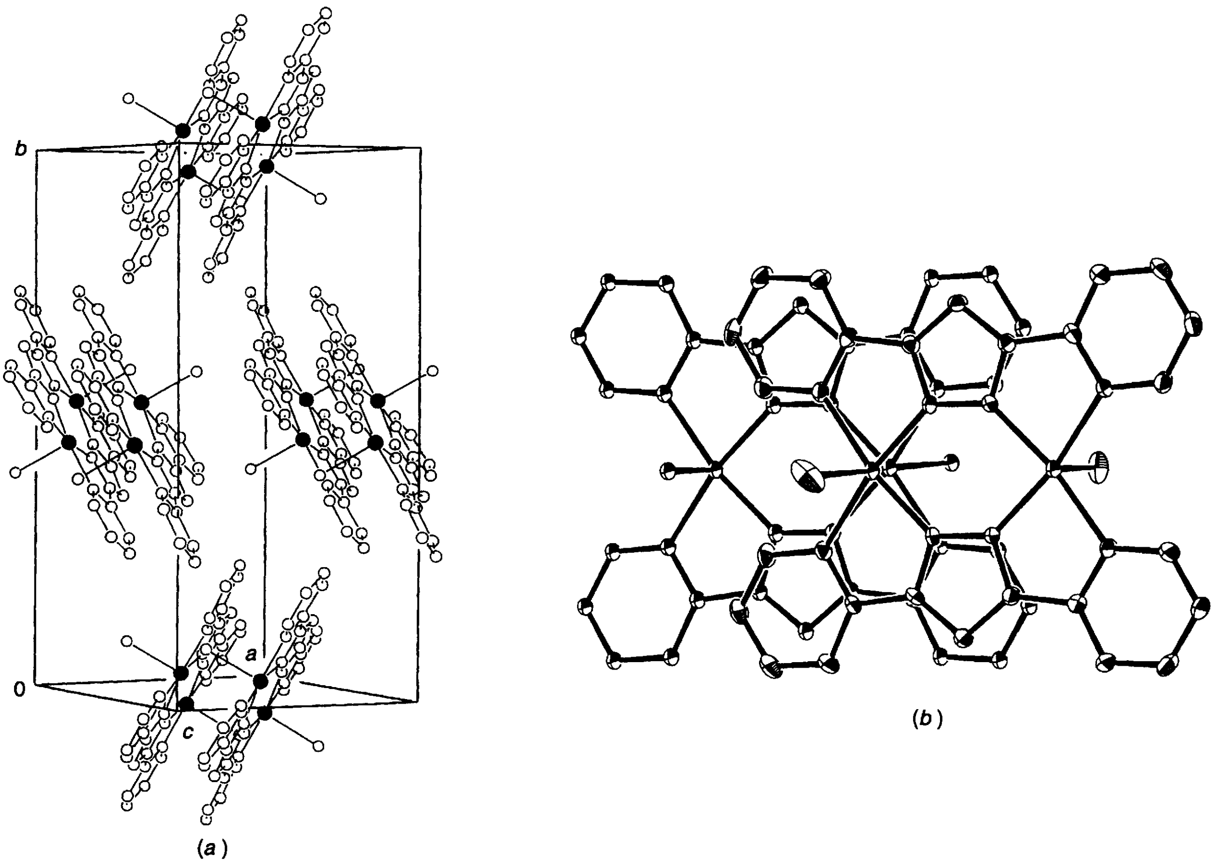


Fig. 4 An ORTEP view of the molecular structure of complex **3** with the labelling scheme. The thermal ellipsoids enclose 50% probability

