Crystal structure of the coordination polymer $[Co(bipy)_{1.5}(NO_3)_2] \cdot CS_2$ (bipy = 4,4′-bipyridine), a new motif for a network sustained by ‘T-shape’ building blocks

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The crystal structure of the coordination polymer $[Co(bipy)_{1.5}(NO_3)_2] \cdot$ **1** (bipy = 4,4′-bipyridine), reveals that, if crystallized in the presence of CS_2, it exists as a novel two-dimensional bilayer motif. This is in contrast to what might have been expected since a one-dimensional molecular-ladder motif is exhibited by **1** when crystallized in the presence of MeCN or $CHCl_3$. A molecule of CS_2 is clathrated inside the bilayer *via* what appear to be C—H···S hydrogen bonds from 4,4′-bipyridine ligands. Adjacent bilayers pack efficiently in a gear-like fashion. The existence of this new structural supramolecular isomer is rationalized on the basis of a template effect from the CS_2 guest molecule.

Crystal engineering in the context of organic solids[1–3] is now a relatively well established area of research that dates to the studies of Schmidt[4] in the context of solid-state photochemistry. It is therefore somewhat surprising that crystal engineering involving transition metals has lagged until very recently, especially when one considers that the metal–ligand bond, being a donor–acceptor interaction, is conceptually related to the hydrogen bond. A pioneer in crystal engineering involving transition metals, coordination polymers, is Prof. R. Robson, whose seminal paper in 1990[5] has been followed by a number of important communications and a recent review.[6] The most common strategy that has thus far been applied in the context of the design of coordination polymers is to generate a coordination polymer network that is a simple extension of transition metal or metal cluster coordination geometry. For this approach to become effective one requires exodentate bifunctional ligands to link metal moieties. The metal coordination environment therefore functions as the node which defines the overall network geometry of the coordination polymer. Such a strategy would, for example, be expected to afford any of the architectures illustrated in Fig. 1. An alternate strategy involves the exploitation of exodentate multitopic ligands which also act as nodes in the network architecture. This strategy is less predictable and requires design of new ligands. Nevertheless, the latter approach has already generated a number of mineralomimetic architectures with interesting properties in terms of inclusion chemistry.[7–9]

We and others have used the former strategy to generate a number of novel architectures by using simple bifunctional ligands such as pyrazine[10–12] and 4,4′-bipyridine (bipy).[10,13–17] The stoichiometry of metal : bipy is a critical factor in terms of defining and limiting the possible architectures that can occur in a coordination polymer. For example, a 1 : 1 ratio limits the architecture to either linear or zig-zag chains whereas a 1 : 2 ratio generates either square grid[13,14] or diamondoid[10,15–17] networks depending upon the metal coordination geometry. For a 1 : 1.5 ratio any one of the four architectures illustrated schematically in Fig. 2 might be encountered if the ligand is bipy or a related ligand such as bis(4-pyridyl)ethane (bipy-Et). The architectures illustrated by motifs (a),[18,19] (b)[19] and (d)[20,21] have already been observed but (c), which could be called a molecular bilayer, was to our knowledge not reported until very recently.[22] In this contribution we report the first example of such a motif in a coordination polymer, the network exhibited by $[Co(bipy)_{1.5}(NO_3)_2] \cdot CS_2$, $\mathbf{1} \cdot CS_2$.

Experimental

Synthesis of $\mathbf{1} \cdot CS_2$

A solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.04 g, 0.1 mmol) in MeOH (25 ml) was added to a solution of bipy (0.06 g, 0.4 mmol) and naphthalene (0.08 g, 0.6 mmol) in CS_2 (5 ml). After standing overnight at room temperature, cranberry-red crystals of **1** were obtained (yield: 0.03 g, 0.07 mmol, 50%). The presence of CS_2 was confirmed by IR spectroscopy. Crystals exposed to the atmosphere become opaque within several hours.

