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Cyano-Bridged 2D Cu^{II}–Cr^{III} Coordination Polymers: Structural Evidence for Formation of a Polymeric Macrocyclic Metallic Compound

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Two unique cyano-bridged 2D coordination polymers have been synthesized and characterized structurally and magnetically. The complexes contain two polyaza Cu(II) units and one novel macromolecular Cu(II) moiety, which have been synthesized via one-pot metal template condensation reactions involving ethylenediamine (en) and formaldehyde. Self-assembly of the polyaza Cu^{II} mixture with $[\mathrm{Cr(CN)_6}]^{3-}$ gave rise to two layered complexes. One complex contains unprecedented covalently linked polymeric Cu^{II} chains and cyano-bridged Cu^{II}–Cr^{III} coordination chains, which are interwoven to form a novel layer. The other complex shows intriguing encapsulation of $[\mathrm{Cr(CN)_6}]^{3-}$ anions. Intermetallic ferromagnetic coupling is operative within the bridged 2D layer. The magnetic susceptibilities of both complexes were simulated using approximate models.

Introduction

One-pot metal template condensation reactions involving amines and formaldehyde have been widely employed in the synthesis of various saturated polyaza macrocyclic metallic complexes,[1−16] some of which show potential use for enzyme mimics, catalysis, and molecular magnetism.[8−14] The complexes thus prepared include small macrocycles with one or two metal ions and big macrocycles with three metal ions, and as far as we know no polymeric macrocycles have been reported.[6,7] Recently, Kang and co-workers reported a macrocyclic Ni^{II} complex $[\mathrm{Ni(H_2L)}](\mathrm{ClO_4})_4$ (L = 1,8-bis(2-aminoethyl)-1,3,6,8,10,13-hexaazacyclotetradecane) which consists of ethylamine pendants.[15] The formation of polymeric Ni^{II} complexes is proposed but not characterized due to the difficulty in purification. A similar reaction using $\mathrm{Cu^{2+}}$ as the template results in a $\mathrm{Cu^{2+}}$ analogue $[\mathrm{Cu(H_2L)}](\mathrm{ClO_4})_4$ together with a polyaza Cu^{II} complex $[\mathrm{CuL'}](\mathrm{ClO_4})_2$ (L′ = 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo[3.3.2]decane).[16] In this paper, we show that several Cu^{II} polyaza complexes were simultaneously synthesized from the simple one-pot template condensation as illustrated in Figure 1. The reaction of the Cu^{II} mixture with $[\mathrm{Cr(CN)_6}]^{3-}$ gives rise to two novel cyano-bridged layered heterometallic Cu^{II}−Cr^{III} complexes

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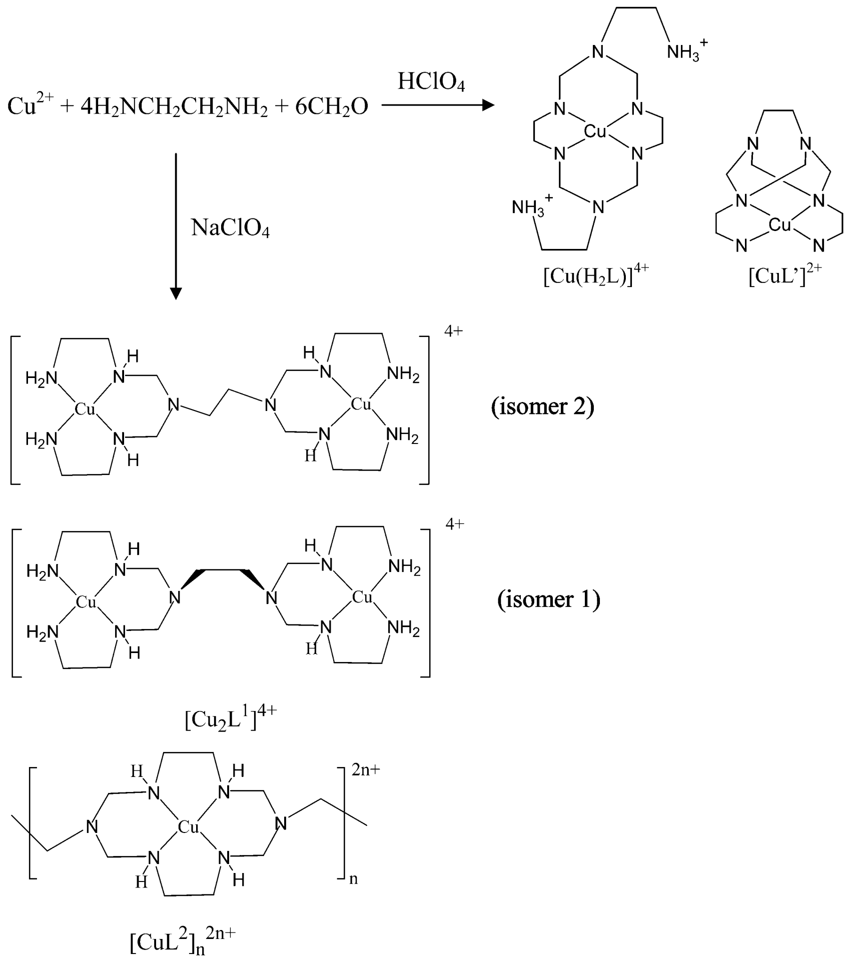