Stacking Conformation of Hbpypz.—Aromatic ring stacking is one type of intramolecular non-covalent interaction between ligands in complexes,[19] which has been investigated extensively by different research groups for ternary complexes of aromatic nitrogen ligands and nucleotides or amino acids.[20,21] As described above, the intramolecular stacking interaction in complex **3** is unique in a sense that it creates a specific structure resulting from coupling of two dimeric fragments into a tetrameric framework, Fig. 5. The two pyrazole rings from each dimer are located approximately parallel to two pyridine rings of the other dimer such that the two dimeric units are attracted by each other through a π–π stacking interaction. This type of stacking mode is similar to that in the previously reported complexes $[Cu(bipy)(\text{L-Trp})]ClO_4$[21c] and $[Cu(phen)(\text{L-Trp})]ClO_4$[22] (bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline and L-Trp = L-tryptophan), where stacking occurs between the aromatic diamine ring and the indole ring of two different ligands. The average spacing of 3.50 Å in **3** is slightly shorter than that for $[Cu(bipy)(\text{L-Trp})]ClO_4$ (3.67 Å) and $[Cu(phen)(\text{L-Trp})]ClO_4$ (3.51 Å), suggesting a stronger interaction in **3**. The UV spectrum of **3** recorded in the solid state shows a broad peak at 340 nm, which is attributable to the charge transfer between stacked aromatic rings in the complex. Similar absorption has been observed at 320 nm in $[Cu(bipy)(\text{L-Trp})]ClO_4$.[21c]

It is noteworthy that in the previously reported crystal structures involving intramolecular stacking there is also strong evidence that the aromatic portion of the ligand tends to occupy space near the metal ion with a close contact between the latter and the carbon atom of 3.29 Å in $[Cu(bipy)(\text{L-Trp})]ClO_4$, 3.20 Å in $[Cu(phen)(\text{L-Trp})]ClO_4$, and 3.23 Å in $[Pd(bipy)(\text{L-Tyr-Gly})]{\cdot}3H_2O$ (L-Tyr-Gly = the dianion of L-tyrosylglycine).[21a] In the nitrate complex containing bpypz a distance of 3.68 Å is reported between the Cu^{II} and one pyrazole ring belonging to the other dimeric unit.[7] By contrast, such ligand–metal



(*a*)

(*b*)

Fig. 5 Molecular packing diagram (*a*) and stacking mode (*b*) of complex **3**

Table 2 Crystal and refinement data for complexes **1–3** *

	1	**2**	**3**
Formula	$C_{58}H_{52}Ag_2Cl_2N_{16}O_{10}$	$C_{13}H_{10}AgClN_4O_4$	$C_{26}H_{20}Cl_2Cu_2N_8O_9$
M	1419.79	429.57	786.47
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	14.937(5)	11.148(4)	10.053(3)
b/Å	16.924(5)	9.018(2)	20.495(3)
c/Å	13.852(6)	14.330(3)	13.574(1)
α/°	110.59(2)	90.0	90.0
β/°	102.80(3)	100.03(2)	94.75(1)
γ/°	101.45(3)	90.0	90.0
$U/Å^3$	3046(2)	1418.6(6)	2787(1)
Z	2	4	4
$D_c/g\ cm^{-3}$	1.548	2.011	1.831
F(000)	1440.0	848.0	1544.0
Crystal size/mm	0.25 × 0.30 × 0.30	0.30 × 0.20 × 0.25	0.50 × 0.30 × 0.40
μ(Mo-Kα)/cm^{-1}	7.92	16.21	17.88
$2\theta_{max}/°$	50.0	55.0	55.0
No. reflections measured	11 155	3825	6948
No. observations [$I > 3.00\sigma(I)$]	5214	2210	3203
No. parameters	793	208	424
R	0.064	0.035	0.043
R′	0.086	0.041	0.045
Goodness of fit	2.96	1.54	1.36

* Details in common: ω–2θ scans; scan rate 8° min^{-1}.

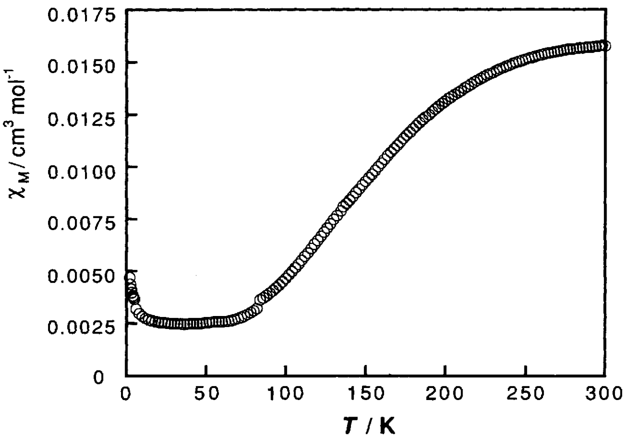


Fig. 6 Plot of magnetic susceptibility *vs.* temperature for complex **3**

interaction is unlikely in **3** as the closest contact between the Cu^{II} and the carbon atoms of the pyrazole ring is 4.02 Å.