X-Ray crystallography

A dark red single crystal of $\mathbf{1} \cdot CS_2$ was placed and sealed in a thin-walled glass capillary and optically centered on an Enraf-Nonius CAD-4 diffractometer. Cell dimensions, obtained from 25 reflections with 2θ angles in the range 41–48°, are found along with other pertinent data collection parameters in Table 1. The intensities were reduced and Lorentz and polarization factors were applied. No corrections were made for extinction but an empirical absorption correction was applied (transmission factors 0.82–0.96). The structure was solved by direct methods and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions with $D_{C\text{–}H} = 1.08$ Å and were fixed during least-squares refinement. Weights based upon counting statistics were used, the weight modifier, k, in kF_o^2 being 0.000 001. All crystallographic calculations were effected with the NRCVAX Crystal Structure System[23] implemented on an IBM-PC compatible computer. Further details are presented in Table 1 and fractional atomic coordinates and interatomic distances and angles are presented in Tables 2 and 3, respectively.

CCDC reference number 440/008.

Results and Discussion

Fig. 3–5 reveal the nature of network formed by $\mathbf{1} \cdot CS_2$. Fig. 3 illustrates a view from above the *ab* plane and reveals how

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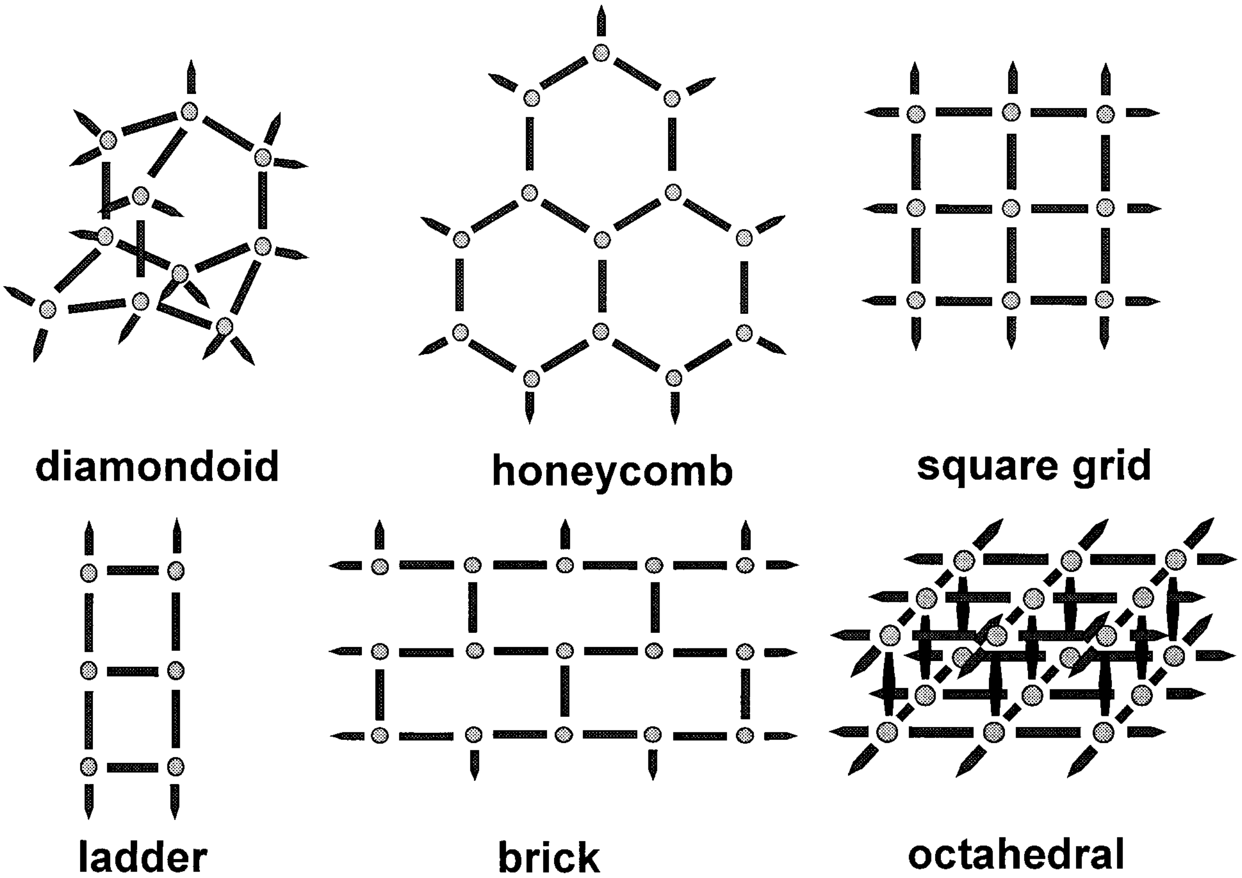

