Inorg. Chem. **2001,** *40,* 1718−1722

Cation Template of Anionic Metal Dicyanamide Networks

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Received August 25, 2000

Introduction

The crystal engineering of coordination polymers aims to gain control of the topology and geometry of the networks formed through judicious choice of ligand and metal precursor geometry.[1] However, other more subtle factors, such as counterion or solvent choice, can also affect the topology of the networks formed. $Cd(CN)_2$, for example, can display a wide range of topologies depending on choice of solvent.[2] Metal oxalates have been shown to form either 2D (6,3) sheets or chiral 3D (10,3)-*a* networks depending on countercation choice.[3]

Metal dicyanamide (dca, $N(CN)_2^-$) coordination polymers are of great current interest because of the interesting magnetic properties recently reported for such systems. The simple binary α-$M(dca)_2$ structures contain rutilelike networks and display ferromagnetism (Co, $T_c = 9$ K; Ni, $T_c = 20$ K), antiferromagnetism (Cr, $T_N = 47$ K; Mn, $T_N = 16$ K; Fe, $T_N = 19$ K), and paramagnetism (Cu).[4] We are currently investigating the use of different methods of modifying the network topology and thus magnetic properties of the metal dicyanamide coordination polymers, most notably through incorporation of coligands (either bridging or terminal) or solvent molecules into the coordination sphere of the metals.[5] We report here the modification of $M(dca)_3^-$ network topology through simple cation templation. The anionic $M(dca)_3^-$ compounds were first reported by Köhler in 1966; however, detailed structural and magnetic studies were not performed.[6]

Table 1. Crystallographic Data for **1**−**3**

	1	**2**	**3**
formula	$C_{30}H_{20}MnN_9P$	$C_{30}H_{20}AsMnN_9$	$C_{25}H_{18}MnN_9P$
fw	592.46	636.41	530.39
space group	$P2/n$ (No. 13)	$P2/n$ (No. 13)	$P2_12_12_1$ (No. 19)
temp, K	123(2)	123(2)	123(2)
a, Å	13.2564(3)	13.3943(4)	13.9593(3)
b, Å	7.5742(1)	7.5841(1)	17.2000(2)
c, Å	14.2386(3)	14.3076(4)	20.8587(3)
β, deg	98.731(1)	99.893(1)	
V, Å^3	1413.08(5)	1431.81(6)	5008.2(2)
Z	2	2	8
ρ_{calcd}, g cm^{-3}	1.392	1.476	1.407
μ, cm^{-1}	5.61	16.45	6.24
R1[a] $[I > 2\sigma(I)]$	0.0293	0.0329	0.059
wR2[b]	0.0650	0.1033	0.0866

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

Experimental Section

Synthesis of 1. Ph_4PBr (0.246 g, 0.50 mmol) in methanol (4 mL) was added to Na(dca) (0.134 g, 1.50 mmol) in water (4 mL). $Mn(NO_3)_2 \cdot 4H_2O$ (0.128 g, 0.51 mmol) was added, stirred until it was dissolved, and covered. After 15 min small rod-shaped colorless crystals of $(Ph_4P)Mn(dca)_3$ started to form, and they were filtered off after several days (0.064 g, 22%). Selected IR (Nujol, cm^{-1}): 2292 (s), 2239 (w), 2224 (sh), 2168 (vs), 1345 (s). Anal. Calcd for **1**, $C_{30}H_{20}MnN_9P$: C, 60.8; H, 3.4; N, 21.3. Found: C, 60.7; H, 3.3; N, 21.3. μ_{Mn} (295 K) = 5.69 μ_B. Powder X-ray diffraction confirmed the bulk was identical to the crystal structure.