Figure 1. Formation of Cu(II) polyaza compounds through one-pot template condensation of en and formaldehyde.

1 and **2**. Herein we present the synthesis, crystal structure, and magnetic properties of the compounds.

Experimental Section

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementar Vario EL. The infrared spectroscopy was performed on a Magna-IR 750 spectrophotometer in the 4000−400 cm^{-1} region. Magnetic measurements were performed on a few manually separated single crystals (ca. 6 mg for **1** and 14 mg for **2**) using a MagLab 2000 magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

Syntheses of 1 and 2. To a methanol (30 mL) suspension of $Cu(Ac)_2 \cdot H_2O$ (2.997 g, 15 mmol) were added 99% ethylenediamine (4.05 mL, 60 mmol) and 40% formaldehyde (4.65 mL, 60 mmol). The mixture was refluxed for 15 h and then cooled to room temperature. An excess amount of sodium perchlorate had been added, resulting in immediate formation of purple solids. The obtained solid was recrystallized from an H_2O−EtOH−MeCN (1:1:1 v/v) solution to give a purple product. Slow diffusion of the Cu^{2+} product (80 mg) in an MeCN−H_2O (1:1) mixture (10 mL) into $K_3[Cr(CN)_6]$[17] (0.1 mmol, 35 mg) in water (10 mL) afforded violet thin platelet single crystals of **1** and deep violet blocks of **2** after a few days. Pure product was obtained by manual separation. Data for **1** are as follows. IR: $\tilde{\nu} = 2096$ sh, 2123 cm^{-1} (C≡N). Anal. Calcd for $C_{36}H_{71}Cr_2Cu_3N_{28}O_{3.5}$: C, 34.68; H, 5.74; N, 31.46. Found: C, 34.49; H, 5.76; N, 31.61. Data for **2** are as follows. IR: $\tilde{\nu} = 2248$ cm^{-1} (C≡N, CH_3CN), 2121, 2134 cm^{-1} (C≡N, CN^-), 1097 cm^{-1} (Cl−O). Anal. Calcd for $C_{44}H_{98}Cl_2Cr_2Cu_4N_{34}O_{14}$: C, 30.09; H, 5.62; N, 27.11. Found: C, 30.19; H, 5.76; N, 27.41.

X-ray Structure Determination. The data collection of **1** and **2** was made on a Bruker Smart CCD (293 K) and a Simens Bruker P4 diffractometer. Intensity data were corrected for *LP* factors. The absorption corrections have been applied by using SADABS (Bruker 2000) for complex **1** and ψ-scans for complex **2**. The structures were solved by direct method SHELXS-97 and refined by full-matrix least squares (SHELXL-97) on F^2. Hydrogen atoms attached to the C and N atoms were added geometrically and refined using a riding model. For complex **1**, the high thermal factors of C4, N22, O4, and O5 indicate that there is some disorder in these atoms, which are treated isotropically. The crystal data are summarized in Table 1.

