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2D and 3D coordination polymers based on 2,2′-bipyrimidine and cyanide bridging ligands incorporating coordinated and guest ammonia molecules. Synthesis, crystal structures, magnetic properties and thermal analysis of $\{[Ni(CN)_4]_2[(Ni(NH_3)_2)_2(bpym)]\cdot 2H_2O\}_n$ and $\{[Cu_2(CN)_2(bpym)]\cdot NH_3\}_n$

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The coordination polymers $\{[Ni(CN)_4]_2[(Ni(NH_3)_2)_2(bpym)]\cdot 2H_2O\}_n$ **1** and $\{[Cu_2(CN)_2(bpym)]\cdot NH_3\}_n$ **2** have been prepared from the reactions of $M(NO_3)_2\cdot nH_2O$ [Cu(II), $n = 3$ and M = Ni(II), $n = 6$] with NaCN and bpym (2,2′-bipyrimidine) in concentrated aqueous ammonia, respectively. The structure of **1** is made of bipyrimidine bridged centrosymmetric dinuclear $[Ni(NH_3)_2(\mu\text{-bpym})Ni(NH_3)_2]$ fragments connected by four $[Ni(CN)_4]^{2-}$ anions giving rise to a 2D framework. Layers, which adopt a stair-like conformation, are stacked with an ABAB… repeat pattern. Water molecules are located in the interlayer space and are involved in hydrogen bond interactions with the non-bridging cyanide groups of the $[Ni(CN)_4]^{2-}$ anions and one of the ammonia molecules. Magnetic measurements clearly show the existence of antiferromagnetic exchange interactions between the local spin triplet states of the octahedral Ni(II) ions mainly mediated by the bpym exchange pathway with a J value of $-16.82\ cm^{-1}$. The structure of **2** consists of $[Cu_2(bpym)]$ centrosymmetric fragments connected by cyanide groups to four neighbouring Cu(I) ions giving rise to a 3D network with channels perpendicular to the *bc* plane. Guest ammonia molecules are located into channels. TG-XRD combined studies show that the structure of **1** is retained after dehydration whereas that of **2**, however, collapses after ammonia elimination.

Introduction

The synthesis and characterization of multidimensional polymetallic coordination networks has been an area of rapid growth in recent years. The aim of this intense activity is the deliberate design of materials to achieve specific properties, for example electronic, magnetic, optical, catalytic, ion exchange, absorption, *etc.*[1] Among these materials, multidimensional cyano-bridged complexes, prepared from the self-assembly of specifically designed precursors (typically a cyanometalate complex that acts as a ligand and a transition metal complex with available coordination sites), are playing an important role in areas such as molecule-based magnets, mineralomimetic materials, magneto-optic materials, ion exchange, materials for storing gases, host–guest chemistry, *etc.*[2] It should be noted that a rich variety of cyano-bridged host–guest systems have been reported so far.[2a] This is because the –M′–CN–M– linkages generate cavities in which molecules of appropriate size and shape can be accommodated, thus stabilizing the crystal structure. In addition to this, small molecules such as water, ammonia, amines, *etc.*, can be coordinated to the metal M′ and exchanged by intercalation. In this regard, 2D and 3D Hoffmann-like frameworks, containing a great variety of cyanometalate and $M'L_n$ complexes (L = ammonia, amines, *etc.*), are of particular interest as inclusion compounds.[2a] Moreover, recently, it has been shown that some Hoffmann clathrates present cooperative spin-crossover behaviour.[3] The structure and function of Hoffmann-like frameworks can be modified by changing the type of $[M(CN)_n]^{m-}$ building block, the M′ coordination centre and the ligand L. A further step in the synthesis of this kind of system could consist of the use of L ligands that are able to bridge two metal ions to generate new and interesting structures and topologies. Following this strategy, we have succeeded in obtaining, in aqueous ammonia medium, two compounds, $\{[Ni(CN)_4]_2[(Ni(NH_3)_2)_2(bpym)]\cdot 2H_2O\}_n$ **1** and $\{[Cu_2(CN)_2(bpym)]\cdot NH_3\}_n$ **2**, containing cyanide and 2,2-bipyrimidine (bpym) bridging ligands. Complex **1** exhibits a 2D structure with coordinated ammonia, whereas complex **2** displays a 3D network structure hosting guest ammonia molecules.