Synthesis of 2. $Ph_4AsCl \cdot H_2O$ (0.218 g, 0.50 mmol) in methanol (3 mL) was added to Na(dca) (0.134 g, 1.50 mmol) in water (3 mL). $Mn(NO_3)_2 \cdot 4H_2O$ (0.126 g, 0.50 mmol) was added, stirred until it was dissolved, and covered. After several days large colorless crystals of $(Ph_4As)Mn(dca)_3$ were isolated (0.062 g, 20%). Selected IR (Nujol, cm^{-1}): 2291 (s), 2239 (w), 2226 (sh), 2169 (vs), 2136 (sh), 1346 (s). Anal. Calcd for **2**, $C_{30}H_{20}AsMnN_9$: C, 56.6; H, 3.2; N, 19.8. Found: C, 56.8; H, 3.1; N, 19.9. μ_{Mn} (295 K) = 5.71 μ_B. Powder X-ray diffraction confirmed the bulk was identical to the crystal structure.

Synthesis of 3. $MePh_3PBr$ (0.357 g, 1 mmol) in methanol (3.5 mL) was added to Na(dca) (0.267 g, 3 mmol) in water (4 mL). $Mn(NO_3)_2 \cdot 4H_2O$ (0.252 g, 1 mmol) was added, swirled until it dissolved, and

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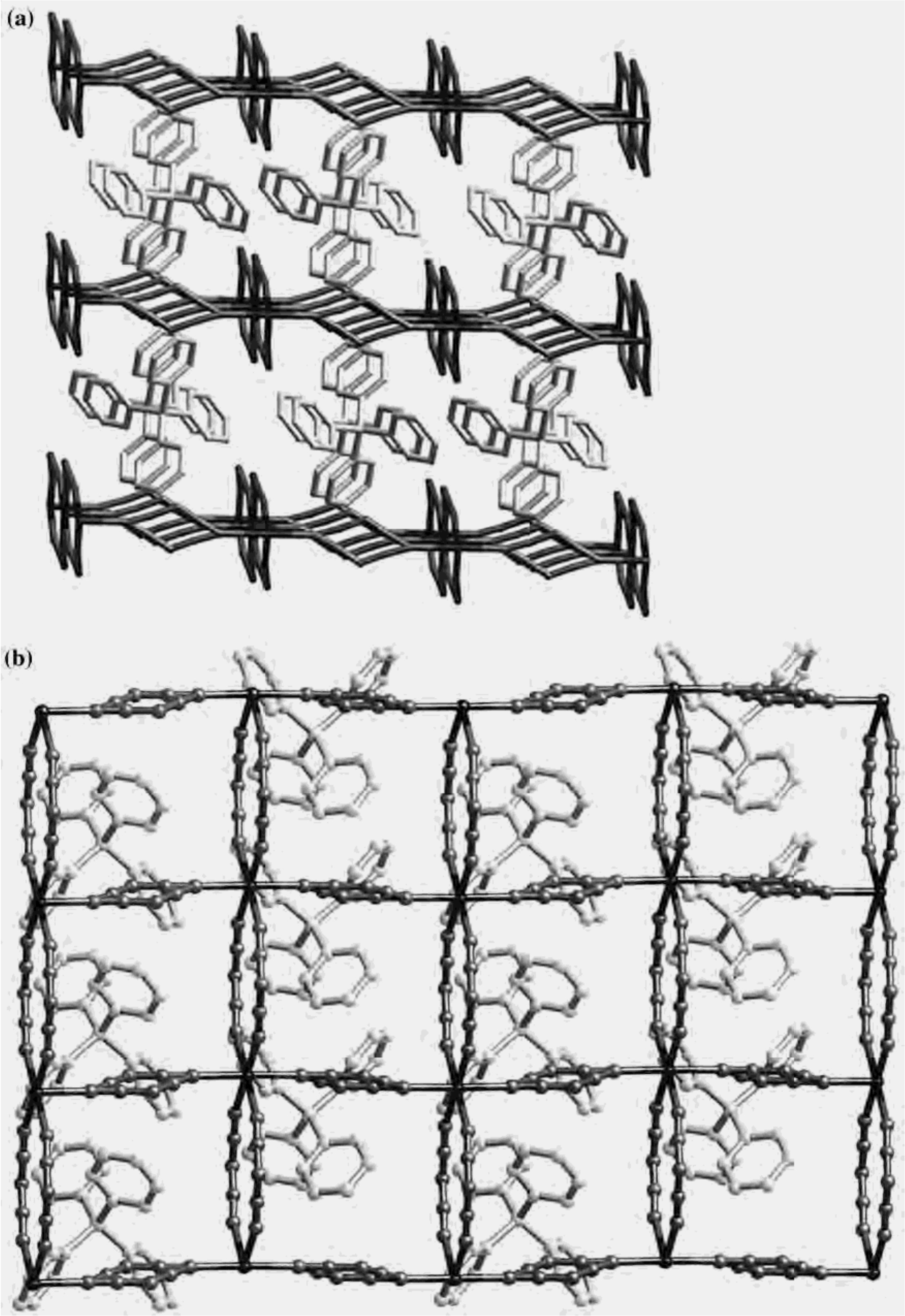