Fig. 1 Schematic representation of several of the network motifs that can be generated by linking transition metals by linear bifunctional 'spacer' ligands. In each example the metal is the node of the resulting network

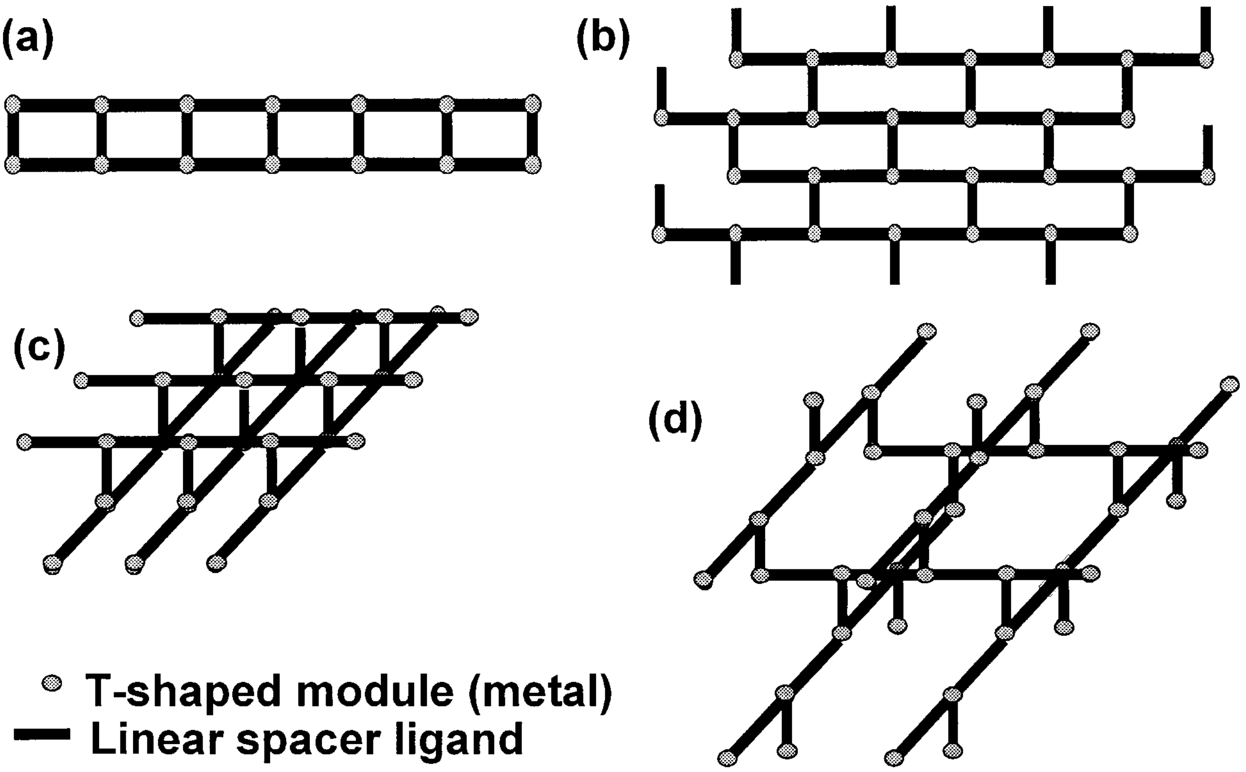

Fig. 2 Four possible architectures that one could expect for coordination polymers based upon a 1 : 1.5 ratio of metal to linear 'spacer' ligand: (a) molecular ladder; (b) molecular brick wall; (c) molecular bilayer; (d) 3D frame