Results and Discussion

Synthesis and General Characterization. It has been shown that the condensation of M^{2+} (M = Cu or Ni), en, and CH_2O in a molar ratio of 1:4:6 gave rise to protonated pendant hexaazamacrocyclic metallic complexes $[M(H_2L)](ClO_4)_4$ in the presence of $HClO_4$. With the employment of $NaClO_4$ instead of $HClO_4$, a purple product was obtained instead of the red crystals of $[Cu(H_2L)](ClO_4)_4$ (Figure 1). The obtained solid was initially thought as deprotonated

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Table 1. Crystal Data for Complexes **1** and **2**

	1	**2**
formula	$C_{36}H_{71}Cr_2Cu_3N_{28}O_{3.5}$	$C_{44}H_{98}Cl_2Cr_2Cu_4N_{34}O_{14}$
fw	1246.83	1756.62
space group	$C2/m$	$C2/c$
a/Å	21.066(8)	20.446(4)
b/Å	31.371(13)	20.476(3)
c/Å	9.250(4)	19.852(3)
β/deg	109.048(7)	113.357(9)
V/Å^3	5778(4)	7630(2)
Z	4	4
ρ_{calcd}/g cm^{-3}	1.433	1.529
μ(Mo Kα)/mm^{-1}	1.510	1.516
data/restraint/params	12 033/0/346	7772/0/460
GOF	1.133	1.069
R1 [$I > 2\sigma(I)$]	0.0859	0.0532
wR2 (all data)	0.1954	0.1259

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

Cu(1)−N(20)	1.964(11)	Cu(1)−N(21)	2.011(16)
Cu(1)−N(6)	2.710(10)	Cu(2)−N(7)	2.370(8)
Cu(2)−N(11)	2.040(6)	Cu(2)−N(12)	1.986(6)
Cu(2)−N(13)	2.016(7)	Cu(2)−N(14)	2.012(6)
Cr(1)−C(2)	2.056(13)	Cr(2)−C(4)	2.085(15)
Cr(1)−C(1)	2.090(10)	Cr(2)−C(5)	2.034(15)
Cr(1)−C(3)	2.073(14)	Cr(3)−C(6)	2.054(10)
Cr(3)−C(8)	2.029(13)	Cr(3)−C(7)	2.090(9)
C(6)−N(6)−Cu(1)	143.8(9)	C(7)−N(7)−Cu(2)	138.6(7)

$[CuL](ClO_4)_2$ and was used for the synthesis of a cyano-bridged $Cu^{II}-Cr^{III}$ complex. The use of the cyano ligand as a bridge has been an intriguing synthetic approach to magneto−optical, porous, catalytic, and magnetic materials due to their remarkable diversities in structural behavior.[14,18,19] When the precursors were slowly diffused into each other in a test tube, two kinds of well-shaped violet single crystals were produced at the interface, thin platelet single crystals of **1** and block single crystals of **2**. Single-crystal X-ray diffraction analyses reveal them to have entirely different structures.

The IR spectra of the complexes are similar and show the splitting of the $\nu(C{\equiv}N)$ bands in the range 2000−2200 cm^{-1}, suggestive of the presence of both bridged and nonbridged CN^- ligands. The peak at 2248 cm^{-1} can be reasonably attributed to the $\nu(C{\equiv}N)$ of CH_3CN, suggestive of the presence of acetonitrile molecules. The appearance of absorption at 1097 cm^{-1} indicates the crystallization of perchlorate anions, consistent with the results of X-ray single-crystal analysis.

Crystal Structures. Selected bond distances and angles for complexes **1** and **2** are listed in Tables 2 and 3, respectively.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**[a]

Cu(1)−N(1)	2.327(3)	Cu(2)−N(2)	2.297(3)
Cu(1c)−N(5)	2.962(3)	Cu(2)−N(4)	2.935(3)
Cu(1)−N(8)	2.010(2)	Cu(2)−N(13)	2.004(3)
Cu(1)−N(10)	2.011(3)	Cu(2)−N(12)	1.999(3)
Cu(1)−N(7)	2.016(3)	Cu(2)−N(15)	2.003(3)
Cu(1)−N(11)	2.019(3)	Cu(2)−N(16)	2.019(3)
Cr(1)−C(2)	2.061(4)	Cr(2)−C(4)	2.074(3)
Cr(1)−C(3)	2.067(3)	Cr(2)−C(5)	2.069(3)
Cr(1)−C(1)	2.068(3)	Cr(2)−C(6)	2.058(4)
C(1)−N(1)−Cu(1)	150.3(2)	C(2)−N(2)−Cu(2)	148.8(3)
C(4)−N(4)−Cu(2)	110.7(3)	C(5)−N(5)−Cu(1c)	105.8(2)

[a] Symmetry operations: (c) $0.5 + x, -0.5 + y, z$.