Close examination of the structure **2** reveals that as the polymeric chain extends along the *b* axis there is no aromatic ring stacking in the molecule. However, in the dimeric structure of **1** a weak interaction does occur between the pyrazole ring and the pyridine ring belonging to two separate monomeric units with average spacing of 3.78 Å, Fig. 1. Compared with the strong intramolecular hydrogen bonds as discussed previously, such ring stacking is not the major driving force for formation of the dinuclear structure.

Co-ordinative Versatility of the Ligand.—The structure determination of the above three complexes has demonstrated the unique co-ordinative versatility of the pyrazole derivative Hbpypz. In the compound with copper(II) perchlorate, **3**, the ligand is deprotonated and the uninegative bpypz anion displays a tetradentate di-μ-pz bridging mode to satisfy the square-planar co-ordination of the Cu^{II}. In the univalent silver(I) complexes **1** and **2** such tetradentate planar conformation of Hbpypz could not be maintained owing to the strong tendency of Ag^{I} to form a four-co-ordinate tetrahedral geometry or three-co-ordinate trigonal-planar stereochemistry. As a compromise the metal ion adopts a severe distortion from idealized geometry and the ligand exhibits a flexibility by twisting the bulky pyridine substituents away from the pyrazole moiety. While each pyridine or pyrazole group in **1** and **2** is planar, they are twisted against each other remarkably in both cases. In **1** the orientation of the co-ordinated pyridine groups, with respect to the pyrazole rings to which they are attached, range from 10.49 to 13.08° for Ag(1) and 7.62 to 11.19° for Ag(2). The two pyridine rings of Hbpypz form angles of 3.64, 1.64° and 11.97, 2.79° for Ag(1) and Ag(2), respectively. In **2** this type of twist is even more prominent due to the steric requirement for formation of a polynuclear structure. As Hbpypz acts as a bridge joining two separate metal centres the two pyridine rings are twisted significantly relative to the pyrazole ring by 15.28 and 38.08°, respectively, and the dihedral angle formed by the two pyridine rings is 53.01°.

Apart from the non-rigidity, Hbpypz also shows versatility in the formation of different types of metal complexes. While it behaves as a tetradentate ligand in **3** using all four available nitrogen atoms, it is bi- and tri-dentate in **1** and **2**, respectively. A pyrazole derivative with four co-ordination sites acting as a bidentate ligand has been previously observed in the complexes of Cr and Mo with 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine.[23] However, the one-dimensional polymeric chain found in **2** in which Hbpypz acts as a tridentate bridge represents an unusual and to our knowledge previously unreported phenomenon in pyrazole chemistry.

ESR and Magnetic Properties of Complex **3**.—The ESR spectra of complex **3** were measured over the temperature range 100–300 K on a powder sample. At room temperature the spectrum shows an isotropic signal with g_{iso} = 2.23. Although this remains resolvable at liquid-nitrogen temperatures its intensity diminishes with temperature. Magnetic susceptibility measurements were performed within the range 2–300 K. A plot of susceptibility *vs.* temperature is shown in Fig. 6. Such behaviour is characteristic of antiferromagnetic exchange between spin-coupled copper(II) centres.[5] Similar results have been reported for the nitrate complex.[7] The coplanarity of the