Results and discussion

Reactions of $M(NO_3)_2\cdot nH_2O$ [Cu(II), $n = 3$ and M = Ni(II), $n = 6$] with NaCN and bpym in concentrated aqueous ammonia gave rise to the complexes $\{[Ni(CN)_4]_2[(Ni(NH_3)_2)_2(bpym)]\cdot$

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$2H_2O\}_n$ **1** and $\{[Cu_2(CN)_2(bpym)]\cdot NH_3\}_n$ **2**. In the former case, the very stable *in situ* generated $[M(CN)_4]^{2-}$ anions can replace some peripheral water or ammonia molecules in the *in situ* generated dinuclear cations $\{[M(L)_4]_2(bpym)\}^{4+}$ leading to complex **1**. In the formation of **2**, despite the stability of the copper(II)-ammonia complexes, Cu(II) is reduced to Cu(II) is reduced to Cu(I). Conversion to a softer and acidic Cu(I) metal cation prevents NH_3 molecules from coordinating to this metal ion. In fact, the stability constants for amminecopper(I) complexes in aqueous solution are small.[4] It should be noted that ammonia plays a remarkable role during the synthesis, as: (a) it can act as an end-cap ligand, blocking metal coordination sites, thus restricting the spatial extension of the structure. In keeping with this, complex **1**, with coordinated ammonia molecules, exhibits a 2D structure, whereas complex **2**, in which ammonia molecules are not coordinated and play a space filling role in the structure, has a 3D host network. (b) Its temporary or definitive coordination helps to dissolve reagents and products and (c) it slowly escapes from the reaction mixture and allows the formation of suitable crystals of the complexes. In fact, when the synthesis is performed in the absence of ammonia, no crystals could be obtained.

Crystal structures

The structure of $\{[Ni(CN)_4]_2[(Ni(NH_3)_2)_2(bpym)]\cdot 2H_2O\}_n$ **1** (Fig. 1) consists of layers, made of Ni(II) ions connected by alternating cyanide and bipyrimidine bridges, and water molecules between the layers. The layer structure can be alternatively described as made of bipyrimidine bridged centrosymmetric dinuclear $[Ni(NH_3)_2(\mu\text{-bpym})Ni(NH_3)_2]$ fragments connected by four $[Ni(CN)_4]^{2-}$ anions (Fig. 1). There are two different Ni(II) ions in the structure, with distorted octahedral NiN_6 and square planar NiC_4 coordination environments. In the former, two nitrogen atoms belonging to a bpym ligand and two nitrogen atoms belonging to two different $[Ni(CN)_4]^{2-}$ anions are coordinated in the plane of the bpym bridging ligand, whereas below and above this plane are coordinated two NH_3 molecules. Ni–N distances are in the range 2.046(4)–2.140(4) Å, whereas *cis* and *trans* N–Ni–N angles are in the ranges 77.26(14)–97.13(16)° and 169.37(15)–178.48(16)°, respectively (Table 1). The distortion of the Ni coordination polyhedron is mainly due to the small bite angle and large N–Ni distances for the bpym ligand. The $[Ni(CN)_4]^{2-}$ square-planar anion is minimally distorted with two *cis*-bridging and two *cis*-terminal cyanide groups. Bond distances and angles in the $[Ni(CN)_4]^{2-}$ anion are in agreement with those reported for other related compounds.[4] The Ni1···Ni1 distance across the bpym ligand is 5.728(3) Å, whereas the Ni1···Ni2 distances across the cyanide ligand are 5.046(2) Å and 5.038(1) Å. The dihedral angle between the bpym ligands of two neighbouring dinuclear $[Ni(NH_3)_2(\mu\text{-bpym})Ni(NH_3)_2]$ fragments connected by $[Ni(CN)_4]^{2-}$ is 34.3°, whereas the mean planes of two neighbouring $[Ni(CN)_4]^{2-}$ anions, those coordinated in *cis* positions on the Ni1 atoms, form a dihedral angle of 27.7°. Owing to this, layers are not fully planar and adopt a stair-like conformation (Fig. 1). Layers are stacked with an ABAB... repeat pattern, the interlayer distance being 4.3 Å. Water molecules, which are located in the interlayer space, are involved in a strong hydrogen bond interaction with one of the non-bridging cyanide groups of the $[Ni(CN)_4]^{2-}$ anion ($N10^{i}\cdots O4 = 2.795$ Å; i = 3/2 − *x*, 1/2 + *y*, 3/2 − *z*) and two weak hydrogen bond interactions involving the other non-bridging cyanide group ($N9^{ii}\cdots O4 = 3.097$ Å; ii = 3/2 − *x*, 1/2 + *y*, 1/2 − *z*) and one of the ammonia molecules ($N5^{iii}\cdots O4 = 3.075$ Å; iii = *x*, *y*, *z*). In a recent report,[5] Gutiérrez-Zorrilla *et al.* summarized the structural types observed for complexes containing group 10 tetracyanometalate coordinated anions. After checking this information, we can conclude that the 2D structure of compound **1** is unique for such a type of compound.

