Inorg. Chem. **2003**, *42*, 2720–2724

Inorganic Chemistry
Article

A New Type of Anionic Metal Dicyanamide Extended Networks through $[Cu(N_4\text{-macrocycle})]^{2+}$ Cation Templation. Structure and Magnetic Properties

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Received December 4, 2002

Two isomorphous anionic metal dicyanamide extended systems $[Cu(pCTH)][M(dca)_4]$ (M = Mn(II), Co(II); dca = dicyanamide; pCTH = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane-4,11-diene) have been prepared through $[Cu(pCTH)]^{2+}$ templation and characterized by X-ray crystallography and magnetic measurements. In these complexes, the $[M(dca)_4]^{2-}$ anions form 2D (4,4) distorted square-gridlike sheets in which each elongated octahedral $M(N_{dca})_6$ metal center is connected to four neighboring ones through single dicyanamide bridges in equatorial positions. $[Cu(pCTH)]^{2+}$ cations lie between the sheets and display weak bonding interactions with the axial dicyanamide ligands on the M centers of two neighboring $[M(dca)_4]_n^{2n-}$ sheets, thus leading to a 3D heterometallic network. Variable-temperature magnetic measurements reveal weak antiferromagnetic interactions between metal centers across $\mu_{1,5}$-dicyanamide bridging ligands. For the cobalt(II) compound, the experimental data for $T > 30$ K match well with the calculated curve by taking into consideration the spin–orbit coupling effect for the $^4T_{1g}$ ground state of the cobalt(II) and an axial distortion of the octahedral geometry. No long-range magnetic order was observed in these compounds above 2 K.

Introduction

In recent years, much research interest has been focused on homoleptic and heteroleptic dicyanamide-bridged extended systems because of their fascinating structural and topological features and interesting magnetic properties. Thus, binary metal−dicyanamide complexes, α-$[M(dca)_2]$, with a 3D-rutile type architecture, magnetically order as ferro- or antiferromagnetic spin-canted systems at T_c lower than 47 K.[1] To modify metal−dca assemblies, monodentate and bridging ligands have been used as coligands, leading to a wide variety of 1D to 3D systems, some of them exhibiting magnetic order.[2] An alternative route to dicyanamide-bridged systems consists of the cation templation of $[M(dca)_3]^-$ and $[M(dca)_4]^{2-}$ networks.[3] In this case, the topology of the final assembly strongly depends on the countercation used in the templation process. Noteworthy, paramagnetic metal complexes can be used as countercations, leading to heterometallic systems.[3e] Following this strategy and by using $[Cu(pCTH)]^{2+}$ (pCTH = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane-4,11-diene) as template paramagnetic countercation, we have succeeded in obtaining a series of polymeric anionic metal−dicyanamide complexes containing $\mu_{1,5}$-bidentate dicyanamide bridges. We

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10.1021/ic026234w CCC: $25.00

report here the structural characterization and magnetic properties of $[Cu(pCTH)][M(dca)_4]$ [M = Co (**1**) and Mn (**2**)], which to our knowledge represent a new type of dicyanamide-bridged complexes.

Experimental Section

Syntheses. To prepare the compounds **1** and **2** the following procedure was used: $Co(NO_3)_2 \cdot 6H_2O$ (27 mg, 0.093 mmol) and Na(dca) (25 mg, 0.28 mmol) were dissolved in 10 mL of water. The resulting solution was slowly layered with a blue solution containing $[Cu(pCTH)]ClO_4$[4] (54 mg, 0.1 mmol) in 10 mL of water. After several days at ambient temperature, suitable blue crystals for X-ray diffraction were growing from the resulting blue solution. For **2**, 23 mg (0.093 mmol) of $Mn(NO_3)_2 \cdot 4H_2O$ was used. Anal. Calcd for **1**, $C_{24}H_{32}N_{16}CoCu$: C, 43.17; H, 4.80; N, 33.58. Found: C, 43.35; H, 5.10; N, 33.70. IR (KBr, cm^{-1}): υ(CN) 2301, 2266, 2254, 2208, 2189, 2146. Anal. Calcd for **2**, $C_{24}H_{32}N_{16}MnCu$: C, 43.42; H, 4.82; N, 33.77. Found: C, 43.27; H, 5.02; N, 33.90. IR (KBr, cm^{-1}): υ(CN) 2301, 2266, 2247, 2206, 2182, 2146.