Table 3 Atomic coordinates for complex **1**

Atom	*x*	*y*	*z*
Ag(1)	0.305 25(7)	0.373 94(7)	0.111 04(9)
Ag(2)	0.803 07(7)	0.210 32(6)	0.308 22(9)
Cl(1)	0.184 1(3)	0.274 9(2)	0.738 9(4)
Cl(2)	0.733 1(3)	0.093 5(2)	0.767 8(3)
O(1)	0.109 9(8)	0.198 6(8)	0.715(1)
O(2)	0.153 4(7)	0.330 6(7)	0.693 3(9)
O(3)	0.214(1)	0.321(1)	0.855(1)
O(4)	0.265 3(8)	0.254 8(7)	0.712(1)
O(5)	0.643 2(8)	0.102 3(9)	0.760(2)
O(6)	0.727(1)	0.039(1)	0.622(1)
O(7)	0.798 2(7)	0.176 2(6)	0.792 2(10)
O(8)	0.761(1)	0.059 8(9)	0.840(1)
O(9)	0.862(1)	0.390 3(10)	0.717(1)
O(10)	−0.010 3(9)	0.082 5(8)	0.270(1)
N(1)	0.179 9(7)	0.258 5(7)	0.076 9(8)
N(2)	0.351 0(7)	0.303 3(6)	0.236 5(8)
N(3)	0.430 2(7)	0.301 4(6)	0.303 5(8)
N(4)	0.576 2(7)	0.261 8(6)	0.427 6(8)
N(5)	0.359 8(8)	0.519 8(6)	0.144 5(7)
N(6)	0.456 9(6)	0.401 0(6)	0.086 8(7)
N(7)	0.525 0(7)	0.356 7(6)	0.081 7(8)
N(8)	0.683 0(7)	0.296 6(7)	0.074 4(7)
N(9)	0.936 0(7)	0.311 2(7)	0.324 4(8)
N(10)	0.779 8(7)	0.352 9(6)	0.377 1(8)
N(11)	0.705 6(7)	0.387 3(6)	0.388 4(8)
N(12)	0.566 2(7)	0.473 9(6)	0.386 2(7)
N(13)	0.738 9(7)	0.086 1(6)	0.327 9(8)
N(14)	0.640 3(7)	0.140 2(7)	0.185 3(8)
N(15)	0.574 8(7)	0.160 4(6)	0.118 8(8)
N(16)	0.411 4(7)	0.174 1(6)	−0.007 7(8)
C(1)	0.094(1)	0.241 1(10)	0.004(1)
C(2)	0.015 9(10)	0.173(1)	−0.019(1)
C(3)	0.023 3(10)	0.121(1)	0.034(1)
C(4)	0.111(1)	0.137 3(9)	0.110(1)
C(5)	0.188 5(8)	0.207 6(8)	0.126 6(9)
C(6)	0.283 5(8)	0.226 7(8)	0.204 7(9)
C(7)	0.319 5(9)	0.174 1(8)	0.255 3(10)
C(8)	0.412 9(8)	0.225 9(8)	0.317 8(9)
C(9)	0.486 6(9)	0.206 5(7)	0.390 3(9)
C(10)	0.463 6(9)	0.140 9(8)	0.423(1)
C(11)	0.534(1)	0.127 4(9)	0.496(1)
C(12)	0.625(1)	0.184(1)	0.534(1)
C(13)	0.643 2(9)	0.249 5(9)	0.497(1)
C(14)	0.309 5(9)	0.578 4(10)	0.164(1)
C(15)	0.346(1)	0.665(1)	0.184(1)
C(16)	0.437(1)	0.695 3(8)	0.182(1)
C(17)	0.490 2(9)	0.636 3(8)	0.162 7(10)
C(18)	0.449 8(9)	0.549 3(8)	0.142 5(9)
C(19)	0.504 4(8)	0.485 4(7)	0.122 3(8)
C(20)	0.600 7(8)	0.496 9(7)	0.130 9(9)
C(21)	0.611 4(8)	0.414 7(7)	0.103 3(9)
C(22)	0.695 4(8)	0.383 8(9)	0.095 1(9)
C(23)	0.781 4(9)	0.437 5(8)	0.104 7(10)
C(24)	0.857 3(10)	0.407(1)	0.091(1)
C(25)	0.844(1)	0.318(1)	0.069(1)
C(26)	0.757(1)	0.264 5(9)	0.061(1)
C(27)	1.014(1)	0.293 0(9)	0.307(1)
C(28)	1.093(1)	0.354(1)	0.312(1)
C(29)	1.091 4(9)	0.441(1)	0.339(1)
C(30)	1.010 9(9)	0.461 6(8)	0.358 4(10)
C(31)	0.933 0(8)	0.395 8(8)	0.351 1(9)
C(32)	0.845 6(8)	0.415 2(7)	0.368 0(9)
C(33)	0.814 7(8)	0.489 4(7)	0.378 1(9)
C(34)	0.726 0(8)	0.469 1(7)	0.390 4(8)
C(35)	0.656 8(8)	0.520 3(8)	0.399 4(9)
C(36)	0.683 5(9)	0.609 0(8)	0.420 1(10)
C(37)	0.614(1)	0.651 9(8)	0.423(1)
C(38)	0.522(1)	0.607 8(8)	0.407 4(10)
C(39)	0.500 4(8)	0.520 2(9)	0.387 5(9)
C(40)	0.788 2(9)	0.051 4(9)	0.390(1)
C(41)	0.748(1)	−0.023(1)	0.407(1)
C(42)	0.653(1)	−0.066 5(9)	0.354(1)
C(43)	0.602 3(9)	−0.030 9(8)	0.290(1)
C(44)	0.645 1(9)	0.041 9(8)	0.274 8(9)
C(45)	0.592 4(8)	0.075 0(7)	0.208 6(9)
C(46)	0.495 4(8)	0.049 7(7)	0.152 2(10)
C(47)	0.484 6(9)	0.103 2(8)	0.095 2(9)
C(48)	0.399 2(8)	0.107 8(8)	0.021 2(9)
C(49)	0.311 5(9)	0.041 9(8)	−0.016(1)
C(50)	0.235 0(9)	0.046 9(9)	−0.087(1)
C(51)	0.246 5(10)	0.114 3(9)	−0.120(1)
C(52)	0.335(1)	0.176 3(9)	−0.077(1)
C(53)	0.907(1)	0.341(1)	0.727(2)
C(54)	0.965(1)	0.354(1)	0.836(2)
C(55)	0.907(1)	0.267(2)	0.630(2)
C(56)	0.044(1)	0.071(1)	0.338(1)
C(57)	0.033(1)	−0.014(1)	0.345(2)
C(58)	0.135(2)	0.140(1)	0.415(2)