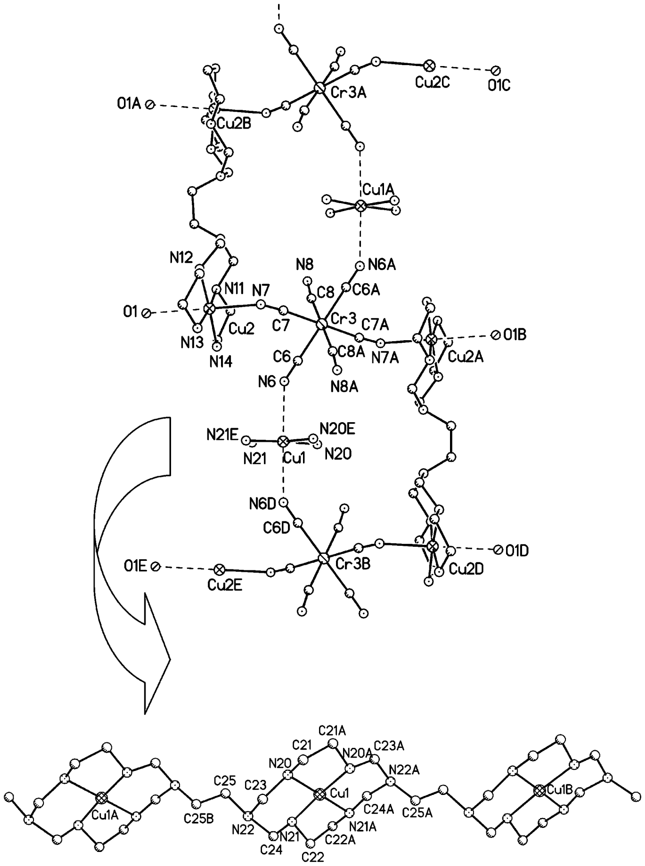

Figure 2. Crystal structure of **1**: top, coordination polymeric chain showing the interaction with the covalently linked chains; bottom, view of the covalently linked chains. Hydrogen atoms and the interstitial water molecules are omitted for clarity.

In **1**, two Cu^{II} building blocks are present: dimeric $[Cu_2L^1]^{4+}$ (isomer 1, Figure 1) and polymeric $[CuL^2]_n^{2n+}$, which are structurally characterized for the first time. The layered structure of **1** can be expressed as interwoven chains: the coordination polymeric $\{[Cu_2L^1][Cr(CN)_6]\}_n^{n+}$ chains and the polymeric $[CuL^2]_n^{2n+}$ chains. The $\{[Cu_2L^1][Cr(CN)_6]\}_n^{n+}$ chain is formed via the cyano bridges. Each $[Cr(CN)_6]^{3-}$ group uses two *trans*-CN^- ligands connecting two $[Cu_2L^1]^{4+}$ moieties, and in turn each $[Cu_2L^1]^{4+}$ cation links to two $[Cr(CN)_6]^{3-}$ anions giving rise to a zigzag chain (Figure 2). The polymeric $[CuL^2]_n^{2n+}$ chain is formed through covalent bonds. The saturated polymeric aza ligand incorporates Cu^{2+} ions that are coordinated by four secondary nitrogen atoms of L^2. The Cu^{II} ions are further bonded to two cyano nitrogen atoms at the axial positions [Cu(1)−