X-ray Structure Determination. Crystallographic data and structural refinement details are presented in Table 1. Single-crystal data collections for **1** and **2** were performed at 298 K on a Siemens P4 diffractometer and at 173 K on a Nonius KappaCCD diffractometer, respectively, using graphite-monochromatized Mo Kα radiation. The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[5] The N18 atom of one of the dicyanamide ligands in both **1** and **2** was disordered on two positions. The hydrogen atoms were treated as riding atoms using the SHELX97 default parameters.

Results and Discussion

Reaction of two aqueous solutions, one containing sodium dicyanamide and the appropriate metal nitrate and the other one containing $[Cu(pCTH)](ClO_4)_2$, results in formation of blue crystals of **1** and **2**. The two crystal structures are isomorphous and consist of anionic 2D (4,4) $[M(dca)_4]_n^{2n-}$ layers and $[Cu(pCTH)]^{2+}$ cations intercalated between the layers. The structure of the 2D system of **2** is given in Figure 1. Within the layers, tetragonally elongated octahedral metal atoms [Co(II) or Mn(II)], which lie on inversion centers, are bonded to four equatorial bidentante dca bridging ligands through the nitrile nitrogens atoms with M−N distances of 2.117(2) and 2.118(2) Å for **1** and 2.199(2) and 2.205(2) Å for **2**, whereas the axial positions are occupied by two monodentate dca ligands with M−N distances of 2.160(3) and 2.262(3) Å, respectively. The dca bridges connect each metal to four neighboring metal atoms, leading to distorted square-gridlike sheets parallel to the *bc* plane. Within the buckled square M_4 units, the equatorial coordination planes of neighboring M atoms are not coplanar but exhibiting dihedral angles of 19.56(6)° and 20.99(5)° for **1** and **2**, respectively. The intralayer M···M separations through the dicyanamide bridge are 8.3037(4) and 8.3558(2) Å, for **1** and **2**, respectively, whereas the M···M distances through the diagonals are different [12.6193(9) and 10.7961(8) Å for **1** and 12.6640(4) and 10.9042(3) Å for **2**], thus indicating that metals in M_4 units adopts a rhombus rather than a square disposition. Copper atoms of the $[Cu(pCTH)]^{2+}$ cations, which also lie on inversion centers, exhibit a square-planar coordination environment with typical Cu−N distances of 1.984(2) and 2.005(2) Å for **1** and 1.984(2) and 2.009(2) Å for **2**. Copper atoms are further semicoordinated at the axial positions by two nitrile nitrogen atoms of the M-axially coordinated dca ligands of neighboring $[M(dca)_4]_n^{2n-}$ sheets [Cu−N distances of 2.767(4) and 2.757(3) Å]. Each copper(II) atom links two M atoms of neighboring sheets that are shifted by a unit in the *a* direction (Figure 1b). If these weak bonding interactions are considered, then $[Cu(pCTH)]^{2+}$ cations act as two connecting nodes linking the $[M(dca)_4]_n^{2n-}$ layers to form a α-Po-like 3D heterometallic network (Figure 2). Note that among the homoleptic dicyanamide-bridged compounds reported so far, as far as we know, only β-Zn-$(dca)_2$ exhibits, like **1** and **2**, a 2D structure with single dicyanamide bridges connecting each metal atom to four

Table 1. Crystallographic Data and Structural Refinement Details for Compounds

	1	2
empirical formula	$C_{24}H_{32}N_{16}CoCu$	$C_{24}H_{32}N_{16}MnCu$
formula weight	667.13	663.14
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	11.1150(7)	11.1574(3)
b (Å)	10.7961(8)	10.9042(3)
c (Å)	12.6193(9)	12.6640(4)
β (deg)	101.621(5)	103.013(2)
V (Å^3)	1483.26(18)	1501.17(7)
Z	2	2
T (K)	298(2)	173(2)
λ (Å)	0.71073	0.71073
ρ (g cm^{-3})	1.494	1.467
μ (mm^{-1})	1.321	1.174
goodness-of-fit	1.039	1.050
R1[a] [$I > 2\sigma(I)$]	0.0364	0.0354
wR2[b] [$I > 2\sigma(I)$]	0.0916	0.0797

