DALTON
FULL PAPER

A variety of one-, two- and three-dimensional copper(I) and silver(I) co-ordination polymers assembled by 1,4-bis(4-pyridyl)butadiyne and 1,4-bis(2-pyridyl)butadiyne †

Masahiko Maekawa,*[a] Hisashi Konaka,[b] Yusaku Suenaga,[b] Takayoshi Kuroda-Sowa[b] and Megumu Munakata[b]

[a] *Research Institute for Science and Technology, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan. E-mail: maekawa@rist.kindai.ac.jp*
[b] *Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan*

Received 21st June 2000, Accepted 13th September 2000
First published as an Advance Article on the web 30th October 2000

Four copper(I) and six silver(I) novel co-ordination polymers linked by 1,4-bis(4-pyridyl)butadiyne (4-bpbd) or 1,4-bis(2-pyridyl)butadiyne (2-bpbd) were prepared and seven structures crystallographically characterized, in order to illustrate the structural versatility of co-ordination polymers assembled by the Group 11 metal ions and rod-like nitrogen bidentate ligands with long spacers. Reaction of appropriate copper(I) and silver(I) salts with the 4-bpbd ligand affords 2-D interwoven copper(I) co-ordination polymers $\{[Cu_2(4\text{-bpbd})_3(CH_3CN)_2]X_2\}_n$ (X = PF_6 **1a**·$2H_2O$ or BF_4 **1b**) and 1-D straight chain silver(I) co-ordination polymers $\{[Ag(4\text{-bpbd})]X\}_n$ (X = NO_3 **2a**·CH_3CN, ClO_4 **2b**·$(CH_3)_2CO$ or CF_3SO_3 **2c**·$(CH_3)_2CO$), respectively. On the other hand, reaction of suitable salts with the 2-bpbd ligand provides a 3-D diamondoid copper(I) co-ordination polymer $\{[Cu(2\text{-bpbd})_2]BF_4\}_n$ **3b**, a 1-D zigzag chain silver(I) co-ordination polymer $\{[Ag(2\text{-bpbd})(NO_3)]\}_n$ **4a** and a 2-D braid sheet silver(I) co-ordination polymer $\{[Ag(2\text{-bpbd})(CF_3SO_3)]\}_n$ **4c**, respectively. On the basis of these structural studies, the unique structural features and the dimensionality of the copper(I) and silver(I) co-ordination polymers are revealed.

Introduction

The construction of solid-state architectures and crystal engineering are rapidly developing areas of research,[1,2] implicated in potential applications of materials to host–guest chemistry,[3] catalysis,[4] and the evolution of optical, magnetic and electron properties.[5,6] During the past ten years, many researchers have attempted to prepare extensive co-ordination polymers with various dimensionalities, sizes, cavities and shapes.[1,2] It has been considered that their structural versatility greatly relates to the nature of the metal center and ligand:[7,8] (1) the oxidation state and co-ordination predisposition of the metal, (2) the ligand geometry including relative orientation of the donor groups and the spacing between donor groups and (3) the influence of the co-ordination anions. To generate multi-dimensional arrays or networks,[1h,9–11] one of the simplest approaches is to use a bifunctional rod-like diatomic anion such as CN^-, or bidentate N,N′-donor linking groups such as pyridine- and pyrazine-based ligands with a preference for binding metals at each end in a linear fashion. Organic building blocks of various connectivities and geometries have been proposed in the preparation of co-ordination polymers.[7] In particular, the 4,4′-bipyridine ligand (4,4′-bpy) is a highly investigated ligand, which has produced a number of 1-D co-ordination polymers[12,13a] in zigzag chain, straight chain and stair-step structures, together with 2-D[12c,13b–d] and 3-D[13] co-ordination polymers in the shape of layers and networks. It is suggested that a degree of structural control may be introduced by manipulation of the disposition of 4-pyridyl groups of the parent 4,4′-bipyridine ligand. Linear rod-like ligands with varying spacer lengths are represented by 1,4-bis(4-pyridyl)-benzene, 1,4-bis(4-pyridyl)butadiyne[14] and 2,7-diazapyrene.[15] The relative orientations of the pyridyl donors should be modified by introduction of appropriate fixed spacers as in 1,2-*trans*-bis(4-pyridyl)ethene,[12b,14a,16] and 4,4′-azobis(pyridine),[16i,17] or by conformationally flexible tethers as in 1,2-bis(4-pyridyl)-ethane[18] and 1,3-bis(4-pyridyl)propane.[19] Thus, systematic investigations of co-ordination polymers with 4,4′-bpy and related compounds are expected to provide useful knowledge, regarding the production of new crystal phases[2] with one-, two-, and three-dimensional motifs such as diamondoid, grid, ladder, brick and railroad. The aim of this study is to illustrate the structural versatility of co-ordination polymers that are built by the Group 11 metal ions (Cu^I and Ag^I) and rod-like nitrogen bidentate ligands with long spacers. According to Scheme 1, using 1,4-bis(4-pyridyl)butadiyne (4-bpbd) and 1,4-bis(2-pyridyl)butadiyne (2-bpbd), we prepared four copper(I) and six silver(I) novel co-ordination polymers and the versatile dimensionality of seven of them was demonstrated crystallographically.

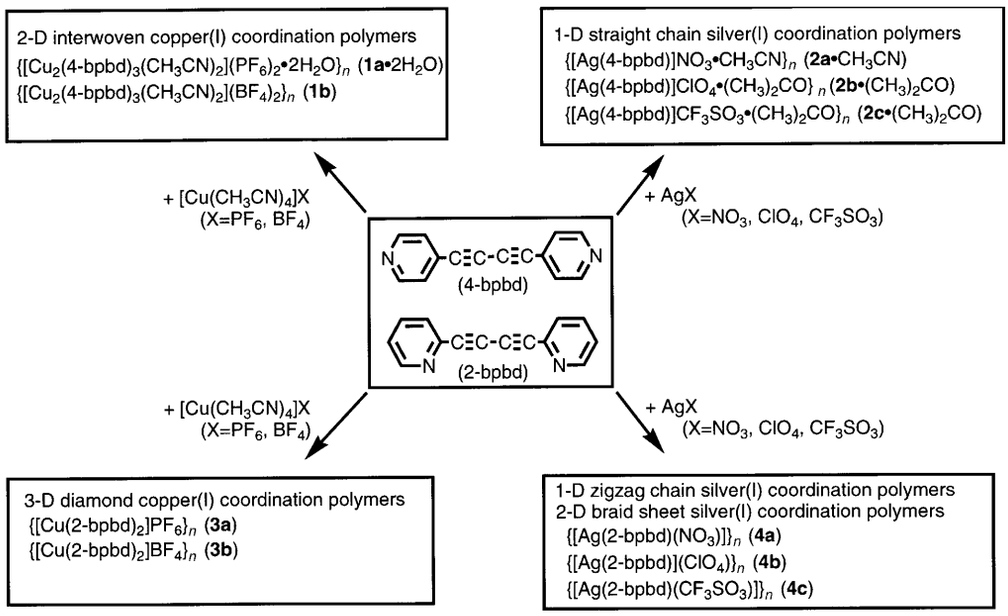
Experimental

General procedures and reagents

All operations were carried out using usual Schlenk techniques under an argon atmosphere. $[Cu(CH_3CN)_4]X$ (X = PF_6 or BF_4) were prepared according to the literature.[20] $AgNO_3$, $AgClO_4$ and $AgCF_3SO_3$ were purchased from Aldrich and used without further purifications. The 4-bpbd and 2-bpbd ligands were synthesized according to the literature.[21] All organic solvents were dried by usual methods and distilled before use. Infrared spectra were recorded with a JASCO 8000 spectrometer as KBr pellets.

† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b005006g/

 DOI: 10.1039/b005006g



Scheme 1

Preparation of silver(I) and copper(I) co-ordination polymers

(a) {[Cu_2(4-bpbd)$_3$(CH_3CN)$_2$][PF_6]$_2$·$2H_2O$)}$_n$ 1a·$2H_2O$. A CH_3CN solution (1 ml) of [Cu(CH_3CN)$_4$]PF_6 (37.2 mg, 0.10 mmol) was mixed with a $(CH_3)_2CO$ solution (9 ml) of 4-bpbd (20.4 mg, 0.10 mmol) for 30 min under Ar. The resultant orange suspension was sealed in a 5 mm diameter glass tube and warmed in hot water (*ca.* 90 °C) to form a clear yellow solution. This was slowly cooled to room temperature in a thermobottle over 3 days and red crystals were obtained. Calc. for $C_{46}H_{32}Cu_2F_{12}N_8OP_2$: C, 48.13; H, 2.99; N, 9.76. Found: C, 48.97; H, 3.06; N, 9.38%.

(b) {[Cu_2(4-bpbd)$_3$(CH_3CN)$_2$][BF_4]$_2$}$_n$ 1b. Complex **1b** was prepared in the same manner as **1a**·$2H_2O$, using [Cu(CH_3CN)$_4$]BF_4 (31.4 mg, 0.10 mmol). Red crystals were collected, which were not suitable for single-crystal X-ray analysis. Calc. for $C_{23}H_{15}BCuF_4N_4$: C, 55.50; H, 3.04; N, 11.26. Found: C, 57.03; H, 3.43; N, 10.49%.

(c) {[Ag(4-bpbd)]NO_3·CH_3CN}$_n$ 2a·CH_3CN. A CH_3CN solution (5 ml) of $AgNO_3$ (8.5 mg, 0.05 mmol) and a THF solution (5 ml) of 4-bpbd (10.2 mg, 0.05 mmol) were prepared in Schlenk tubes under Ar. The $AgNO_3$ solution was introduced into one compartment of a 5 mm diameter h-shaped glass tube and the 4-bpbd solution into the second compartment under Ar. These solutions were bridged by *n*-pentane and the h-shaped glass tube was sealed. It was allowed to stand at 5 °C for 6 months and colorless crystals were obtained. Calc. for $C_{16}H_{11}AgN_4O_3$: C, 46.29; H, 2.67; N, 13.50. Found: C, 45.06; H, 2.51; N, 12.39%.

(d) {[Ag(4-bpbd)]ClO_4·$(CH_3)_2CO$}$_n$ 2b·$(CH_3)_2CO$. A $(CH_3)_2$-CO solution (5 ml) of $AgClO_4$ (10.3 mg, 0.05 mmol) and a CH_2Cl_2 solution (5 ml) of 4-bpbd (10.2 mg, 0.05 mmol) were prepared in Schlenk tubes under Ar. 2 ml samples of the 4-bpbd solution, $(CH_3)_2CO$ solvent and the $AgClO_4$ solution were triply layered in a 5 mm diameter glass tube. The glass tube was sealed and allowed to stand at 5 °C for 3 days. Colorless crystals were obtained. Calc. for $C_{17}H_{14}AgClN_2O_5$: C, 43.48; H, 3.00; N, 5.79. Found: C, 42.27; H, 2.76; N, 7.10%.

(e) {[Ag(4-bpbd)]CF_3SO_3·$(CH_3)_2CO$}$_n$ 2c·$(CH_3)_2CO$. $AgCF_3$-SO_3 (12.8 mg, 0.05 mmol) in CH_3CN solution (5 ml) was mixed with 4-bpbd (5.1 mg, 0.025 mmol) in $(CH_3)_2CO$ solution (5 ml) for 30 min under Ar. The reaction solution was filtered and the filtrate introduced into one compartment of a 5 mm diameter h-shaped glass tube. Diethyl ether was introduced into the second compartment. The glass tube was sealed and allowed to stand at 5 °C for 3 days. Colorless crystals were obtained. Calc. for $C_{18}H_{14}AgF_3N_2O_4$: C, 41.64; H, 2.72; N, 5.39. Found: C, 40.09; H, 2.51; N, 6.04%.

(f) {[Cu(2-bpbd)$_2$]PF_6}$_n$ 3a. [Cu(CH_3CN)$_4$]PF_6 (37.2 mg, 0.10 mmol) was treated with 2-bpbd (20.4 mg, 0.10 mmol) in CH_3CN–$(CH_3)_2CO$ (10 ml, 1 : 9 v/v). After stirring for 30 min, the solution was filtered. The filtrate was introduced into a 5 mm glass tube and layered with *n*-pentane. The glass tube was sealed and allowed to stand at 5 °C for 1 week. The orange crystals were collected, but were not suitable for single-crystal X-ray analysis. Calc. for $C_{28}H_{16}CuF_6N_4P$: C, 54.51; H, 2.61; N, 9.08. Found: C, 53.34; H, 2.73; N, 9.35%.

(g) {[Cu(2-bpbd)$_2$]BF_4}$_n$ 3b. Complex **3b** was prepared in the same manner as **3a**, using [Cu(CH_3CN)$_4$]BF_4 (31.4 mg, 0.10 mmol). Orange crystals were collected. Calc. for $C_{28}H_{16}$-$BCuF_4N_4$: C, 60.18; H, 2.89; N, 10.03. Found: C, 59.64; H, 3.00; N, 10.07%.

(h) {[Ag(2-bpbd)(NO_3)]}$_n$ 4a. $AgNO_3$ (17.0 mg, 0.10 mmol) was mixed with 2-bpbd (20.4 mg, 0.10 mmol) in CH_3CN–CH_2Cl_2 (10 ml, 1 : 1 v/v). After stirring for 30 min the solution was filtered. The filtrate was introduced into a 5 mm glass tube and layered with *n*-pentane. The glass tube was sealed and allowed to stand at 5 °C for 3 days. Pale yellow crystals were collected. Calc. for $C_{14}H_8AgN_3O_3$: C, 44.95; H, 2.16; N, 11.23. Found: C, 44.31; H, 2.21; N, 11.16%.

(i) {[Ag(2-bpbd)]ClO_4}$_n$ 4b. Complex **4b** was prepared in the same way as **4a**, using $AgClO_4$ (20.6 mg, 0.10 mmol). Pale yellow crystals were collected, but were not suitable for single-crystal X-ray analysis. Calc. for $C_{14}H_8AgClN_2O_4$: C, 40.86; H, 1.96; N, 6.81. Found: C, 40.78; H, 2.12; N, 6.92%.

(j) {[Ag(2-bpbd)(CF_3SO_3)]}$_n$ 4c. 5 ml $(CH_3)_2CO$ solutions of $AgCF_3SO_3$ (6.4 mg, 0.025 mmol) and 2-bpbd (5.1 mg, 0.025 mmol) were prepared in Schlenk tubes under Ar. A 2 ml sample of each solution was layered in a 5 mm diameter glass tube, sealed and allowed to stand at 5 °C for 3 days. Colorless crystals were obtained. Calc. for $C_{15}H_8AgF_3N_2O_3S$: C, 39.07; H, 1.75; N, 6.07. Found: C, 40.27; H, 1.77; N, 5.91%.