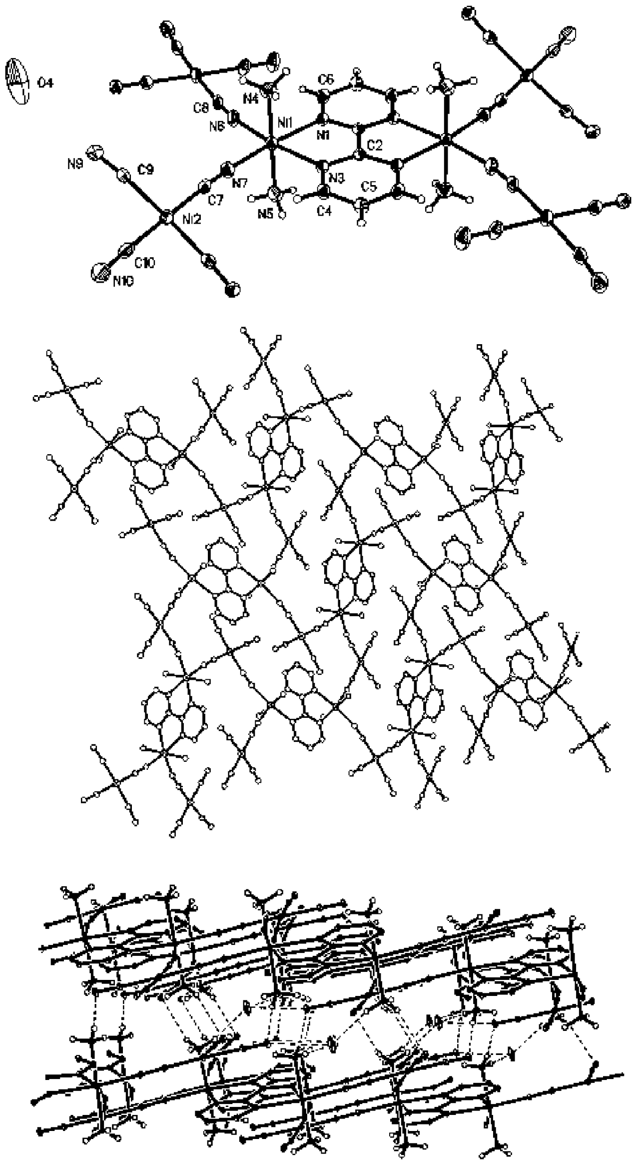

Fig. 1 Perspective views of the structure of **1**: centrosymmetric dinuclear unit (top), a layer (middle) and hydrogen bonding network between water molecules and two neighbouring layers (bottom).