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

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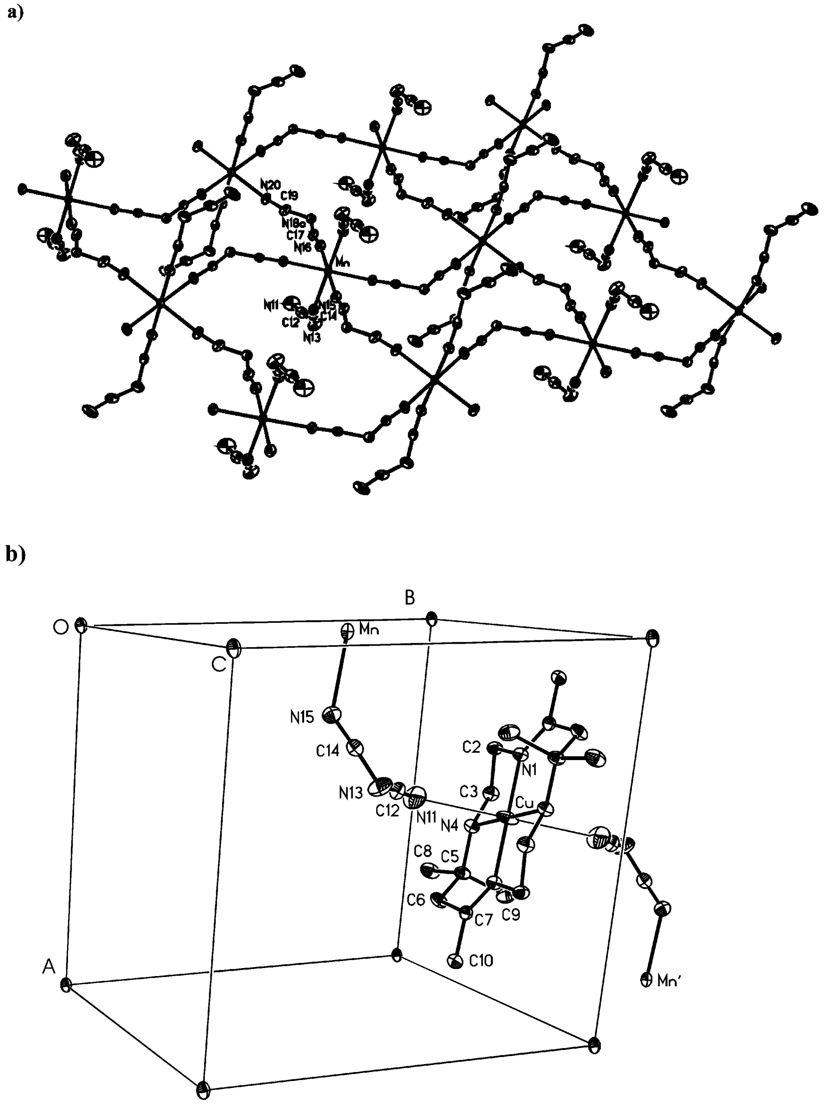

Figure 1. (a) A fragment of the anionic 2D (4,4) $[M(dca)_4]_n^{2n-}$ sheets of **2** (**1** is isomorphous). N18b with minor occupancy is omitted for clarity. (b) Bonding interactions between Mn−axially coordinated dca ligands of two neighboring sheets and $[Cu(pCTH)]^{2+}$ cations leading to a 3D bimetallic network. Nonlabeled atoms at the corners of the unit cell represent Mn atoms.

neighboring ones.[6] In this compound due to the tetrahedral Zn^{II} centers, the layers are markedly buckled. Several 3D heteroleptic dicyanamide compounds such as $M(dca)_2(pyz)$ [pyz = pyrazine, M = Mn(II) and Cu(II)][7] have, as a part of their structure, square-gridlike layers similar to those found for **1** and **2**.