Crystal structure determinations

X-Ray measurement of complex **1a**·$2H_2O$ was made with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) at 23 °C on a Quantum CCD area detector coupled with a Rigaku AFC-7 diffractometer. The data were corrected for Lorentz and polarization effects. **2a**·CH_3CN, **2b**·$(CH_3)_2CO$, **2c**·$(CH_3)_2CO$, **3b**, **4a** and **4c** were attached to ends of glass fibers and mounted on a Rigaku AFC-7R automated diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). The structures were solved by direct methods (SAPI 91[22a] for **1a**·$2H_2O$, **2a**·CH_3CN, **2c**·$(CH_3)_2CO$ and **4c**; SIR 88[22b] for **2b**·$(CH_3)_2CO$, **3b** and **4a**) and expanded using Fourier techniques.[22c] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically for **4a** and included but not refined for other complexes. The F atom of the PF_6 and BF_4 anion for **1a**·$2H_2O$ and **3b** and the O atom of solvated H_2O molecule of **1a**·$2H_2O$ are disordered. Atomic scattering factors and anomalous dispersion terms were taken from ref. 23. All calculations were performed using TEXSAN.[24] Crystal data and details of the structure determination are summarized in Table 1.

CCDC reference number 186/2192.

See http://www.rsc.org/suppdata/dt/b0/b005006g/ for crystallographic files in .cif format.

Results and discussion

2-D interwoven copper(I) co-ordination polymer: 1a·$2H_2O$

The reaction of the 4-bpbd ligand with $[Cu(CH_3CN)_4]X$ afforded red-brown crystals of $\{[Cu_2(4\text{-bpbd})_3(CH_3CN)_2]X_2\}_n$ (X = PF_6 **1a**·$2H_2O$ or BF_4 **1b**). The crystal structure of **1a**·$2H_2O$ was characterized crystallographically. It shows an undulating polycatenated molecular ladder involving fully interwoven 2-D sheets. The whole structural motif bears a close resemblance to that described for $\{[Cu_2(pybut)_3(CH_3CN)_2][PF_6]_2\cdot 0.5MeCN\cdot 0.5Et_2O\}_n$ (pybut = 1,4-bis(4-pyridyl)butadiyne), which was prepared by another procedure.[2f,14e] The structural difference is that the PF_6^- anion and two H_2O molecules are interposed between the fourfold interpenetrated 2-D sheets. The molecular structure of **1a**·$2H_2O$ was deposited as ESI, together with the bond distances and angles. Recently the features of ordered interpenetrating networks were reviewed by Batten and Robson.[2g] Molecular ladders have been observed for relatively few related systems and the metal junction of the ladder is pseudo-octahedral in $\{[Co_2(4,4'\text{-bpy})_3(NO_3)_4]\}_n$[25] and $\{[Cd_2(L)_3](NO_3)_4\}_n$ (L = 1,4-bis(4-methylpyridyl)benzene).[26] It was indicated that the 2-D ladder structure with linkage of the tetrahedral metal centers can be produced by combination of copper(I) ion and a rod-like ligand with a long spacer.

1-D straight chain silver(I) co-ordination polymers: 2a·CH_3CN, 2b·$(CH_3)_2CO$ and 2c·$(CH_3)_2CO$

A series of 1-D straight chain silver(I) co-ordination polymers $\{[Ag(4\text{-bpbd})]X\}_n$ (X = NO_3 **2a**·CH_3CN, ClO_4 **2b**·$(CH_3)_2CO$ or CF_3SO_3 **2c**·$(CH_3)_2CO$) were obtained by reaction of appropriate silver(I) salts with the 4-bpbd ligand. Similar co-ordination polymers $\{[Ag(pybut)]X\}_n$ (X = PO_2F_2 or NO_3) were reported as unpublished data in a recent report.[2f] The fragment structure of **2a**·CH_3CN, **2b**·$(CH_3)_2CO$ and **2c**·$(CH_3)_2CO$ is shown in Fig. 1, together with the atomic labeling scheme. Selected bond distances and angles are listed in the caption. In Fig. 1(b) complex **2b**·$(CH_3)_2CO$ has an inversion center of symmetry on the Ag(1) atom. Each Ag is co-ordinated by two N atoms of the 4-bpbd ligand in a completely linear geometry to form a 1-D straight chain structure of alternating silver(I) ions and 4-bpbd ligands. The ClO_4 anion is not co-ordinated, the Ag(1)···O(2) distance being 2.840(1) Å. Similarly, complexes **2a**·CH_3CN and **2c**·$(CH_3)_2CO$ afforded 1-D straight chain structures, although they are slightly wavy at the N–Ag–N angles of 169.5(1) and

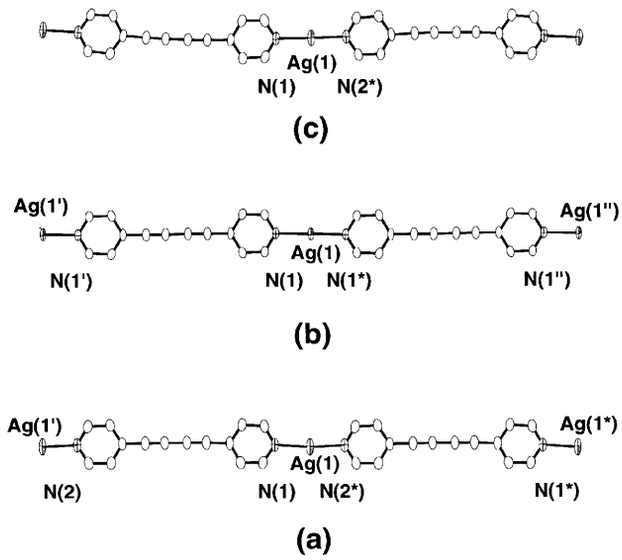


Fig. 1 The fragment structure of complexes **2a**·CH_3CN (a), **2b**·$(CH_3)_2CO$ (b) and **2c**·$(CH_3)_2CO$ (c). Selected bond distances (Å) and bond angles (°): **2a**·CH_3CN Ag(1)–N(1) 2.174(3) and Ag(1)–N(2*) 2.172(3); N(1)–Ag(1)–N(2*) 169.5(1); **2b**·$(CH_3)_2CO$ Ag(1)–N(1) 2.162(2) and Ag(1)–N(1*) 2.162(2); N(1)–Ag(1)–N(1*) 180.0; **2c**·$(CH_3)_2CO$ Ag(1)–N(1) 2.160(4) and Ag(1)–N(2*) 2.171(4); N(1)–Ag(1)–N(2*) 178.9(2).