Figure 1. (a) Crystal structure of **1** (**2** is isomorphous), showing polymeric $Mn(dca)_3^-$ (4,4) sheets separated by layers of Ph_4P^+ cations. (b) Top view of a single $Mn(dca)_3^-$ layer in foreground with the packing of Ph_4P^+ cations shown in the background. Note the disorder in the dca ligands bridging in the horizontal direction. Note also the intercation 4-fold phenyl embraces, which generate columns in the vertical direction, and the $\pi-\pi$ interactions in the horizontal direction (between the phenyl groups located under the disordered dca ligands (in this view) and the phenyl groups located under the metal atoms of the $Mn(dca)_3^-$ sheet).

covered. After 24 h large colorless crystals of $(MePh_3P)Mn(dca)_3$ were isolated (0.284 g, 54%). Selected IR (Nujol, cm^{-1}): 2287 (s), 2243 (w), 2235 (w), 2229 (w), 2183 (vs), 2157 (vs), 1353 (w), 1342 (w). Anal. Calcd for **3**, $C_{25}H_{18}MnN_9P$: C, 56.6; H, 3.4; N, 23.8. Found: C, 56.6; H, 3.3; N, 24.0. μ_{Mn} (295K) = 5.88 μ_B. Powder X-ray diffraction confirmed the bulk was identical to the crystal structure.