two copper atoms and two ligand molecules in the complex contributes to an efficient antiferromagnetic spin coupling through the pyrazolate bridge.[2b]

Experimental

General Methods.—Preparations were performed using usual Schlenk techniques. All solvents were dried and distilled by standard methods before use. The standard chemicals and 3,5-bis(2-pyridyl)pyrazole were obtained from Wako Chemical Co., Japan, and used without further purification. Infrared and electronic spectra were measured as KBr discs on JASCO FT/IR-8000 and Hitachi 150–20 spectrometers, ESR spectra in the liquid-nitrogen range on a JES-TE200 spectrometer. Variable-temperature magnetic data were collected in the liquid-helium range at 3 T with a SQUID susceptometer (Quantum Design, San Diego, CA) interfaced with an HP Vectra computer system.

CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts should be prepared, and handled with great care.

Syntheses.—$[Ag_2(Hbpypz)_4][ClO_4]_2 \cdot 2Me_2CO$ **1**. To a solution of Hbpypz (44.5 mg, 0.2 mmol) in acetone (10.0 cm^3) was added $AgClO_4$ (20.7 mg, 0.1 mmol). The resultant white

Table 4 Atomic coordinates for complex **2**

Atom	*x*	*y*	*z*
Ag	0.727 68(4)	0.857 01(4)	0.555 81(3)
Cl	0.946 9(1)	0.441 4(1)	0.195 31(8)
O(1)	1.058 5(4)	0.414 9(5)	0.259 4(3)
O(2)	0.894 7(4)	0.575 8(5)	0.223 2(3)
O(3)	0.968 8(4)	0.460 6(4)	0.100 8(3)
O(4)	0.864 6(5)	0.322 9(5)	0.197 4(3)
N(1)	0.702 2(3)	0.601 9(4)	0.512 3(2)
N(2)	0.658 2(3)	0.733 2(4)	0.675 1(2)
N(3)	0.646 8(3)	0.765 0(4)	0.764 7(2)
N(4)	0.660 2(3)	0.547 6(4)	0.974 7(2)
C(1)	0.707 7(4)	0.541 9(5)	0.427 4(3)
C(2)	0.670 8(4)	0.398 3(5)	0.403 4(3)
C(3)	0.625 1(4)	0.311 3(5)	0.469 0(3)
C(4)	0.620 0(4)	0.371 2(4)	0.556 7(3)
C(5)	0.657 8(3)	0.516 5(4)	0.576 0(3)
C(6)	0.650 4(3)	0.585 9(4)	0.667 8(3)
C(7)	0.631 2(4)	0.523 3(4)	0.753 1(3)
C(8)	0.629 1(3)	0.640 7(4)	0.813 9(3)
C(9)	0.609 9(4)	0.653 0(4)	0.912 7(3)
C(10)	0.541 4(4)	0.768 1(5)	0.940 2(3)
C(11)	0.525 7(4)	0.779 7(5)	1.033 2(3)