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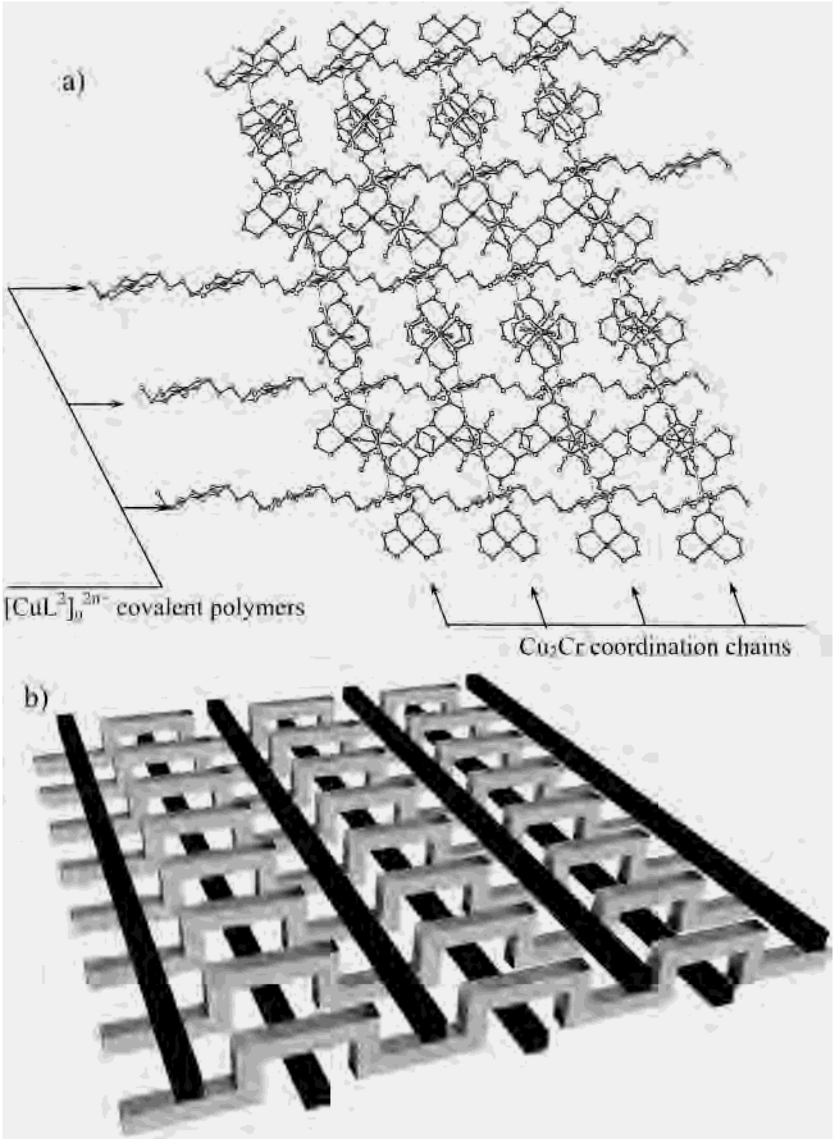

Figure 3. (a) Layered structure of **1** (along the crystallographic *b* axis). (b) Schematic view of the cross-linked chains (black sticks, covalent polymers; gray zigzag sticks, coordination polymers).

N_{cyano} = 2.710(10) Å]. Therefore, the interwoven chains extend to generate a 2D layer with Cu(1) at the knots (Figure 3). Adjacent layers are connected by the weak Cu−O_{water} contacts [Cu(2)−O(1) = 2.952(2) Å] yielding a 3D molecular network (see Supporting Information). The $[Cr(CN)_6]^{3-}$ counteranions occupy the formed cavities and are hydrogen-bonded to the water molecules or the primary amine groups of $[Cu_2L^1]^{4+}$. The bridging bond angles are 143.8(9)° for C(6)−N(6)−Cu(1) and 138.6(7)° for C(7)−N(7)−Cu(2). It is worth noting that the latter linkage has an unusual low bond angle for a strong bridging bond [Cu(2)−N(7) = 2.370(8) Å]. The adjacent Cu−Cr distances are 5.568(2) Å for Cu(1)−Cr(3) and 5.143(2) Å for Cu(2)−Cr(3). The Cu−Cu separations within the ligands are 9.034(4) Å for $[Cu_2L^1]^{4+}$ and 9.250(4) Å for $[CuL^2]_n^{2n+}$.