Table 1 Crystallographic data for **1** · CS_2

Compound	1
Colour	Dark red
Formula	$[Co(NO_3)_2(N_2C_{10}H_8)_{1.5}] \cdot CS_2$
f.w./g mol^{-1}	493.35
Space group	*Ccca*
a/Å	12.1829(10)
b/Å	19.1078(14)
c/Å	17.4642(13)
U/Å^3	4065.5(5)
Z	8
d_{calc}/g cm^{-3}	1.612
Crystal size/mm	0.20 × 0.30 × 0.40
μ(Mo-Kα)/mm^{-1}	1.08
T/K	290
No. unique reflections	1796
Reflections used ($I > 3\sigma I$)	1349
R_f	0.051
R_w	0.044
$2\theta_{max}$/°	49.8
G.o.f.	4.72
$(shift/error)_{max}$	0.000

Table 2 Atomic parameters for **1** · CS_2

Atom	x	y	z
Co	0	1/4	0.576 45(5)
O1	0.1529(4)	0.1816(3)	0.563 40(24)
O2	0.2320(4)	0.1346(3)	0.6614(3)
O3	0.0979(3)	0.205 28(20)	0.6737(3)
N1	0.1632(4)	0.1716(3)	0.6317(3)
N21	−0.0920(3)	0.154 68(19)	0.581 03(25)
N11	0.0000	0.2500	0.4531(3)
C11	0.0888(4)	0.2326(3)	0.4129(3)
C12	0.0919(4)	0.2321(3)	0.3341(3)
C13	0.0000	0.2500	0.2921(3)
C21	−0.0995(5)	0.1119(3)	0.5211(3)
C22	−0.1601(5)	0.0510(3)	0.5220(3)
C23	−0.2159(4)	0.032 47(21)	0.5874(3)
C24	−0.2042(4)	0.074 60(22)	0.6502(3)
C25	−0.1417(4)	0.134 89(23)	0.6446(3)
C31	0.0000	0.0302(6)	0.2500
S31	0.065 42(22)	0.027 49(23)	0.179 44(19)
H11	0.158	0.220	0.441
H12	0.162	0.219	0.305
H21	−0.063	0.127	0.471
H22	−0.162	0.019	0.475
H24	−0.242	0.062	0.700
H25	−0.132	0.165	0.693

two crystallographically related $[Co(bipy)]_n$ chains are cross-hatched. These chains are cross-linked by a crystallographically unrelated bipy molecule which forms the bottom portion of the T-shape moiety. The overall network architecture can therefore be described and classified as being a two-dimensional (2D) bilayer. There appears to be little strain in the structure since the torsion angles in the bipy molecules are 35.4 and 34.1°, respectively, and the N—Co—N angles around Co are 92.1 and 175.7°. The CS_2 guest molecules lie between the upper and lower chains and are oriented so that they appear to be hydrogen bonded to C—H groups of the bipy ligands. The existence and structural importance of weak C—H···X hydrogen bonds is now well established.[24] The C—H···S and C···S distances, 2.969 and 3.742 Å, respectively, are comparable to typical C—H···O hydrogen bonds when the relative van der Waals radius of sulfur is considered.