178.9(2)°, respectively. The Ag(1)···O(1)(NO_3) 2.706(4) Å and Ag(1)···O(4) (CF_3SO_3) 2.869(8) Å distances are not indicative of co-ordination of the counter anion. In all of the silver(I) 4-bpbd complexes the two pyridyl groups of the co-ordinating 4-bpbd ligand are coplanar through the diyne portion. These 1-D straight chain co-ordination polymers assembled by the linkage of two-co-ordinate metal centers are structurally significant, since it seems that 1-D co-ordination polymers are generally assembled by linkage of square-planar and octahedral metal centers.[2d,e]

The molecular structures of complexes **2a**·CH_3CN and **2b**·$(CH_3)_2CO$ are depicted in Figs. 2 and 3, and that of **2c**·$(CH_3)_2CO$ is deposited as ESI. As mentioned above, the parallel 1-D straight chains constructed alternately by Ag atoms and 4-bpbd ligands are *ca.* 7.64 Å apart in **2a**·CH_3CN. The counter anion NO_3^- and the CH_3CN molecule lie between these chains. Similarly, the 1-D straight chains are *ca.* 7.94 and 8.91 Å apart in **2b**·$(CH_3)_2CO$ and **2c**·$(CH_3)_2CO$. The counter anion and solvent molecule {ClO_4^- and $(CH_3)_2CO$ and $CF_3SO_3^-$ and $(CH_3)_2CO$} are situated between the 1-D co-ordination chains for **2b**·$(CH_3)_2CO$ and **2c**·$(CH_3)_2CO$, respectively. Incidentally, Schröder and co-workers recently reported the effect of ligand functionality and anion functionality on 1-D silver(I) co-ordination polymers.[2f] In $\{[Ag(4,4'\text{-bpy})]BF_4\}_n$ 1-D linear chains of alternating silver(I) ions and 4,4′-bpy ligands lie parallel within the crystal structure but are staggered, minimizing Ag···Ag contacts and π–π interactions between adjacent chains. The structure of $\{[Ag(pybut)](PO_2F_2)\}_n$ contains pairs of 1-D linear chains of alternating silver(I) ions and bipyridyl ligands, resembling a ladder structure with π–π interactions of 3.394 Å and Ag···Ag interactions of 3.1929(10) Å. A similar ladder-like motif has been found in $\{[Ag(4\text{-pytz})]X\}_n$ (4-pytz = 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine, X = BF_4 or PF_6)[13a] and $\{[Ag(3\text{-pytz})]CF_3SO_3\}_n$[2f] with Ag···Ag interactions of 3.312(1), 3.230(1) and 3.2199(13) Å, respectively. In $\{[Ag(pybut)](NO_3)\}_n$ the Ag···Ag and π-π interactions are also replaced by weak interactions involving the NO_3^- anion. The 1-D linear chains no longer link pairwise to form ladders with Ag···Ag interactions. The weakly co-ordinating NO_3^- anions bridge between adjacent chains so as to form staggered pairs of chains. On the other hand, the side views of **2a**·CH_3CN, **2b**·$(CH_3)_2CO$ and **2c**·$(CH_3)_2CO$ reveal that the

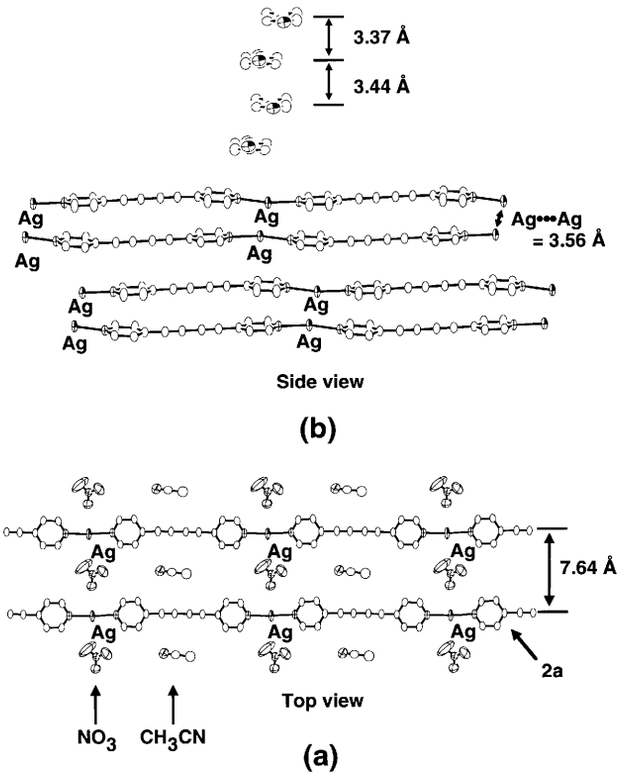


Fig. 2 The molecular structure of complex **2a**·CH_3CN. Top view (a) and side view (b).

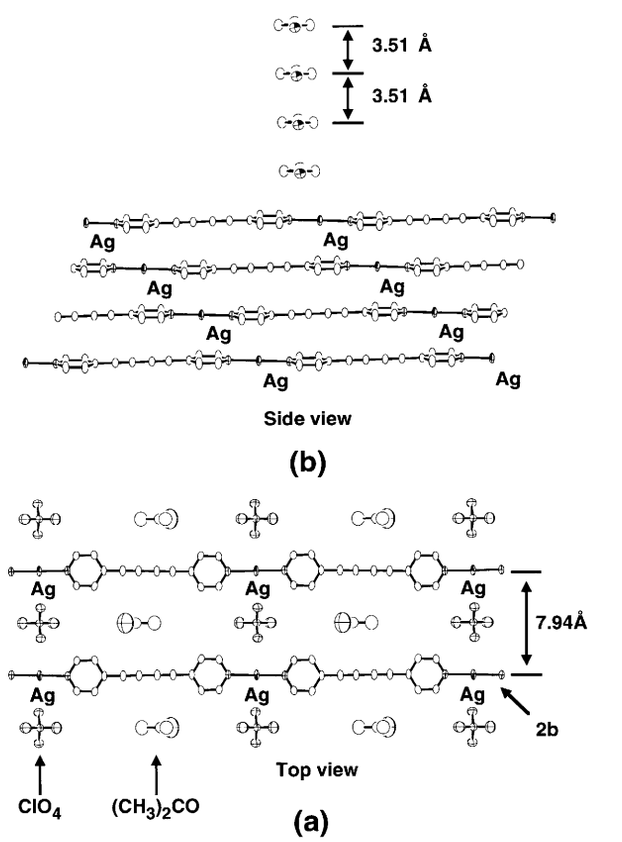


Fig. 3 The molecular structure of complex **2b**·$(CH_3)_2CO$. Top view (a) and side view (b).

parallel 1-D straight chains of **2a**·CH_3CN are nearly overlapping at *ca.* 3.37 and 3.44 Å, and the Ag···Ag separation of 3.56 Å is not bridged by the NO_3^- anions. Moreover, the parallel 1-D straight chains of **2b**·$(CH_3)_2CO$ and **2c**·$(CH_3)_2CO$ are not ladder-like motifs but are staggered at *ca.* 3.51 and 3.33 Å, respectively. Thus, structural differences with $\{[Ag(pybut)]X\}_n$ ($X = PO_2F_2$ or NO_3)[2f] are probably derived from the occurrence of solvent molecules between the 1-D straight chains. It was demonstrated that the accommodation of solvent molecules is greatly related to an essential factor in the construction of longer-range silver(I) arrays, in addition to the effects of ligand functionality and anion functionality.[2f]