The structure of $\{[Cu_2(CN)_2(bpym)]\cdot NH_3\}_n$ **2** (Fig. 2) consists of a 3D host network and guest ammonia molecules. The host network is made of distorted tetrahedral Cu(I) ions connected through two disordered cyanide ligands and one bisdidentate bpym ligand to three neighbouring copper(I) ions. As in **1**, the distortion of the Cu coordination polyhedron is mainly caused by the small bite angle and large Cu–N distances for the bpym ligand (Table 2). Alternatively, the 3D network can be described as $[Cu_2(bpym)]$ centrosymmetric fragments connected by cyanide groups to four neighbouring Cu(I) ions. The Cu···Cu distance across the bpym ligand is 5.729 Å, whereas there are two almost equal Cu···Cu distances across the cyanide ligands (4.964 Å and 4.965 Å). When viewed down the *a* axis, the structure seems to be made of fused hexagonal rings (Fig. 2). However, a closer examination reveals that these rings are not closed (Fig. 2) but that the Cu atoms are distributed in the *a* direction in a spiral manner leading to chiral hexagonal channels of approximate dimensions 9 × 9.5 $Å^2$. The guest ammonia molecules are located in the channels, thus achieving the space filling. It should be noted that the host

Table 1 Selected bond lengths (Å) and angles (°) for **1**[a]

Ni(1)–N(7)	2.046(4)	Ni(1)–N(6)	2.056(4)
Ni(1)–N(5)	2.065(4)	Ni(1)–N(4)	2.086(4)
Ni(1)–N(3)	2.136(4)	Ni(1)–N(1)	2.140(4)
Ni(2)–C(7)	1.862(5)	Ni(2)–C(9)	1.864(6)
Ni(2)–C(8)#1	1.867(6)	Ni(2)–C(10)	1.870(5)
N(3)–C(4)	1.331(6)	N(3)–C(2)	1.347(5)
N(7)–Ni(1)–N(6)	97.13(16)	N(7)–Ni(1)–N(5)	90.99(16)
N(6)–Ni(1)–N(5)	90.36(18)	N(7)–Ni(1)–N(4)	87.96(16)
N(6)–Ni(1)–N(4)	90.86(17)	N(5)–Ni(1)–N(4)	178.48(16)
N(7)–Ni(1)–N(3)	93.43(15)	N(6)–Ni(1)–N(3)	169.39(15)
N(5)–Ni(1)–N(3)	88.40(16)	N(4)–Ni(1)–N(3)	90.57(16)
N(7)–Ni(1)–N(1)	170.47(16)	N(6)–Ni(1)–N(1)	92.22(15)
N(5)–Ni(1)–N(1)	90.76(15)	N(4)–Ni(1)–N(1)	90.09(15)
N(3)–Ni(1)–N(1)	77.26(14)	C(7)–Ni(2)–C(9)	91.3(2)
C(7)–Ni(2)–C(8)#1	90.5(2)	C(9)–Ni(2)–C(8)#1	177.2(2)
C(7)–Ni(2)–C(10)	178.2(2)	C(9)–Ni(2)–C(10)	88.8(2)
C(8)#1–Ni(2)–C(10)	89.3(2)		

[a] Symmetry transformations used to generate equivalent atoms; #1 $-x + 3/2$, $y - 1/2$, $-z + 1/2$. #2 $-x + 3/2$, $y + 1/2$, $-z + 1/2$.

network in **1** is very similar to that found for the compound [$Cu_2(CN)_2$(mbpym)] (mbpym is 4-methyl-2,2′-bipyrimidine),[6] which was prepared using hydrothermal methods. In this latter compound, however, the methyl group of the ligand, which is oriented toward the centre of the channel, fills the space. Moreover, all channels have the same helicity as a consequence of the lack of centre of symmetry. In **2**, however, each row of homochiral channels along the *b* direction is related by centres of symmetry with two neighbouring rows of opposite helicity and therefore the crystal as a whole is racemic. The framework comprised of tri-connected Cu(I) nodes has a (10,3)-$ThSi_2$ topology.[7] Although some thermal desolvated compounds have been shown to be able of incorporating ammonia[8] and one of them has been structurally characterized,[8c] **2** is, to the best of our knowledge, the first example of a fully structurally characterized 3D polymer containing guest ammonia molecules.