In complex **2**, only dimeric $[Cu_2L^1]^{4+}$ (isomer 2, Figure 1) is included. The differences in spatial configuration of the isomers are responsible for formation of a molecular structure different from that of **1**. The structure of **2** consists of cyano-bridged layers with the repeating unit of $\{[Cu_2L]_2[Cr(CN)_6]\}^{5+}$, one $[Cr(CN)_6]^{3-}$, and two perchlorate counteranions, interstitial MeCN, and water molecules. The layer contains two different $[Cr(CN)_6]^{3-}$ anions [Cr(1) and Cr(2)] (Figure 4). Cr(1) is linked to four different $[Cu_2L^1]^{4+}$ through four equatorial cyano ligands, and each $[Cu_2L^1]^{4+}$ group is bonded to two $[Cr(CN)_6]^{3-}$ anions. The Cu−N_{cyano} bond distances are 2.327(3) Å for Cu(1)−N(1) and 2.297(3) Å for Cu(2)−N(2). The arrangement of cyano-bridged $[Cr(CN)_6]^{3-}$ and $[Cu_2L^1]^{4+}$ building blocks affords a planar layer with large cavities (Figures 5 and 6). The other $[Cr(CN)_6]^{3-}$ anions [Cr(2)] are embedded in the cavities and weakly bonded to the Cu^{II} ions of the neighboring $[Cu_2L^1]^{4+}$ groups via four equatorial cyano ligands [Cu−N_{cyano} = 2.935(3) and 2.962(3) Å]. The bridging bond angles rang from 148.8(3) to 150.3(2)° for the strong bridging linkages and from 105.8(2) to 110.7(3)° for the weak bridging linkages. The adjacent Cu−Cr distances are 5.332(1) Å for Cr(1)−Cu(1), 5.268(1) Å for Cr(1)−Cu(2), 5.077(1) Å for Cr(2)−Cu(2), and 4.966(1) Å for Cu(1)−$Cr(2)^{\#1}$. The ClO_4^- anions, MeCN, and the water molecules are situated between the

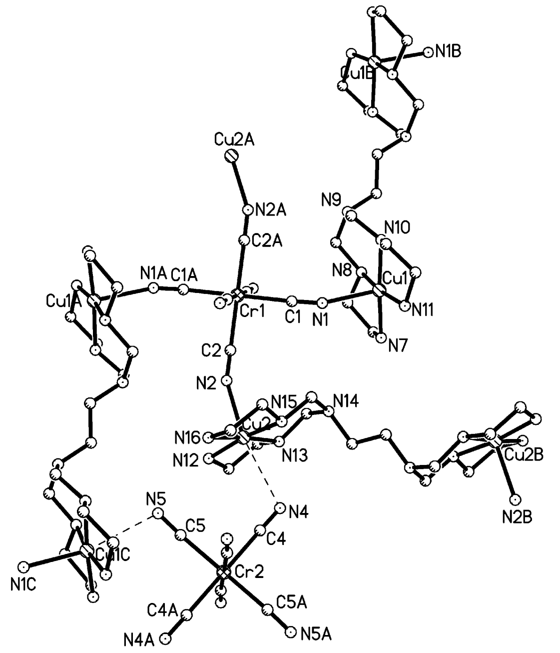

Figure 4. View of the ligand−metal environment in complex **2**.

layers (see Supporting Information). Unlike complex **1**, the Cu−Cu separations within the $[Cu_2L^1]^{4+}$ ligand (isomer 2) are 9.289(1) and 9.291(1) Å, which are close to that for the polymeric $[CuL^2]_n^{2n+}$.

The hexacyanochromate(III) ion is approximately octahedral, and the Cr−C and C≡N bond distances and Cr−C≡N bond angles do not deviate greatly from the normal values.

Magnetic Properties. Magnetic susceptibilities of **1** and **2** were measured in the temperature range 2−300 K on a bunch of manually selected single crystals. Figure 7 shows the χ_mT vs T plots for two complexes. The increase of χ_mT with a decrease of temperature suggests the presence of ferromagnetic interactions between adjacent metal ions.

On the basis of the structural information of **1** and **2**, the layer of **1** can be treated as strongly interacting Cu_2Cr trimers and a Cu^{II} monomer between which a weak interaction is present, while that of **2** is composed of strongly interacting Cu_4Cr pentamers and a $Cr(CN)_6^{3-}$ monomer between which a weak magnetic coupling is neglected. Hence, the magnetic susceptibilities can be simulated on the basis of the isotropic spin Hamiltonian $\hat{H} = -2JS_{Cr}(S_{Cu1} + S_{Cu2})$ for the Cu_2Cr trimer of **1**.[18] The best fit to the magnetization data (10−300 K) gives $g = 2.00$, $J = +19.0$ cm^{-1}, and $zJ' = +0.14$ cm^{-1}, among which zJ' accounts for the intermolecular interaction.