C(12)	0.576 5(4)	0.673 1(5)	1.096 3(3)
C(13)	0.642 6(4)	0.558 3(5)	1.065 6(3)

Table 5 Atomic coordinates for complex **3**

Atom	*x*	*y*	*z*
Cu(1)	0.438 58(7)	0.038 72(3)	0.850 214(5)
Cu(2)	0.608 40(7)	−0.033 04(3)	0.612 50(5)
Cl(1)	0.812 1(2)	−0.143 20(8)	0.752 4(1)
Cl(2)	0.166 3(2)	0.134 3(1)	0.781 2(1)
O(1)	0.936 6(5)	−0.178 5(2)	0.742 2(3)
O(2)	0.703 1(5)	−0.188 7(3)	0.734 0(4)
O(3)	0.809 8(7)	−0.120 5(3)	0.849 6(4)
O(4)	0.794 9(5)	−0.092 4(3)	0.682 2(4)
O(5)	0.270 8(5)	0.095 0(2)	0.752 7(3)
O(6)	0.165 3(6)	0.141 4(3)	0.882 4(4)
O(7)	0.106 0(9)	0.172 5(5)	0.718 5(6)
O(8)	0.047 5(9)	0.082 3(6)	0.768 9(8)
O(9)	0.263(2)	0.202 6(6)	0.780(1)
N(1)	0.496 3(5)	0.122 4(2)	0.927 2(3)
N(2)	0.579 6(5)	0.068 2(2)	0.772 0(3)
N(3)	0.632 1(4)	0.046 1(2)	0.690 8(3)
N(4)	0.745 0(5)	0.016 2(2)	0.532 9(3)
N(5)	0.546 5(5)	−0.116 1(2)	0.532 5(3)
N(6)	0.469 4(5)	−0.063 4(2)	0.691 1(3)
N(7)	0.416 8(5)	−0.040 8(2)	0.773 1(3)
N(8)	0.305 1(5)	−0.010 8(2)	0.932 1(3)
C(1)	0.450 7(6)	0.148 5(3)	1.009 8(5)
C(2)	0.497 4(7)	0.205 1(3)	1.053 2(5)
C(3)	0.598 3(7)	0.237 9(3)	1.011 4(5)
C(4)	0.646 4(6)	0.213 2(3)	0.926 8(4)
C(5)	0.595 0(6)	0.155 6(3)	0.886 5(4)
C(6)	0.640 3(6)	0.124 7(3)	0.797 7(4)
C(7)	0.735 1(6)	0.140 6(3)	0.733 1(4)
C(8)	0.724 7(6)	0.088 6(3)	0.665 9(4)
C(9)	0.788 6(5)	0.072 0(3)	0.575 6(4)
C(10)	0.882 3(6)	0.111 7(3)	0.536 5(5)
C(11)	0.933 4(7)	0.092 8(4)	0.449 4(5)
C(12)	0.891 2(6)	0.036 0(4)	0.404 8(4)
C(13)	0.797 8(7)	−0.001 3(3)	0.448 3(4)
C(14)	0.588 5(7)	−0.141 4(3)	0.449 5(5)
C(15)	0.546 6(7)	−0.200 6(4)	0.411 3(5)
C(16)	0.456 6(7)	−0.236 1(3)	0.459 5(5)
C(17)	0.410 8(7)	−0.211 3(3)	0.544 3(5)
C(18)	0.456 9(6)	−0.151 0(3)	0.578 4(4)
C(19)	0.411 4(6)	−0.120 6(3)	0.667 6(4)
C(20)	0.318 5(6)	−0.136 3(3)	0.734 0(4)
C(21)	0.326 7(6)	−0.084 4(3)	0.799 3(4)
C(22)	0.259 6(6)	−0.066 7(3)	0.887 0(4)
C(23)	0.158 9(6)	−0.103 3(3)	0.922 0(5)
C(24)	0.104 5(6)	−0.084 8(3)	1.007 7(5)
C(25)	0.153 2(7)	−0.029 7(3)	1.055 9(5)
C(26)	0.251 6(7)	0.006 2(3)	1.015 4(4)