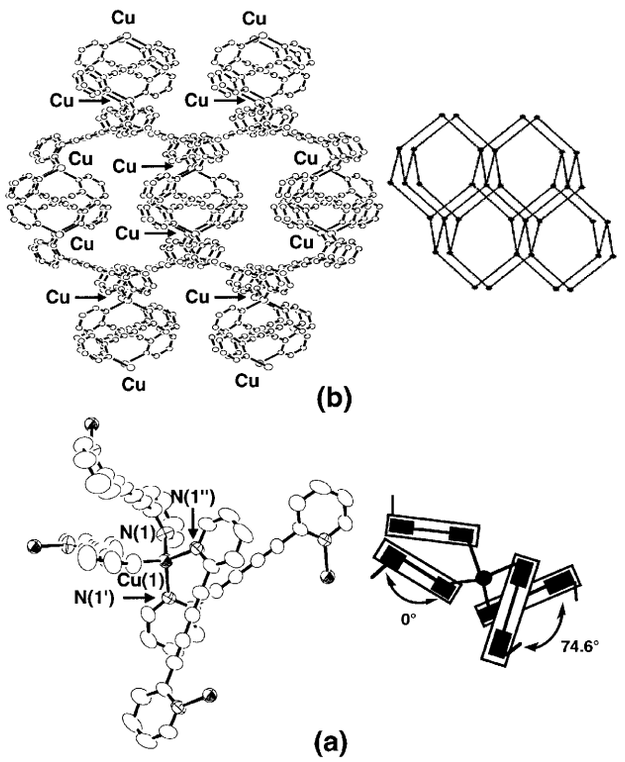


Fig. 4 The fragment structure (a) and the molecular structure (b) of complex **3b**. Selected bond distances (Å) and angles (°): Cu(1)–N(1) 2.070(6), Cu(1)–N(1′) 2.070(6), Cu(1)–N(1″) 2.070(6) and Cu(1)–N(1*) 2.070(6); N(1)–Cu(1)–N(1′) 105.7(1), N(1)–Cu(1)–N(1″) 105.7(1), N(1)–Cu(1)–N(1*) 117.4(3), N(1′)–Cu(1)–N(1″) 117.4(3), N(1′)–Cu(1)–N(1*) 105.7(1), N(1″)–Cu(1)–N(1*) 105.7(1), Cu(1)–N(1)–C(1) 122.4(5) and Cu(1)–N(1)–C(5) 122.4(5).

3-D diamondoid copper(I) co-ordination polymer: 3b

On the basis of the above crystallographic studies, it was obvious that the 4-bpbd ligand can provide a remarkable 2-D interwoven and 1-D straight chain structure for Cu^I and Ag^I, respectively. The 2-bpbd ligand is expected to produce an even more attractive co-ordination structure, since it can be co-ordinated in a *cisoid* or *transoid* conformation, similar to the 3,3′-dicyanodiphenylacetylene ligand.[27] According to the Experimental section, the reaction of $[Cu(CH_3CN)_4]BF_4$ with 2-bpbd afforded a 3-D diamondoid copper(I) co-ordination polymer $\{[Cu(2\text{-}bpbd)_2]BF_4\}_n$ **3b**. The fragment structure and the molecular structure of **3b** are shown in Fig. 4. Selected bond distances and angles are listed in the caption. Each Cu atom is co-ordinated by four equivalent N atoms from the 2-bpbd ligand in a tetrahedral geometry. The Cu–N distance of 2.070(6) Å and the N–Cu–N angles of 105.7(1) and 117.4(3)° are almost equal to those of typical tetrahedral copper(I) complexes.[28] The pyridyl groups of the 2-bpbd ligands are coplanar through the diyne portion. The dihedral angle between the planes defined by two 2-bpbd ligands is *ca.* 74.6° *via* the Cu atom. The tetrahedral copper centers are in helices joined by the 2-bpbd ligands in a *transoid* conformation. The most remarkable feature is that the framework of the linkage of Cu atoms reveals a 3-D diamondoid structure with a $Cu^I \cdots Cu^I$ separation of 8.34 Å, which is not indicative of an attractive intermolecular interaction. The BF_4^- counter anions occupy vacant space in the crystal packing, which is not concurrent with interpenetration and π–π stacking.

Several co-ordination polymers with diamondoid and related frameworks have recently been reported.[2b,g,29] In particular, the copper(I) and silver(I) ions having d^{10} electronic configuration are suitable for tetrahedral geometries in a diamondoid framework. Diamond-related frameworks have been constructed by combination of a tetrahedral metal ion and a bridging ligand, *e.g.* pyrazine,[30] 4,4′-bipyridine,[13d–f] bisnitrile ligand[27,31] and related compounds,[15,16a] which in many cases generates a π–π interaction (stacking) and an interpenetrated structure. For instance, pyrazine (pz) and its derivatives are the shortest bridging ligands. The copper(I) ion in $[Cu(2,5\text{-}Me_2pz)_2]PF_6$[30] has a tetrahedral geometry with co-ordination of four N atoms of 2,5-dimethylpyrazine (2,5-Me_2pz). Coordination of the other N atoms of each 2,5-Me_2pz to other copper(I) ions results in the formation of a diamondoid framework with the shortest $Cu^I \cdots Cu^I$ separation of 6.99 Å. The presence of the PF_6^- counter anion and methyl groups in 2,5-Me_2pz prevents interpenetration of any other framework. On the other hand, 4,4′-bipyridine provided fourfold interpenetrated diamondoid frameworks for both Cu^I and Ag^I. The copper(I) compound $[Cu(4,4'\text{-bpy})_2]PF_6$[13d] exists as four independent concatenated diamondoid frameworks with Cu ··· Cu separations of 11.16 Å, in which the PF_6^- counter anions occupy channels. The silver(I) compound $[Ag(4,4'\text{-bpy})_2]CF_3SO_3$[13e] contains four interpenetrating diamondoid frameworks with a $Ag^I \cdots Ag^I$ intraframework separation of *ca.* 11.6 Å. The copper(I) complex $[Cu(4,4'\text{-bpy})_{1.5}]NO_3 \cdot 1.25H_2O$[13f] showed sixfold interpenetrated frameworks with an interconnection of trigonal copper(I) centers through 4,4′-bpy by hydrothermal synthesis. A 1,2-*trans*-bis(4-pyridyl)ethene (4-bpe) ligand with a long spacer and a specific directionality afforded the copper(I) compound $[Cu(4\text{-bpe})_2]BF_4 \cdot 0.5CH_2Cl_2$[16a] with fivefold interpenetrated diamondoid frameworks. The Cu ··· Cu distances bridged by 4-bpe ranged from 13.33 to 13.82 Å to create large cavities within the diamondoid framework. All five independent frameworks are polycatenated with channels throughout the structure, and these channels accommodate BF_4^- counter anions and CH_2Cl_2 solvent molecules. A *transoid* conformation of 3,3′-dicyanodiphenylacetylene (3,3′-dcpa) afforded the silver(I) compound $[Ag(3,3'\text{-dcpa})_2]ClO_4 \cdot H_2O$ with eightfold interpenetrated diamondoid frameworks,[27] which possessed the long $Ag^I \cdots Ag^I$ distance of *ca.* 17.0 Å. A majority of the large amount of void space created in a single diamondoid framework is filled through interpenetration. The remaining space within the lattice is filled by perchlorate ions and water. Thus, in many cases interpenetration and accommodation of solvent molecules or counter anions fill the vacant space in crystal packing. It has been suggested that the degree of interpenetration in a diamondoid structure is strongly correlated with the bridging M ··· M distance, counter anion size and π–π stacking distance. This is supported by a model study; it was found that the longer the M ··· M distance, the greater is the degree of interpenetration.[29c] In contrast, in our crystallographic study, it is remarkable that complex **3b** did not display interpenetration and π–π stacking, regardless of the use of the 2-bpbd ligand with a rigid long spacer and a specifically co-ordinative orientation. Although the $Cu^I \cdots Cu^I$ separation of 8.34 Å is longer than that (6.99 Å) of 3-D interpenetrated copper(I) co-ordination polymers of 2,5-Me_2pz,[30] the separation is rather shorter than those of the 3-D interpenetrated copper(I) and silver(I) co-ordination polymers[13d–f,16a,27] of 4,4′-bpy, 4-bpe and 3,3′-dcpa mentioned above. This result is in good agreement with the above suggestions. It was proposed that the specifically co-ordinative orientation of 2-bpbd and the favorable counter anion size of BF_4^- might prevent interpenetration of other frameworks.[29c]