Magnetic Properties. The temperature dependence of the $\chi_M T$ product of **1** between 2 and 300 K is given in Figure 3. The value of $\chi_M T$ at 300 K of 3.48 $cm^3\ mol^{-1}$ K substantially exceeds the spin only value of 2.250 $cm^3\ mol^{-1}$ K expected for uncoupled high-spin Co^{II}(S=3/2) and Cu^{II} (S=1/2) ions with $g = 2$, thus indicating that an important orbital contribution due to Co(II) with a $^4T_{1g}$ ground state exists. In a magnetic field of 1 T, the $\chi_M T$ values gradually decrease with the temperature as a consequence of both the spin−orbit coupling effects and weak antiferromagnetic interactions. In a field of 0.025 T, however, the $\chi_M T$ values rise sharply at around 9 K to reach a maximum of 2.62 $cm^3\ mol^{-1}$ K at 7 K and then decreasing rapidly toward 2.54 $cm^3\ mol^{-1}$ K at 2 K. This low-temperature behavior might be due either to a spin-canting antiferromagnetism (weak ferromagnetism) or to traces of α-[Co(dca)],[1a−c] which shows ferromagnetic order at 9 K. It should be noted that two additional samples of hand-picked single crystals showed the same low-temperature dependence pattern. The high temperature (30−300 K) magnetic behavior of **1** most likely follows that of a magnetically isolated six-coordinated high-spin Co(II). The single-ion excited states for high-spin Co^{II} in O_h symmetry are well-separated from the $^4T_{1g}$ ground state ($^4T_{1g} - {}^4T_{2g} \approx 9000\ cm^{-1}$) and they can be neglected. The $^4T_{1g}$ ground state is split into a sextet, a quartet, and a Kramer's doublet

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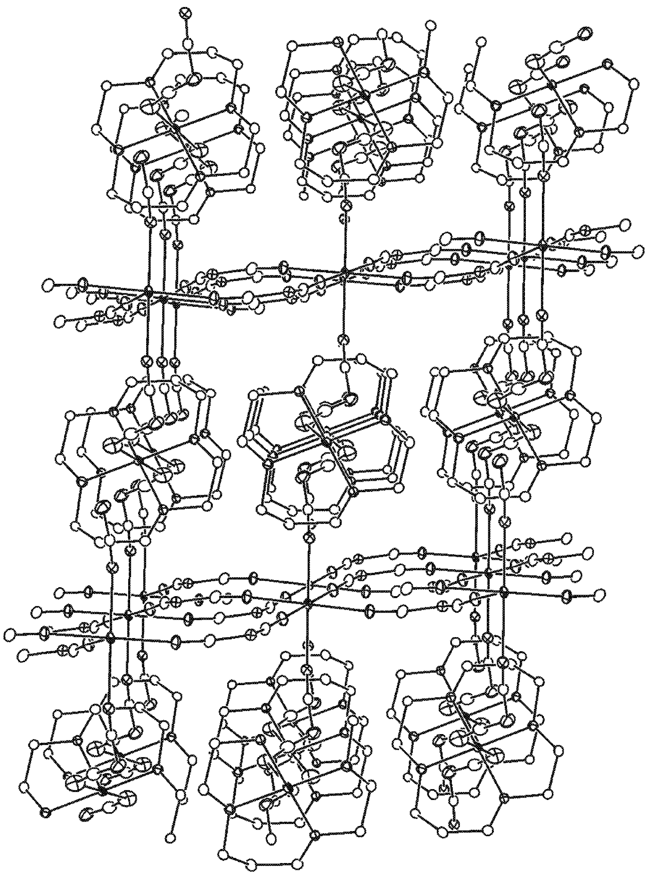

Figure 2. The 3D network in the structures of **1** and **2**.

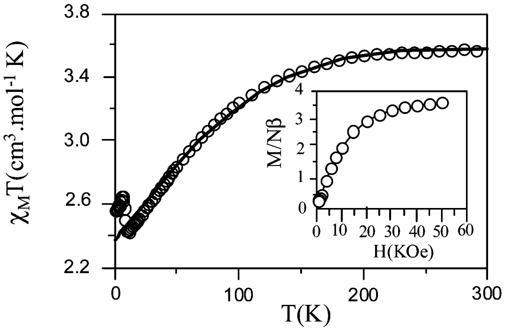

Figure 3. Temperature dependence of $\chi_M T$ and field dependence of M (inset) for **1**.