Magnetic properties of 1

The temperature dependence of χ_M and $\chi_M T$ (χ_M is molar magnetic susceptibility for the dimer) for **1** are plotted in Fig. 3. The value of $\chi_M T$ at room temperature is 2.079 $cm^3\ mol^{-1}$ K, which agrees well with that expected for two isolated Ni(II) ions with $S = 1$ and $g = 2$ (2.0 $cm^3\ mol^{-1}$ K). As the sample is cooling down, the $\chi_M T$ product decreases smoothly until 50 K and then sharply to 0.11 $cm^3\ mol^{-1}$ K at 2 K. This behaviour is indicative of an antiferromagnetic interaction between the local spin triplet states of the octahedral Ni(II) ions. The maximum in the χ_M *vs.* T plot at 24 K, confirms the antiferromagnetic interaction in **1** (inset Fig. 3). It is well known that the $[Ni(CN)_4]^{2-}$ anion is a very poor mediator of the magnetic exchange interaction[4,9] and therefore the antiferromagnetic exchange interaction in **1** is mainly due to the bpym exchange pathway. In keeping with this and the crystal structure of **1**, magnetic data were analyzed through the expression for a dinuclear Ni(II) system ($S_A = S_B = 1$) derived from the isotropic spin Hamiltonian $H = -JS_AS_B$:

$$\chi_M = \frac{2N\beta^2g^2}{kT}\left[\frac{\exp\left(\frac{J}{kT}\right) + 5\exp\left(\frac{3J}{kT}\right)}{1 + 3\exp\left(\frac{J}{kT}\right) + 5\exp\left(\frac{3J}{kT}\right)}\right](1 - P) + \frac{4N\beta^2g^2}{3kT}P$$

where a P parameter was included to take into account the presence of a mononuclear impurity. Interdimeric interactions through the tetracyanonickelate bridges were accounted for by addition of a mean field term to the above equation:

$$\chi = \chi_M \Big/ \left(1 - \frac{2k}{Ng^2\beta^2}zJ'\chi_m\right)$$

where J' is the interdimer coupling and z is the number of interacting neighbours. The best fit of the magnetic susceptibility data to the theoretical equation led to the following values: $J = -16.82(2)\ cm^{-1}$, $g = 2.060(1)$, $p = 0.015(0)$ and $zJ' = -1.01(3)\ cm^{-1}$. The exchange parameter J calculated for the interaction through the bpym ligand is comparable to those reported for other systems containing bpym bridged octahedral Ni(II) ions, with values in the range $-11\ cm^{-1}$ to 16.5 cm^{-1}.[10] Owing to the planarity of the Ni–bpym–Ni fragment in **1**, the in-plane overlap between the $d_{x^2-y^2}$ magnetic orbitals on each octahedral Ni(II) ion (the x and y axes lying on the Ni–Nbpym bonds) through the HOMO of the bpym bridging ligand is favoured and so too is the magnetic exchange interaction. This is the reason why the J value for **1** is in the upper limit of the values found for other complexes containing the Ni–bpym–Ni exchange pathway. The very weak antiferromagnetic exchange interaction through the tetracyanonickelate bridge is similar to that found in related systems.[4,9] Nevertheless, the calculated J' value may be somewhat overestimated because the effects of the zero-field splitting of the $^3A_2$ ground state in the octahedral Ni(II) ion, which are important at very low temperature, have not been taken into account.

Thermogravimetric analysis

The thermogravimetric analysis of **1** and **2** was performed under flowing air, from room temperature up to 900 °C. The TG curve for **1** shows three weight-loss steps in the 90–160 °C, 250–350 °C and 380–450 °C temperature ranges. The first weight-loss step of 4.7% is consistent with the loss of the two crystallization water molecules (calculated value of 5.12%), whereas the second one of 9.5% corresponds well with the calculated value of 9.7% for the loss of four coordinated ammonia molecules per formula unit. The third weight-loss effect is due to the simultaneous pyrolysis of the cyanide and bpym ligands. The IR analysis of the gas evolved during each weight-loss step supported the above assignments. The dehydrated compound was exposed to liquid ammonia condensed into a Schlenk flask at −60 °C. The resulting mixture was kept aside for 15 min, during which time the excess of ammonia was allowed to evaporate. Elemental analysis of the resulting pink solid, revealed the intercalation of two molecules of ammonia. The TG diagram shows a weight-loss step of 5.08% in the 90–130 °C temperature range, which corresponds to the elim-