1-D zigzag chain silver(I) co-ordination polymer: 4a

The reaction of $AgNO_3$ with the 2-bpbd ligand provided an interesting 1-D zigzag chain silver(I) co-ordination polymer $\{[Ag(2\text{-bpbd})(NO_3)]\}_n$ **4a**, in contrast to the 1-D straight chain co-ordination polymer **2a**·CH_3CN provided by $AgNO_3$ and the 4-bpbd ligand. The fragment structure of **4a** is shown in Fig. 5(a). Selected bond distances and angles are listed in the caption. Each Ag atom is co-ordinated by two N atoms of the 2-bpbd ligand and the O atom of the NO_3^- anion in a Y-shaped trigonal geometry:[32] The Ag(1)–O(1) distance of 2.532(1) Å is longer than other distances of Ag(1)–N(1) 2.240(2) and Ag(1)–N(2) 2.274(2) Å, whereas the O(1)–Ag(1)–N(2) angle of 88.30(6)° is smaller than other angles of N(1)–Ag(1)–N(2) 130.81(5) and O(1)–Ag(1)–N(1) 139.69(6)°. The silver center is linked by 2-bpbd ligands in a *transoid* conformation to provide a 1-D zigzag chain structure. The pyridyl groups of the 2-bpbd ligands are coplanar through the diyne portions. The dihedral angle between the planes defined by the two 2-bpbd ligands is 97.5° through each Ag atom. Therefore, the ligands intersect at nearly right angles to each other.

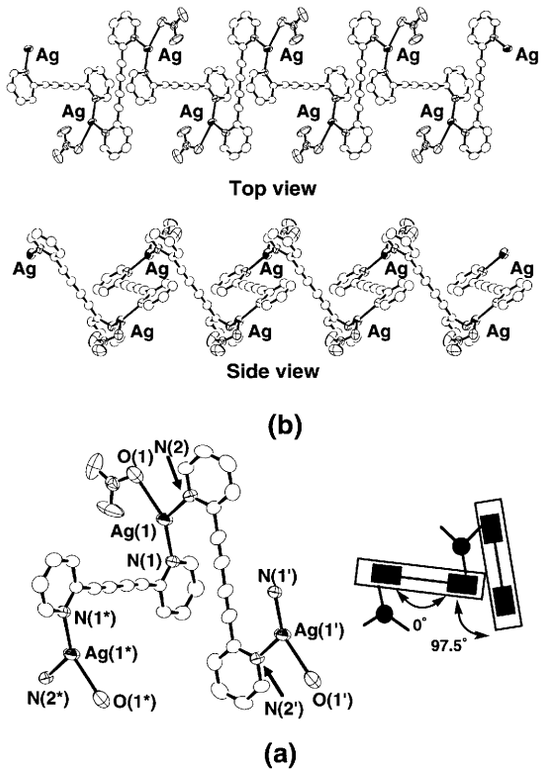


Fig. 5 The fragment structure (a) and the molecular structure (b) of complex **4a**. Selected bond distances (Å) and angles (°): Ag(1)–O(1) 2.532(1), Ag(1)–N(1) 2.240(2) and Ag(1)–N(2) 2.274(2); O(1)–Ag(1)–N(1) 139.69(6), O(1)–Ag(1)–N(2) 88.30(6), N(1)–Ag(1)–N(2) 130.81(5), Ag(1)–O(1)–N(3) 103.1(1), Ag(1)–N(1)–C(1) 120.6(2), Ag(1)–N(1)–C(5) 122.3(1), Ag(1)–N(2)–C(10) 121.2(1) and Ag(1)–N(2)–C(14) 120.9(1).

The molecular structure is shown in Fig. 5(b). The 1-D zigzag chains are completely separated and no intermolecular interaction was found between them. It has recently been reported that the 1-D silver(I) co-ordination polymer $\{[Ag(2\text{-bpbd})(NO_3)]\}_n$,[33] which has the same components and the two pyridine rings attached to each tetrahedral Ag approximately coplanar, has a ribbon-like metallopolymeric structure. It resembles the structural motif in the 1-D silver(I) co-ordination polymer $\{[Ag(2,2'\text{-dcpa})(CF_3SO_3)]\}_n$[34] of 2,2′-dicyanodiphenylacetylene (2,2′-dcpa), in which 2,2′-dcpa co-ordinates to a distorted trigonal Ag atom in a *transoid* conformation, resulting in a half-bow-tie motif for chains and a flat 1-D silver(I) infinite chain constructed by the alternate arrangement of Ag atoms and 2,2′-dcpa. In contrast, the 2-bpbd ligands of **4a** in our crystallographic study are not coplanar to each Ag atom but intersect at nearly right angles to each other. Consequently,

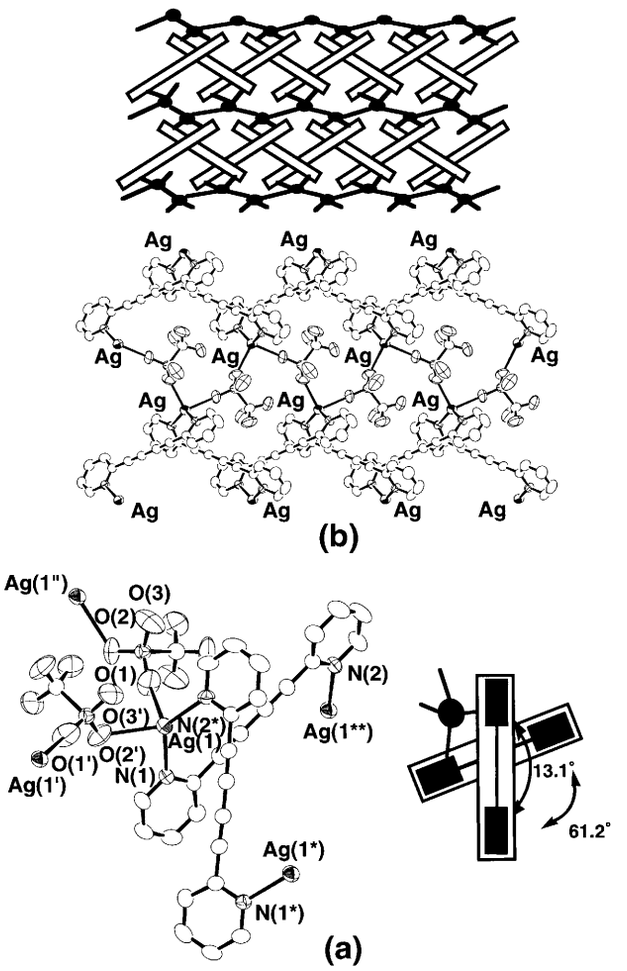


Fig. 6 The fragment structure (a) and the molecular structure (b) of complex **4c**. Selected bond distances (Å) and angles (°): Ag(1)–O(2′) 2.572(4), Ag(1)–O(1) 2.445(4), Ag(1)–N(1) 2.258(3) and Ag(1)–N(2*) 2.239(3); O(2′)–Ag(1)–O(1) 86.6(1), O(2′)–Ag(1)–N(1) 88.1(1), O(2′)–Ag(1)–N(2*) 136.2(1), O(1)–Ag(1)–N(1) 106.5(2), O(1)–Ag(1)–N(2*) 98.4(2), N(1)–Ag(1)–N(2*) 130.6(1), Ag(1)–O(2′)–S(1′) 111.4(2), Ag(1)–O(1)–S(1) 164.2(4); Ag(1)–N(1)–C(1) 123.8(3), Ag(1)–N(1)–C(5) 118.6(2), Ag(1)–N(2*)–C(10*) 119.5(3) and Ag(1)–N(2*)–C(14*) 122.4(3).

the whole motif of **4a** is greatly different from those found in $\{[Ag(2\text{-bpbd})(NO_3)]\}_n$[33] and $\{[Ag(2,2'\text{-dcpa})(CF_3SO_3)]\}_n$.[34] Thus the structural differences are probably attributable to conditions of preparation, *i.e.* the solvents used and the reaction temperature.