suspension was stirred for 1 h with all apparatus covered by aluminium foil. The white precipitate was filtered off to give a colourless filtrate which was transferred to a glass tube and layered with pentane. After standing in the dark at room temperature for 1 week colourless brick crystals were obtained (Found: C, 49.0; H, 3.85; N, 15.15. Calc. for $C_{58}H_{52}Ag_2Cl_2N_{16}O_{10}$: C, 49.0; H, 3.65; N, 15.8%).

$\{[Ag(Hbpypz)](ClO_4)\}_\infty$ **2**. To a solution of Hbpypz (22.2 mg, 0.1 mmol) in MeOH (10.0 cm^3) was added $AgClO_4$ (20.7 mg, 0.1 mmol). The resultant white suspension was stirred for 1 h with all apparatus covered by aluminium foil. The white precipitate was filtered off to give a colourless filtrate which was transferred to a glass tube. After standing in the dark at room temperature for 3 weeks pale yellow plate crystals were isolated (Found: C, 37.5; H, 2.85; N, 13.65. Calc. for $C_{13}H_{10}AgClN_4O_4$: C, 36.3; H, 2.30; N, 13.05%).

$[Cu_4(bpypz)_4(ClO_4)_4]\cdot 2H_2O$ **3**. The single crystals of complex **3** for X-ray analysis were obtained accidentally from reoxidation of the corresponding copper(I) species. Copper(II) perchlorate hexahydrate (37.1 mg, 0.1 mmol) was reduced with copper wire to Cu^I in methanol (10 cm^3) under ethylene. The compound Hbpypz (44.5 mg, 0.2 mmol) was added and a clear colourless solution was formed. After standing at room temperature for 1 week the colour gradually changed to blue and deep blue prism crystals were isolated. Complex **3** can also be prepared by direct reaction of equimolar Hbpypz and $Cu(ClO_4)_2\cdot 6H_2O$ in MeOH followed by recrystallization of the crude product from dimethylformamide (Found: C, 40.0; H, 2.85; N, 14.0. Calc. for $C_{26}H_{20}Cl_2Cu_2N_8O_9$: C, 39.65; H, 2.55; N, 14.25%).

Crystallography.—Details of the crystal data collection and processing, structure analysis and refinement for complexes **1**–**3** are given in Table 2. The unit-cell data and intensities were collected on a Rigaku AFC-5R four-circle diffractometer, with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å). The structures were solved by a direct method (MITHRIL)[24] and refined by full-matrix least-squares minimization of $\Sigma w(|F_o| - |F_c|)^2$ with anisotropic thermal parameters for all the non-hydrogen atoms. Isotropic hydrogen atoms were located by Fourier difference synthesis and refined on the associated atoms. All of the calculations were performed using the TEXSAN package[25] on a micro VAX computer. Reliability factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, where $w = 4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors and anomalous dispersion terms were taken from ref. 26. The final atomic coordinates are given in Tables 3–5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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