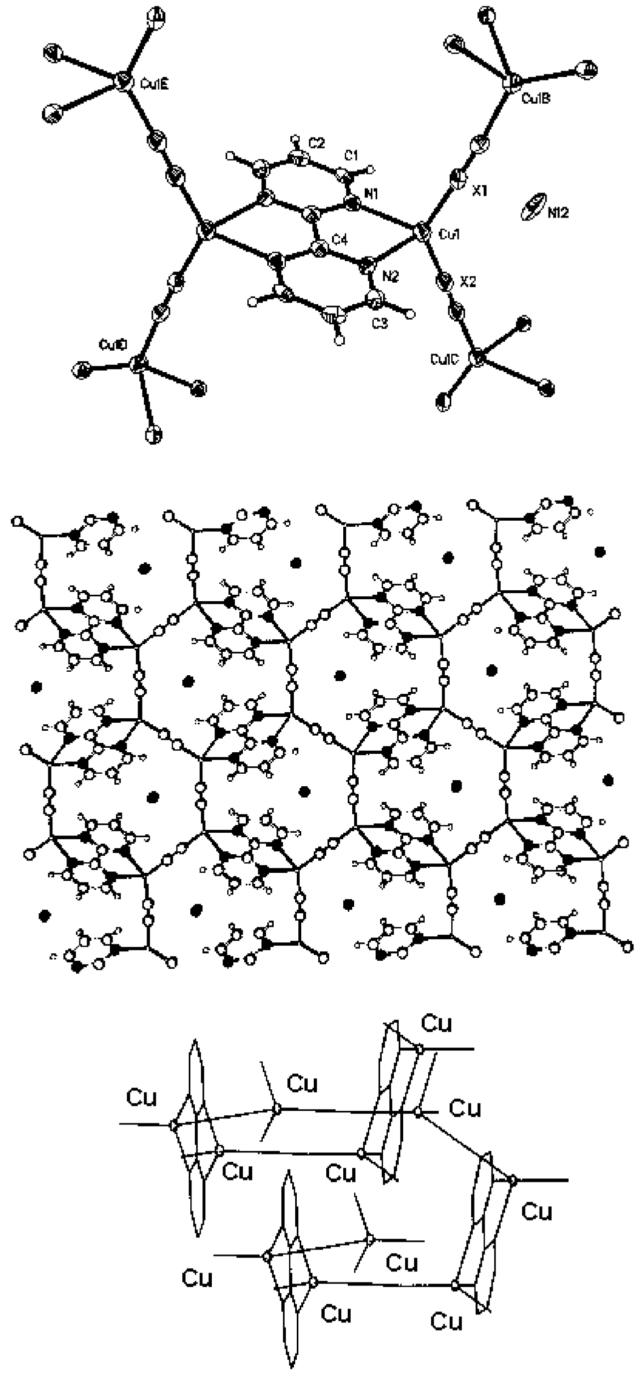

Fig. 2 Perspective views of the structure of **2**: centrosymmetric dinuclear unit (top). View of the 3D network down the *a* axis showing the channels and guest ammonia molecules (middle). Spiral distribution of Cu(I) atoms along the *a* axis (bottom).

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

Cu(1)–X1	1.900(8)
Cu(1)–X2	1.901(8)
Cu(1)–N(2)	2.143(8)
Cu(1)–N(1)	2.171(8)
X1–Cu(1)–X2	131.3(3)
X1–Cu(1)–N(2)	107.9(4)
X2–Cu(1)–N(2)	108.6(3)
X1–Cu(1)–N(1)	109.2(3)
X2–Cu(1)–N(1)	109.1(3)
N(2)–Cu(1)–N(1)	77.8(3)