2-D braid sheet silver(I) co-ordination polymer: 4c

It is known that a counter anion such as NO_3, ClO_4 or CF_3SO_3 can act as a useful bridging ligand. The 2-D braid sheet silver(I) co-ordination polymer $\{[Ag(2\text{-bpbd})(CF_3SO_3)]\}_n$ **4c** was constructed by the use of $AgCF_3SO_3$ (instead of $AgNO_3$), compared with the 1-D zigzag chain silver(I) co-ordination polymer formed by $AgNO_3$ and the 2-bpbd ligand. The fragment structure of **4c** is shown in Fig. 6(a). Selected bond distances and angles are listed in the caption. Each Ag atom is co-ordinated by two N atoms of the 2-bpbd ligand and two O atoms of CF_3SO_3 in a distorted tetrahedral geometry. The tetrahedral silver centers are connected by 2-bpbd ligands in a *transoid* conformation. The pyridyl groups of the 2-bpbd ligand are slightly twisted through the diyne portions at 13.1°, and this structural feature is unique among the copper(I) and silver(I) co-ordination polymers of 2-bpbd and 4-bpbd in this study. The dihedral angle between the mean planes defined by each 2-bpbd ligand is 61.2° *via* the Ag atom. Consequently, a 1-D braid chain structure is formed by the alternating Ag atoms and

Table 1 Crystallographic data and details of the structure determination

	1a·2H_2O	**2a**·CH_3CN	**2b**·$(CH_3)_2CO$	**2c**·$(CH_3)_2CO$	**3b**	**4a**	**4c**
Formula	$C_{46}H_{34}Cu_2F_{12}N_8O_2P_2$	$C_{16}H_{11}AgN_4O_3$	$C_{17}H_{14}AgClN_2O_5$	$C_{18}H_{14}AgF_3N_2O_4S$	$C_{28}H_{16}BCuF_4N_4$	$C_{28}H_{16}Ag_2N_6O_6$	$C_{15}H_8AgF_3N_2O_3S$
Formula weight	11147.85	415.16	469.63	519.24	558.81	748.2	461.16
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Tetragonal	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/m$	$P2_1/c$	$I4_1/a$	$P\bar{1}$	$P2_1/c$
a/Å	12.639(2)	14.739(6)	5.296(2)	11.399(3)	10.626(3)	9.918(3)	15.870(4)
b/Å	15.558(2)	7.644(4)	15.876(6)	17.818(1)		10.625(3)	10.912(4)
c/Å	16.5787(5)	7.582(5)	10.889(3)	10.157(3)	25.718(3)	7.398(3)	9.457(5)
α/°	113.349(1)	75.66(5)				95.33(2)	
β/°	91.187(2)	89.36(5)	100.47(4)	104.98(2)		102.96(3)	99.32(3)
γ/°	106.020(1)	80.00(4)				113.84(2)	
V/Å^3	2845.3(5)	814.7(8)	900.3(6)	1992(1)	2903.8(10)	680.0(4)	1616(1)
Z	2	2	2	4	4	1	4
μ(Mo-Kα)/cm^{-1}	8.84	12.55	12.95	11.68	7.99	14.91	14.22
T/K	296	296	296	296	296	296	296
Measured reflections	12379	4004	1829	4824	1853	3308	3943
Observed reflections ($I > 2\sigma(I)$)	6748	2644	1424	2583	701	2529	2578
R	0.111	0.041	0.024	0.055	0.093	0.029	0.041
R_w	0.358	0.123	0.071	0.180	0.297	0.073	0.103

2-bpbd ligands. The 1-D braid chains are further bridged by CF_3SO_3 anions to provide a quite interesting 2-D braid sheet structure. The molecular structure is shown in Fig. 6(b). So far, various motifs of 2-D copper(I) and silver(I) co-ordination polymers have been reported,[2] including hexagonal, helical (spiral), zigzag, square grid, rectangular grid, ladder (railroad-like), rhombic and honeycomb grid. However, to the best of our knowledge, complex **4c** is the first 2-D co-ordination polymer having a braid sheet structure. It is considered that the specifically co-ordinative direction of functional groups and the rigid long spacer in the rod-like 2-bpbd ligand greatly contributed to the formation of the 2-D braid sheet structure.

Acknowledgements

We thank Mr. Koji Okuno and Mr. Shigeru Maeda for their respective assistances. This work was partially supported by a Grant-in-Aid for Science Research from the Ministry of Education, Science, Culture and Sports in Japan.