by spin−orbit coupling. The Hamiltonian describing the spin−orbit coupling is given by eq 1

$$\mathbf{H}_{SO} = -A\kappa\lambda \boldsymbol{LS} \tag{1}$$

where κ and λ are the orbital reduction and spin−orbit coupling parameter, respectively. The inclusion of the A factor is due to the use of T−P isomorphism. That is, A appears to distinguish between the matrix elements of the orbital angular momentum operator calculated with the wave functions of the ground $^4T_{1g}$ term with those calculated with the use of P-basis ($|1, -1\rangle$, $|1, 0\rangle$, and $|1, -1\rangle$). So, A can be defined by the symbolic equation: $\mathbf{L}(T_{1g}) = -A\mathbf{L}(P)$. Comparing the matrixes calculated in both ways, one arrives at the following expression (eq 2)

$$A = \frac{3/2 - c^2}{1 + c^2} \tag{2}$$

which describes the dependence of A on the strength of the cubic crystal field. c is the mixing coefficient of the $^4T_{1g}$ (F) and $^4T_{1g}$ (P) terms (eq 3).

$$\psi(^4T_{1g}) = \frac{1}{\sqrt{1 + c^2}}[\varphi^0(^4T_{1g},F) + c\varphi^0(^4T_{1g},P)] \tag{3}$$

The c value can be determined from the cubic ligand-field (Dq) and interelectronic repulsion (B) parameters (eq 4).

$$c = 0.75 + 1.875\frac{B}{Dq} - 1.25\left[1 + 1.8\frac{B}{Dq} + 2.25\left(\frac{B}{Dq}\right)^2\right]^{1/2} \tag{4}$$

In our case is not possible to obtain the corresponding spectrum of the CoN$_6$ core due to the presence of the Cu-(p-CTH) chromophore.

In the weak crystal-field limit ($B \gg$ Dq), one obtains that $c = 0$ ($A = 3/2$, the value used in most of the studies dealing with the magnetism of Co(II) compounds), whereas in the strong crystal-field limit ($B \ll$ Dq), one gets $c = -1/2$ ($A = 1$).

In **1**, the six-coordinated Co^{II} ion is axially distorted (four equatorial bismonodentate dca bridges with M−N distances of 2.12 Å and two axial monodentate dca ligands with M−N distances of 2.16 Å), being roughly D_{4h}. Under an axial distortion, the triplet orbital $^4T_{1g}$ ground state splits into a singlet $^4A_{2g}$ and a doublet ^4E_g level with an energy gap of D. The one-center operator responsible for an axial distortion can be expressed as (eq 5)

$$H_{ax} = D\left[L_Z{}^2 - \frac{1}{3}L(L + 1)\right] \tag{5}$$

The full Hamiltonian involving the spin−orbit coupling, axial distortion and Zeeman interaction is given in eq 6.

$$H = -A\kappa\lambda LS + D\left[L_z{}^2 - \frac{1}{3}L(L + 1)\right] + \beta(-A\kappa L + g_e S)H \tag{6}$$

No analytical expression for the magnetic susceptibility, which depends on A, k, λ, and D, can be derived. Matrix diagonalization techniques allowed us to determine the values of these parameters. The best-fit parameters using $g_{Cu} = 2.07$ and the experimental data for $T > 30$ K are $A = 1.43$ (B/Dq $= 1.05$ and $c = -0.18$), $k = 0.91$, $\lambda = -160$ cm^{-1}, and $D = 800$ cm^{-1}. The calculated curve matches well the experimental data in the temperature range $30 \le T \le 300$ K. At $T < 30$ K, the magnetic data are below the calculated curve, suggesting that a very small antiferromagnetic interaction between the Co^{II} ions occurs. This, together with the fact that the structure is centrosymmetric, seems to support that the rise in $\chi_M T$ at 9 K is due to traces of α-[Co(dca)$_2$] rather than to spin-canted antiferromagnetism. The values of the parameters obtained by the previous fit are within the