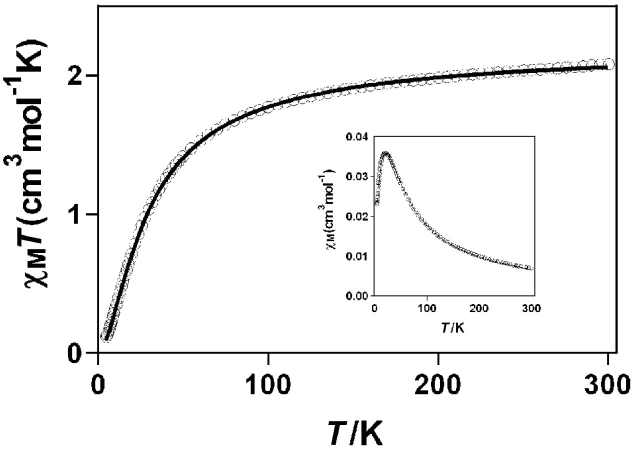

Fig. 3 Temperature dependence of $\chi_M T$ and χ_M (inset) for **1**. Solid lines are the best fit to the model (see text).

ination of two molecules of ammonia (calculated value of 4.83%). The IR analysis of the gas evolved during this weight-loss supports the ammonia elimination. The powder XRD pattern of the ammonia soaked sample is different from that of **1**, thus showing that the structure is not retained after ammonia incorporation. However, the XRD patterns after dehydration and after elimination of the NH_3 molecules are the same, thus showing that the ammonia incorporation–elimination process is reversible.

The TG plot of **2** exhibits four weight-loss effects centred at 200, 305, 360 and 560 °C. The first weight-loss effect of 5.20% corresponds well to the loss of the guest ammonia molecule (calculated value of 4.8%), which was confirmed by IR analysis of the gas evolved during this weight-loss effect. After this elimination process, the colour of the crystals becomes slightly darker but their external shape remains unchanged. The second and third overlapping weight-loss effects of 5.1 and 9.0%, are consistent with the loss of the two cyanide ligands (calculated value of 14.7%), whereas the fourth weight-loss step corresponds to the pyrolysis of the bpym ligand. It should be outlined that the powder XRD pattern shows a change in the structure after elimination of ammonia. To see if this structural change was reversible, ammonia gas was condensed into a Schlenk flask containing the freshly degassed compound. The resulting mixture was kept aside for 15 min and then the ammonia was allowed to evaporate. The TG diagram of the resulting solid showed a considerable increase in the onset of the first weight-loss compared to the parent sample **2**. The weight-loss effect of 9.6% is in good agreement with the incorporation of two molecules of NH_3 per formula unit. Moreover, the ammonia elimination takes place in the 120–220 °C temperature range and therefore starts at lower temperature than in **2**. This indicates that at least one of the ammonia molecules is less tightly bound than that in **2**. The XRD patterns of the ammonia incorporated sample and the parent sample **2** show that their structures are different. The XRD patterns before and after the first cycle of ammonia incorporation–elimination are, however, the same, thus pointing out the reversibility of the process.

Conclusions

We have shown in this paper that the use of aqueous ammonia allows the crystallization of 2D and 3D coordination polymers containing cyanide and bipyrimidine bridging ligands and either coordinated or guest ammonia molecules. It seems that the reaction takes place by substitution of the peripheral ligands of the $[M_2(bpym)(L)_4]^{4+}$ units by cyanide bridging ligands. This strategy opens the door toward analogous systems with non-innocent cyanometalate bridging groups, such as paramagnetic octa- and hexametalates or dicyanoaurate,

Table 3 Crystallographic data and structural refinement details for compounds **1** and **2**^{1}†

	1	**2**
Empirical formula	C8 H9 N8 Ni2 O	C10 H9 Cu2 N7
Formula weight	352.67	354.32
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)
a (Å)	9.1210(8)	5.8736(12)
b (Å)	11.4690(10)	17.266(3)
c (Å)	13.5610(12)	12.983(3)
β (°)	104.623(2)	93.40(2)
V (Å^3)	1372.6(2)	1314.3(5)
Z	4	4
T (°C)	20 °C	−80
λ (Å)	0.71069	0.71069
ρ (g cm^{-3})	1.697	1.791
μ (mm^{-1})	2.747	3.231
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0363	0.0743
w$R_2{}^b$ [$I > 2\sigma(I)$]	0.0731	0.1702

^{a} $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. ^{b} w$R_2 = \{\Sigma[\mathrm{w}(F_o^2 - F_c^2)^2]/\Sigma[\mathrm{w}(F_o^2)^2]\}^{1/2}$.

which might lead to extended networks with intriguing magnetic properties or aurophilic interactions, respectively. Work along this line is in progress in our laboratory.