Analogously, the magnetic susceptibilities of complex **2** can be simulated on the basis of the isotropic spin Hamiltonian $\hat{H} = -2JS_{Cr}(S_{Cu2} + S_{Cu2} + S_{Cu3} + S_{Cu4})$ for the Cu_4-Cr pentamer. The best fit to the magnetization data (10−300 K) gives $g = 2.19$, $J = +11.0$ cm^{-1}, and $\Theta = +5.5$ K.

The $Cu^{II}-Cr^{III}$ coupling constant is comparable to that ($J = 45$ cm^{-1}) for a cyano-bridged Cu_6Cr complex[20] and

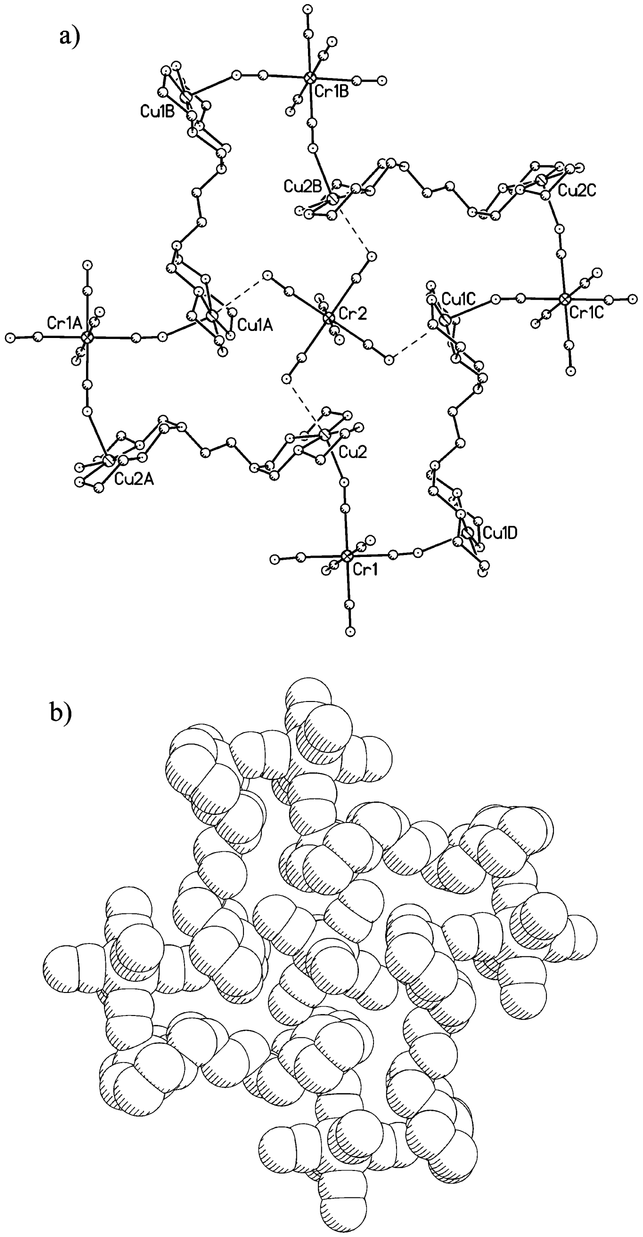

Figure 5. (a) Layered structure of complex **2** with the encapsulated $[Cr(CN)_6]^{3-}$ ion. (b) Space-filling diagram.

slightly higher than the reported values for cyano-bridged 1D CuCr complex $\{[Cu(L^3)][Cu(L^3)Cr(CN)_6]ClO_4 \cdot 2H_2O\}_n$ (L^3 = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) ($J = +4.82$ cm^{-1}), $\{[Cu(cyclam)]_3[Cr(CN)_6]_2 \cdot 4H_2O\}_n$, and $[Cu(edma)]_3Cr(CN)_6$ (edma$^-$ = ethylenediaminemonoacetate) ($J = +9.16$ cm^{-1}).[18] It should be noted that the fitting model is rough because the weakly interacted $Cu^{II}-Cr^{III}$ ions ferromagnetically couple to a certain extent.[21] However, the fitting including two different coupling constants was complicated and no appropriate models for such species can be used. This may be the reason low-temperature data (<10 K) could not be satisfactorily fitted.