Table 3 Interatomic distances (Å) and angles (°) for **1** · CS_2

Co—O1	2.287(5)	N11—C11a	1.331(6)
Co—O1a	2.287(5)	C11—C12	1.377(7)
Co—O3	2.245(4)	C12—C13	1.382(6)
Co—O3a	2.245(4)	C13—C12a	1.382(6)
Co—N21	2.140(3)	C13—C13b	1.470(12)
Co—N21a	2.140(3)	C21—C22	1.378(7)
Co—N11	2.154(5)	C22—C23	1.376(7)
O1—N1	1.214(7)	C23—C23c	1.493(7)
O2—N1	1.214(7)	C23—C24	1.369(6)
O3—N1	1.259(8)	C24—C25	1.384(6)
N21—C21	1.331(7)	C31—S31	1.468(3)
N21—C25	1.320(6)	C31—S31d	1.468(3)
N11—C11	1.331(6)		
O1—Co—O1a	168.56(15)	O1—N1—O2	125.7(6)
O1—Co—O3	54.91(16)	O1—N1—O3	115.3(5)
O1—Co—O3a	136.53(16)	O2—N1—O3	119.0(5)
O1—Co—N21	86.76(17)	Co—N21—C21	112.0(3)
O1—Co—N21a	93.66(17)	Co—N21—C25	121.1(3)
O1—Co—N11	84.28(11)	C21—N21—C25	117.0(4)
O1a—Co—O3	136.53(16)	Co—N11—C11	121.8(3)
O1a—Co—O3a	54.91(16)	Co—N11—C11a	121.8(3)
O1a—Co—N21	93.66(17)	C11—N11—C11a	116.4(5)
O1a—Co—N21a	86.76(17)	N11—C11—C12	123.4(4)
O1a—Co—N11	84.28(11)	C11—C12—C13	120.4(4)
O3—Co—O3a	81.63(18)	C12—C13—C12a	115.9(5)
O3—Co—N21	85.75(15)	C12—C13—C13b	122.1(3)
O3—Co—N21a	91.00(15)	C12a—C13—C13b	122.1(3)
O3—Co—N11	139.18(12)	N21—C21—C22	123.2(5)
O3a—Co—N21	91.00(15)	C21—C22—C23	119.4(5)
O3a—Co—N21a	85.75(15)	C22—C23—C23c	119.3(4)
O3a—Co—N11	139.18(12)	C22—C23—C24	117.5(4)
N21—Co—N21a	175.71(17)	C23c—C23—C24	123.2(4)
N21—Co—N11	92.14(12)	C23—C24—C25	119.3(4)
N21a—Co—N11	92.14(12)	N21—C25—C24	123.4(4)
Co—O1—N1	94.4(4)	S31—C31—S31d	176.0(9)
Co—O3—N1	95.1(4)		

The nitrate ligands are almost symmetrically bidentate with Co—O distances of 2.245(4) and 2.287(5) Å. The overall coordination geometry can be regarded as trigonal bipyramidal if the nitrates are assumed to occupy only one coordination site. These distances and angles are expected since statistically identical distances have been observed in the related discrete complex $[Co(py)_3(NO_3)_2]$ (py = pyridine).[25] Fig. 4 and 5 reveal the bilayer architecture from a side perspective. As Fig. 4 shows, the CS_2 molecules lie equidistant between the upper and lower chains of $[Co(bipy)]_n$. Fig. 5 illustrates how there are grooves in the bilayer. These grooves appear to control the efficient crystal packing of adjacent bilayers.

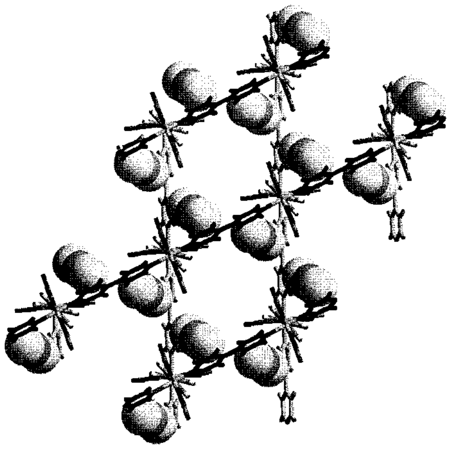

Fig. 3 An overhead view of a single network of **1** · CS_2. The CS_2 guest molecules are illustrated in space-filling mode