References

1 (*a*) E. C. Constable, *Adv. Inorg. Chem.*, 1989, **34**, 1; (*b*) *Supramolecular Chemistry*, eds. V. Balzani and L. De Cola, Kluwer, Dordrecht, 1992; (*c*) L. Fabbrizzi and A. Poggi, *Transitional Metals in Supuramolecular Chemistry*, eds. L. Fabbrizzi and A. Poggi, Kluwer Academic Publishers, Dordrecht, 1994; (*d*) F. Vögtle, *Supramolecular Chemistry*, Wiley, Chichester, 1993; (*e*) *Comprehensive Supramolecular Chemistry*, ed. J.-M. Lehn, Pergamon Press, Oxford, 1995, vol. 9; (*f*) E. C. Constable, *Prog. Inorg. Chem.*, 1994, **2**, 92; (*g*) J.-M. Lehn, in *Perspectives in Coordination Chemistry*, eds. A. F. Williams, C. Floriani and A. E. Merbach, VHCA, Basel, 1992; (*h*) R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskin and J. Liu, *Supramolecular Architecture*, ed. T. Bein, American Chemical Society, Washington, DC, 1992, ch. 19, p. 256.
2 (*a*) M. Munakata, L.-P. Wu and T. Kuroda-Sowa, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1727; (*b*) M. Munakata, L.-P. Wu and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, 1999, **46**, 173; (*c*) S. Kitagawa and M. Munakata, *Trends Inorg. Chem.*, 1993, 3; (*d*) S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1739; (*e*) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; (*f*) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; (*g*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, 37, 1460.
3 M. Fujita, Y. J. Kwon, S. Washiza and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.
4 E. T. Bein, *ACS Symp. Ser.*, 1992, 499.
5 O. Ermer, *Adv. Mater.*, 1991, 3, 608.
6 K. Inoue, T. Hayamizu, H. Iwamura, D. Hashizume and Y. Ohashi, *J. Am. Chem. Soc.*, 1996, **118**, 1803.
7 R. Robson, in *Comprehensive Supramolecular Chemistry*, eds. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle and J.-M. Lehn, Pergamon, New York, 1996, vol. 6, p. 733.
8 J.-M. Lehn, *Pure Appl. Chem.*, 1994, **66**, 1961.
9 G. R. Desiraju, *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam, 1989.
10 M. C. Etler, *Acc. Chem. Res.*, 1990, 23, 120.
11 G. R. Desiraju, *The Crystal as a Supramolecular Entity*, Wiley, New York, 1995; G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
12 (*a*) A. S. Batsanov, M. J. Begley, P. Hubberstey and J. Stroud, *J. Chem. Soc., Dalton Trans.*, 1996, 1947; (*b*) A. J. Blake, S. J. Hill, P. Hubberstey and W.-S. Li, *J. Chem. Soc., Dalton Trans.*, 1998, 909; (*c*) D. Hagrman, C. Zubieta, D. J. Rose, J. Zubieta and R. C. Haushalter, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 873; (*d*) M. Li, Z. Xu, X. You, Z. Dong and G. Guo, *Polyhedron*, 1993, **12**, 921; (*e*) J. Lu, G. Crisci, T. Niu and A. J. Jacobson, *Inorg. Chem.*, 1997, **36**, 5140; (*f*) P.-J. Prest and J. S. Moore, *Acta Crystallogr., Sect. C*, 1996, **52**, 2176.
13 (*a*) M. A. Withersby, A. J. Blake, N. R. Champress, P. Hubberstey, W.-S. Li and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2327; (*b*) J. Y. Lu, B. R. Cabrera, R.-J. Wang and J. Li, *Inorg. Chem.*, 1999, **3**, 4608; (*c*) O. M. Yaghi and G. Li, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 207; (*d*) L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1994, 1325; (*e*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1994, 2755; (*f*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401; (*g*) T. Soma, H. Yuge and T. Iwamoto, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1665; (*h*) F. Robinson and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1995, 2413; (*i*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295.
14 (*a*) M. Maekawa, K. Sugimoto, T. Kuroda-Sowa, Y. Suenaga and M. Munakata, *J. Chem. Soc., Dalton Trans*, 1999, 4357; (*b*) J. T. Lin, M.-F. Yang, C. Tsai and Y. S. Wen, *J. Organomet. Chem.*, 1998, **564**, 257; (*c*) J. R. Allan, M. J. Barrow, P. C. Beaumont, L. A. Macindoe, G. H. W. Milburn and A. R. Werninck, *Inorg. Chim. Acta*, 1988, **148**, 85; (*d*) B. F. Abrahams, M. J. Hardie, B. F. Hoskins, R. Robson and E. E. Sutherland, *J. Chem. Soc., Chem. Commun.*, 1994, 1049; (*e*) A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovskii, W.-S. Li and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1997, 2027; (*f*) J. T. Lin, S.-S. Sun, J. J. Wu, L. Lee, K.-J. Lin and Y. F. Huang, *Inorg. Chem.*, 1995, **34**, 2333; (*g*) M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi and K. Ogura, *J. Chem. Soc., Chem. Commun.*, 1996, 1535.
15 A. J. Blake, N. R. Champness, A. N. Khlobystov, D. A. Lemenovsk, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 1339.
16 (*a*) A. J. Blake, N. R. Champness, S. S. M. Chung, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 1005; (*b*) Y.-B. Dong, R. C. Layland, M. D. Smith, N. G. Pschirer, U. H. F. Bunz and H.-C. zur Loye, *Inorg. Chem.*, 1999, **38**, 3056; (*c*) D. Hagrman, R. P. Hammond, R. Haushalter and J. Zubieta, *Chem. Mater.*, 1998, **10**, 2091; (*d*) M. J. Irwin, J. J. Vittal, G. P. A. Yap and R. J. Puddephatt, *J. Am. Chem. Soc.*, 1996, **118**, 13101; (*e*) G. Mago, M. Hinago, H. Miyasaka, N. Matsumoto and H. Okawa, *Inorg. Chim. Acta*, 1997, **254**, 145; (*f*) G. D. Munno, D. Armentano, T. Poerio, M. Julve and J. A. Real, *J. Chem. Soc., Dalton Trans.*, 1999, 1813; (*g*) J. A. Real, E. Andres, M. C. Munoz, M. Julve, T. Granier, A. Bousseksou and F. Varret, *Science*, 1995, **268**, 265; (*h*) S. Wang, H.-L. Tsai, K. Folting, J. D. Martin, D. N. Hendrickson and G. Christou, *J. Chem. Soc., Chem. Commun.*, 1994, 671; (*i*) L. Carlucci, G. Ciani and D. M. Proserpio, *J. Chem. Soc., Dalton Trans.*, 1999, 1799.
17 S. Noro, M. Kondo, T. Ishii, S. Kitagawa and H. Matsuzaka, *J. Chem. Soc., Dalton Trans.*, 1999, 1569.
18 Y. B. Dong, M. D. Smith, R. C. Layland and H.-C. zur Loye, *Inorg. Chem.*, 1999, **38**, 5207; M. L. Hernandez, M. G. Barandika, M. K. Urtiaga, R. Cortes, L. Lezama, M. I. Arriortua and T. Rojo, *J. Chem. Soc., Dalton Trans.*, 1999, 1401; C. S. Hong, S.-K. Spn, Y. S. Lee, M.-J. Jun and Y. Do, *Inorg. Chem.*, 1999, **38**, 5602.
19 T. Soma and T. Iwamoto, *Acta Crystallogr., Sect. C*, 1997, **53**, 1819; L. Carlucci, G. Ciani, D. W. v. Gudenberg and D. M. Proserpio, *Inorg. Chem.*, 1997, **36**, 3812.
20 G. J. Grubus, *Inorg. Synth.*, 1979, **19**, 90.
21 L. D. Ciana and A. Haim, *J. Heterocycl. Chem.*, 1984, **21**, 607; U. Fritzsche and S. Hunig, *Tetrahedron Lett.*, 1972, 4831; J. G. Rodriguez, R. Martin-Villamil, F. H. Cano and I. Fonseca, *J. Chem. Soc., Perkin Trans. 1*, 1997, 709.
22 (*a*) F. Hai-Fu, SAPI 91. Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, 1991; (*b*) SIR 88, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, *J. Appl. Crystallogr.*, 1989, **22**, 389; (*c*) P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, The DIRDIF 94 program system. Technical Report of the Crystallography Laboratory, Univeristy of Nijmegen, 1994.
23 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. IV.
24 TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.
25 P. Losier and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2779.
26 M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 7287.
27 K. A. Hirsch, S. R. Wilson and J. S. Moore, *Inorg. Chem.*, 1997, **36**, 2960.
28 B. J. Hathaway, *Comprehensive Coordination Chemistry*, ed. S. G. Wilkinson, Pergamon Press, Oxford, 1987, vol. 5, sect. 53, pp. 533–774.
29 (*a*) M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, **23**, 283; (*b*) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546; (*c*) K. A. Hirsch, S. R. Wilson and J. S. Moore, *Eur. J. Chem.*, 1997, **3**, 765.
30 T. Otieno, S. J. Rettig, R. C. Thompson and J. Trotter, *Inorg. Chem.*, 1993, **32**, 1607.
31 T. Kuroda-Sowa, T. Horino, M. Yamamoto, Y. Ohno, M. Maekawa and M. Munakata, *Inorg. Chem.*, 1997, **36**, 6382.
32 M. Munakata, M. Maekawa, S. Kitagawa and S. Matsuyama, *Inorg. Chem.*, 1989, **28**, 4300.
33 C. Richardson and P. J. Steel, *Inorg. Chem. Commun.*, 1998, **1**, 260.
34 K. A. Hirsch, S. R. Wilson and J. S. Moore, *J. Am. Chem. Soc.*, 1997, **119**, 10401.