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(21) We have tried a two-dimensional model by including the Cu(1)---Cr(2) magnetic coupling in the fitting for complex **2**, and unfortunately, a bad fitting result was obtained. This indicates that the interlayer magnetic coupling is present, and therefore, the employment of the parameter Θ seems more appropriate.

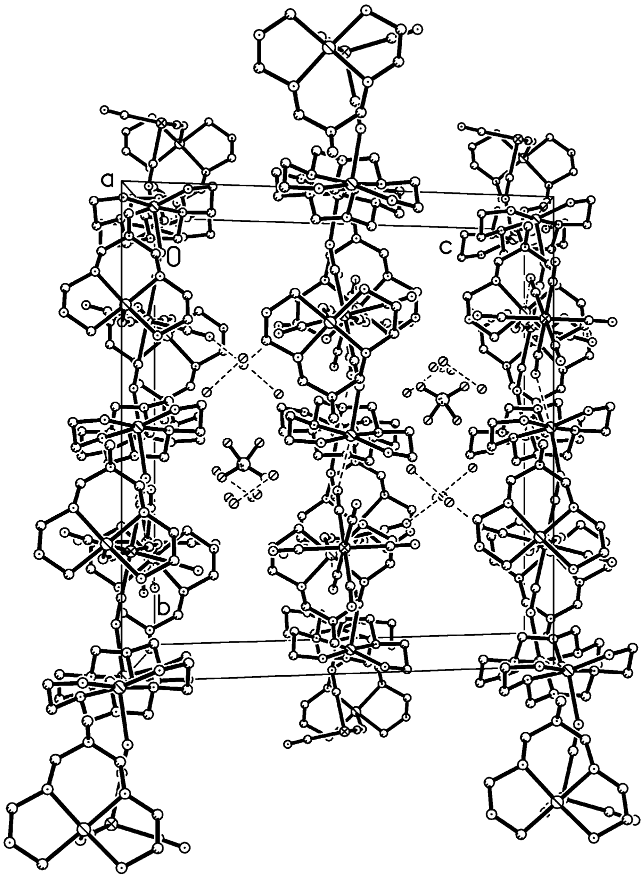

Figure 6. Cell packing diagram of **2** (along the *a* axis).

Conclusions

The present research presents two novel cyano-bridged bimetallic coordination polymers. Structural studies clearly show that a macromolecular metallic compound has formed in the course of one-pot metal template condensation reaction involving ethylenediamine (en) and formaldehyde. Polymeric ligands containing metal ions have been studied extensively; however, to the best of our knowledge, no species have been elucidated by single-crystal X-ray diffraction analysis due to the insolubility of the compounds.[22] Attempts to separate the Cu^{2+} mixture (column chromatogram and recrystallization) have been unsuccessful. Recent reports have shown that the isomeric organic ligands or complexes could be separated via the coordination chemistry method.[23] The present research adds an interesting example of the separation of isomeric complexes. We anticipate that by altering the reactants and the reaction conditions more polyaza transition metal complexes can be synthesized.[7] Furthermore, these complexes might find their use in the construction of porous materials of tunable sizes. Interestingly the possible inclusion of the covalently linked polymeric Cu^{2+} building block might enhance the stability of porous species. Work along this line is under way in our laboratory.

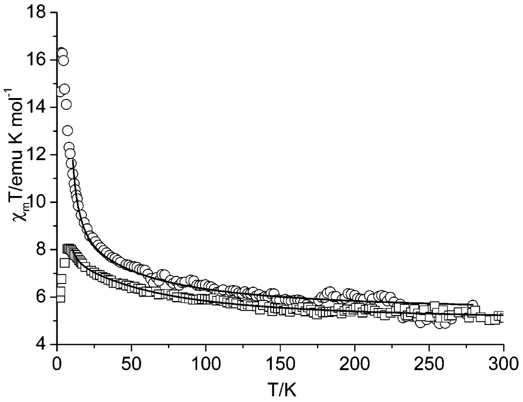

Figure 7. Plot of $\chi_M T$ vs T for **1** (□) and **2** (○). The solid line represents the theoretical values based on the parameters described in the text.

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Supporting Information Available: Cell packing diagrams for **1** and **2** and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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