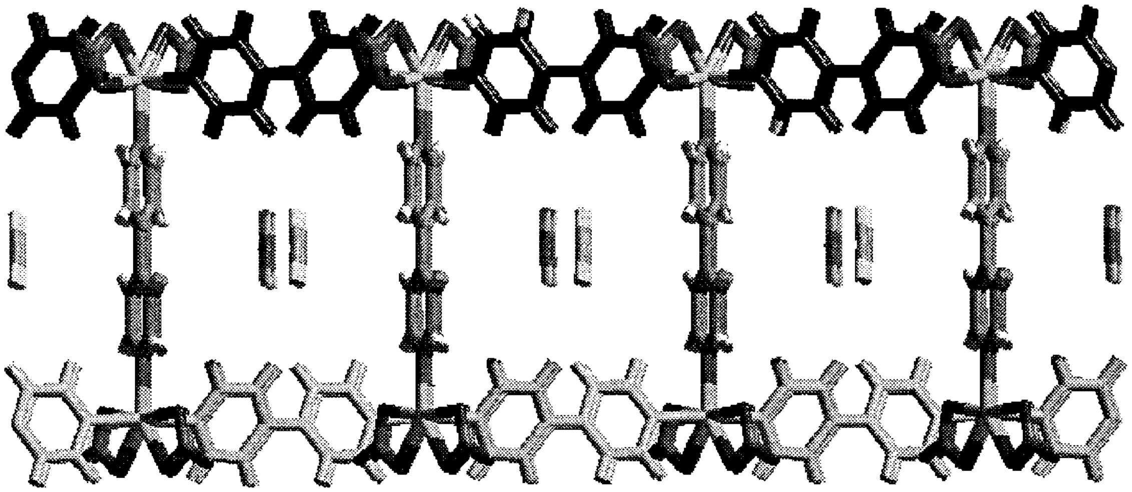

Fig. 4 A side view of a single network of **1** · CS_2. The CS_2 guest molecules lie equidistant between C—H groups of bipy ligands

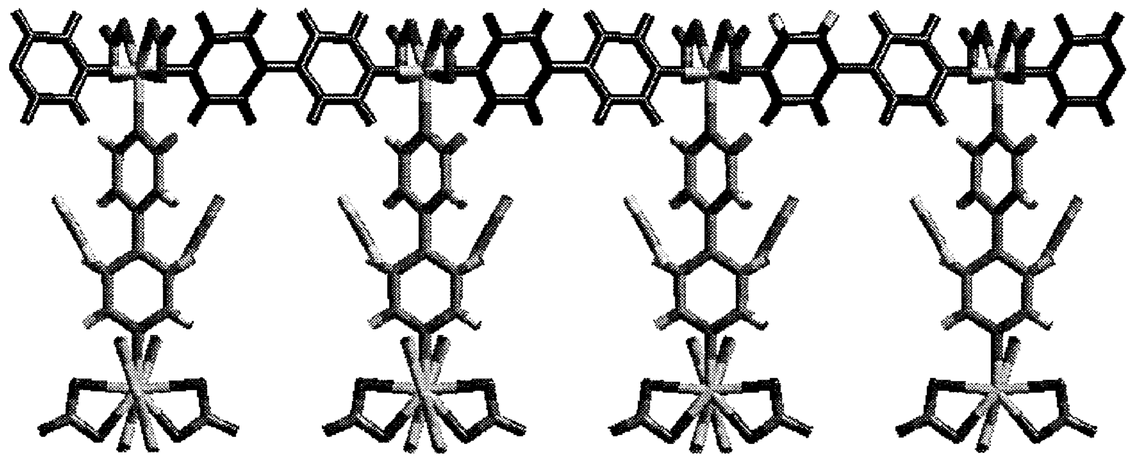

Fig. 5 A different side view of a single network of **1** · CS_2. The open spaces are partially filled by interdigitation of adjacent networks and partially filled by CS_2 guest molecules as illustrated in Fig. 4