Experimental

Preparation of the compounds

{[Ni(CN)$_4$]$_2$[(Ni(NH$_3$)$_2$)$_2$(bpym)]·2H$_2$O}$_n$ 1. To 40 ml of water containing 5 ml of concentrated ammonia, were successively added Ni(NO$_3$)$_2$·6H$_2$O (58 mg, 0.2 mmol), NaCN (19.6 mg, 0.4 mmol) and 2,2′-bipyrimidine (15.8 mg, 0.1 mmol). The resulting solution was filtered to eliminate any insoluble material and transferred to a crystallizing dish, which was covered by a watch glass. After ten days pink crystals of **1** appeared, which were collected by filtration and dried in air. Yield: 28.2 mg (80%). Calcd for $C_8H_{11}N_8Ni_2O$, C 27.26, H 3.12, N 31.81%; found C 27.65, H 3.23, N 31.53%. FT-IR (KBr, cm^{-1}): 3634, ν(OH); 3366, 3277, ν(NH); 2157, 2134, 2122 ν(CN).

{[Cu$_2$(CN)$_2$(bpym)]·NH$_3$}$_n$ 2. To a solution of Cu(NO$_3$)$_2$·3H$_2$O (24.1 mg, 0.1 mol) and NaCN (24.5 mg, 0.5 mmol) in 10 ml of water containing 2 ml of concentrated ammonia, was added with stirring a solution of Cu(NO$_3$)$_2$·3H$_2$O (12.2 mg, 0.05 mol) and 2,2′-bipyrimidine (7.9 mg, 0.05 mmol). The resulting solution was filtered to eliminate any insoluble material and transferred to a crystallizing dish, which was covered by a watch glass. After five days dark-red crystals of **2** appeared, which were collected by filtration and dried in air. Yield: 9.0 mg (51%). Calcd for $C_{10}H_9N_7Cu_2$, C 33.90; H 2.56; N 27.67%; found C 34.05, H 2.87 N 27.92%. FT-IR (KBr, cm^{-1}): 3354, 3260, ν(NH); 2142, 2096 ν(CN).

Physical measurements

Elemental analyses were carried out at the Instrumentation Scientific Centre of the University of Granada on a Fisons-Carlo Erba analyser model EA 1108. IR spectra were recorded on a MIDAC progress-IR spectrometer using KBr pellets. Magnetization and variable-temperature (1.9–300 K) magnetic susceptibility measurements on polycrystalline samples were carried out with a Quantum Design SQUID operating at different magnetic fields. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal's tables.

Crystallography

Single-crystal diffraction data for **1** and **2** were measured on a Bruker Smart Apex diffractometer and on a Stoe Image Plate Diffraction system, respectively, using graphite monochromatized Mo-Kα radiation. All data sets were corrected for Lorentz and polarization effects. In addition, in the case of **2** an empirical absorption correction was applied using the DIFFABS routine in PLATON.[11]

A total of 6205 and 5034 reflections giving 1967 and 1257 unique reflections were collected ($R_{\mathrm{int}} = 0.0645$ and 0.2081) for **1** and **2**, respectively. The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[12] For **2**, refinement of each CN bridge between two Cu(I) atoms indicated disordering with respect to the C and N termini. The site occupation parameters of the bridging CN were fixed to 50% C and 50% N. The disordered CN atom positions were labelled in tables and drawings with X1, X2, X3 and X4. For both structures, the non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms were treated as riding atoms using the SHELX97 default parameters. Crystallographic data for **1** and **2** are given in Table 3.†

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