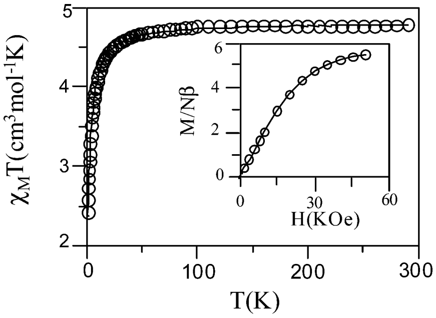

Figure 4. Temperature dependence of $\chi_M T$ and field dependence of M (inset) for **2**.

range of those reported for high-spin octahedral Co(II) complexes. The value of λ is slightly smaller than that of the free ion ($\lambda_0 = -180$ cm^{-1}) due to covalent effects. The value of A about 1.43 is in agreement with the weak ligand-field expected for the Co(II) ion in **1**. Finally, the energy gap ($D = 800$ cm^{-1}) between the orbital singlet, $^4A_{2g}$, and the orbital doublet, ^4E_g ($D > 0$ means that $^4A_{2g}$ is the ground term), indicates a low distortion, in agreement with the high magnetic moment at room temperature.

The magnetization vs H plot at 2.0 K of a polycrystalline sample of **1** is shown in the inset of Figure 3. At 50 kOe, compound **1** shows a saturation M_s value of 3.20 μ_B, that is, 2.17 μ_B per cobalt(II) ion and about 1.03 μ_B per Cu(II). The M_s value for cobalt(II) is smaller than the M_s expected value of 3 for $g = 2$. This difference is due to the fact that only the ground Kramers doublet is populated at 2.0 K to which an effective spin $S_{eff} = 1/2$ with a $g = (10 + 2Ak)/3$ can be associated. So, for $A = 1.43$ and $k = 0.91$ a M_s value of 2.10 μ_B is calculated. This value is closer to the experimental one.

The magnetic properties of **2** in the form of $\chi_M T$ vs T plot are shown in Figure 4. At room temperature in a field of 0.1 T, the $\chi_M T$ has a value of 4.80 cm^3 mol^{-1} K, which is in excellent agreement with the expected value of 4.76 cm^3 mol^{-1} K for isolated Mn^{II}(S=5/2) and Cu^{II}(S=1/2) with $g = 2$. Upon cooling, $\chi_M T$ values slightly decrease between 300 and 50 K and then decrease more rapidly to 2.41 cm^3 mol^{-1} K at 2 K. This behavior is indicative of weak antiferromagnetic coupling mainly occurring between Mn(II) ions through $\mu_{1,5}$-dicyanamide bridges combined with very small single-ion zero-field splitting effects.[3a,e,7b] In view of the long Cu−N distance involving the intersheets Mn−NCNCN−Cu pathway, magnetic data were fit to two models for a 2D classical square lattice Heisenberg ($\mathbf{H} = 2J\mathbf{S1S2}$) antiferromagnet (Lines's[8] and Curely's[9] models), including a Curie term to account for the copper(II) contribution. The best fit values were as follows: Lines, $g = 2.00$, $J = -0.11$ cm^{-1}; Curely $g = 1.99$, $J = -0.12$ cm^{-1} (in both cases, the Curie constant, C, for Cu(II) was fixed to 0.4, with $g = 2.07$). This small J value is similar to those observed for other 2D Mn(II) complexes containing either double or double and single five-atoms dicyanamide bridges.[3a,e,7b] The M vs H plot at 2 K (see inset Figure 3) is almost linear up to 3 T and then undergoes a curvature to reach a value of 5.47$N\beta$ at 5 T. This value is only slightly lower than the expected value of 6$N\beta$ for $S_{Mn} + S_{Cu} = 5/2 + 1/2 = 3$.

These and other cation-templated coordination polymers clearly reveal that the features of the cation such as size, shape, charge, available coordination positions, ability to form hydrogen bonding, etc. play a key role in the formation of the architecture of the coordination polymer. In this case, the [Cu(pCTH)]$^{2+}$ cation promotes the formation of a new type of anionic bimetallic dicyanamide network. Cation templation of anionic metal dicyanamide bridged assemblies by other metal−macrocycle complexes are currently under study.

Acknowledgment. This work was supported by the Spanish Ministerio de Ciencia y Tecnología (through projects BQU2001/3221 and BQU2001/2928), Junta de Andalucía, and the Academy of Finland (project 41519, R.K.).

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

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