What is not overtly clear from this study is why **1** exists in the 'bilayer' motif rather than any of the other three likely motifs. As Table 4 reveals, there are no obvious structural differences between coordination polymers based upon the T-shape motif. One would therefore assume that solvent and/or guest molecules are critical in influencing the network architecture. Indeed, in the absence of CS_2 and the presence of either MeCN,[18] $CHCl_3$ [18] or dioxane,[26] **1** generates open-framework molecular ladders. It is therefore reasonable to assume that there is a templating effect of the guest molecule that affects nucleation and/or self-assembly of the T-shape moieties. This is supported by the observation that the CS_2 guest molecules are apparently hydrogen bonded between the two $[Co(bipy)]_n$ chains. Furthermore, the size of the cavities in the bilayer and ladder structures are slightly different and correspond to the slightly different sizes of the CS_2 and MeCN guests, respectively. For example, the relevant H—H contacts across the cavities are 8.796 and 8.002 Å, respectively, and the C—C separations are 9.861 and 10.252 Å, respectively.

The existence of more than one network architecture for a

Table 4 A comparison of salient distances (Å) and angles (°) in T-shape coordination polymers

Compound	M—N	M—O	N—M—N	bipy torsion
1[a]	2.140(3)	2.287(5)	92.1	34.1
	2.154(5)	2.245(4)	175.9	35.4
$[Co(bipy)_{1.5}(NO_3)_2]_n \cdot 2CHCl_3$ [b]	2.136(4)	2.207(4)	89.38(14)	0.8
	2.162(4)	2.228(3)	94.39(14)	41.2
	2.164(3)	2.226(4)	176.14(14)	
$[Co(bipy)_{1.5}(NO_3)_2]_n \cdot MeCN$[b]	2.142(5)	2.128(4)	91.94(12)	45.0
	2.144(3)		176.12(17)	46.3
$[Ag(bipy)] [NO_3]$[c]	2.163(6)	2.789(21)	86.9	2.0
		2.888	173.7(3)	
$[Co(bipy\text{-}Et)_{1.5}(NO_3)_2]_n \cdot MeCN$[b]	2.134(5)	2.183(5)	89.15(17)	
	2.140(4)	2.286(6)	92.15(17)	
	2.142(4)	2.247(5)	172.85(20)	
$[Co(bipy\text{-}Et)_{1.5}(NO_3)_2]_n \cdot 3CHCl_3$ [b]	2.122(4)	2.157(4)	92.08(15)	
	2.132(4)	2.230(4)	96.18(15)	
	2.148(4)	2.251(4)	170.94(16)	

[a] Bilayer. [b] Ladder. [c] 3D Framework.

coordination polymer is closely related to the phenomenon of polymorphism and allotropism but it remains quite rare. However, we recently observed the effects of conformational freedom in ligands on network architecture and used the term 'conformational supramolecular isomerism' to describe this situation.[22] A bilayer architecture similar to that reported herein was one of three supramolecular isomers observed. One could reasonably draw an analogy between the results described herein and the existence of structural isomers at the molecular level. Hence, we might apply the term 'structural supramolecular isomerism' to describe the existence of more than one network architecture for a given asymmetric unit and molecular formula. It is too early to tell how common supramolecular isomerism will be in the context of coordination polymers, however, the results described herein suggest that it might be possible to manipulate and control network morphology by careful selection of solvent and guest molecules.

Note added at proof. The crystal structure of the hydrate analogue of $1 \cdot CS_2$, *ie.*, $\mathbf{1} \cdot H_2O$, was recently reported and is isostructural.[27]

Acknowledgements

We gratefully acknowledge the financial support of the N.S.E.R.C. (Canada) and the Environmental Science and Technology Alliance of Canada.

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Received 3rd *February* 1997; *Paper* 7/07640A