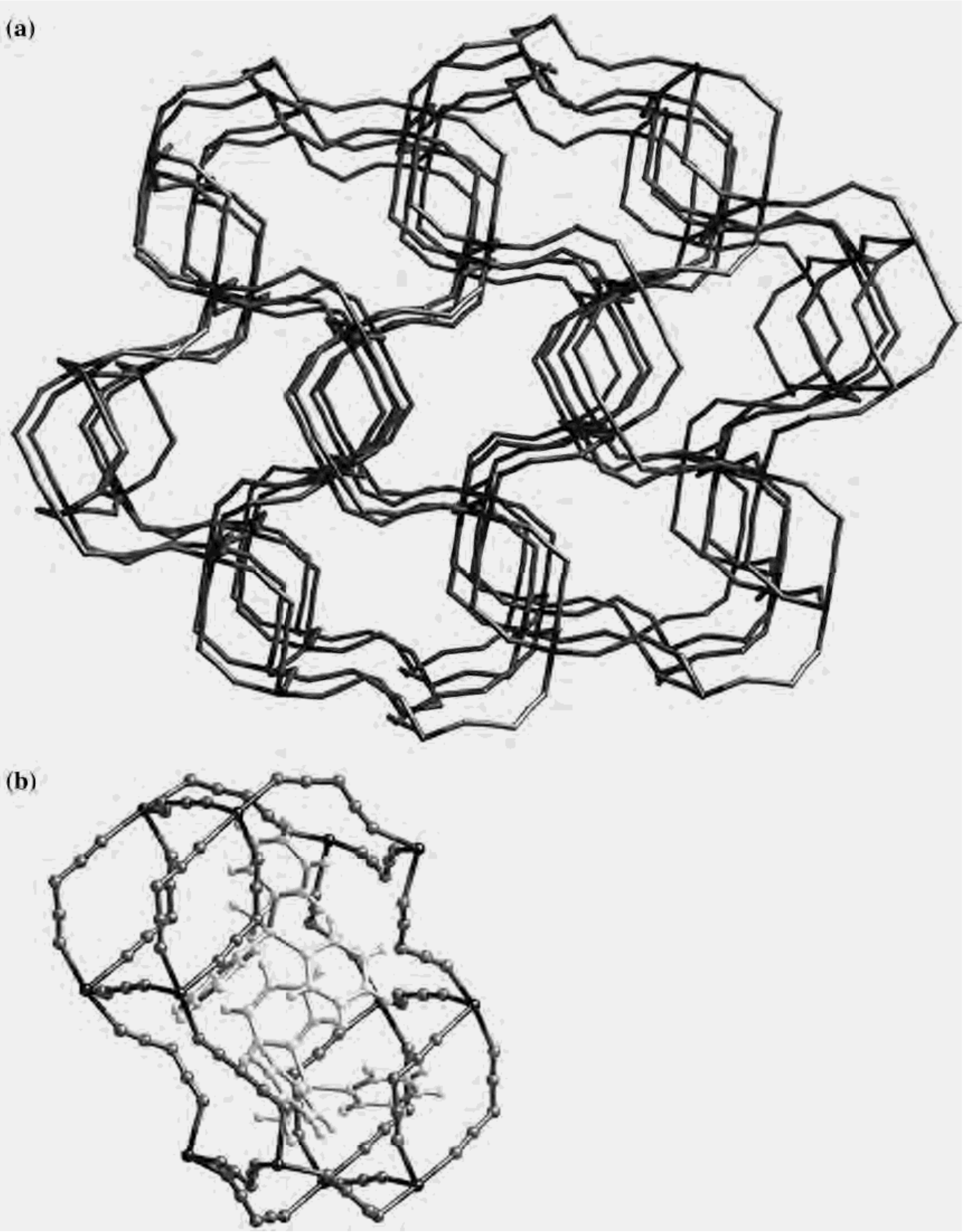

Figure 2. (a) The 3D anionic Mn(dca)$_3^-$ network in the structure of **3**, viewed down *b*. (b) Two MePh$_3$P$^+$ cations inside a single cavity in the structure of **3**.

X-ray Structure Determinations. Crystal data and details of the structure determinations are presented in Table 1. Data were collected at 123(2) K on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Absorption corrections (face-indexed) were applied only to the data for **1** (min/max transmission factors 0.902/0.935) and **3** (min/max transmission factors 0.847/0.913). Solutions were obtained by direct methods using SHELXS-97,[7] and the structures were refinement against $|F^2|$ using SHELXL-97.[7] Hydrogens were included at calculated positions but not refined (C$-$H = 0.95 Å (aryl) or 0.98 Å (methyl)), and H···C/N distances quoted in the text are calculated using these C$-$H distances. One of the dca ligands in both **1** and **2** was disordered over a center of symmetry such that there are only four unique atoms. CCDC reference numbers are CCDC-146448 (**1**), CCDC-146449 (**2**), and CCDC-146450 (**3**).

Results and Discussion

Reaction of Ph$_4$PBr or Ph$_4$AsCl·H$_2$O, sodium dicyanamide, and Mn(NO$_3$)$_2$·4H$_2$O resulted in precipitation of colorless crystals of (Ph$_4$E)Mn(dca)$_3$, E = P (**1**), As (**2**). The structures were determined by X-ray crystallography and found to be isomorphous. The structures consist of anionic Mn(dca)$_3^-$ 2D (4,4) sheets separated by layers of Ph$_4$E$^+$ cations (Figure 1a). They stack in the ($-$101) direction. The Mn(dca)$_3^-$ networks are composed of square sheets of Mn atoms bridged in the (101)

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direction by single dca bridges (Mn···Mn = 8.980 Å (**1**), 8.947 Å (**2**)) and in the (010) direction by double dca bridges (Mn···Mn = b = 7.5742(1) Å (**1**), 7.5841(1) Å (**2**)), giving an overall octahedral coordination geometry for the metal (Figure 1b). The single dca bridges are disordered about a center of symmetry, as shown in the figure. In the Co and Ni analogues of **1** and **2** the two positions of these dca ligands are in fact ordered and a doubling of the b axis occurs.[8]

The occurrence of multiple phenyl embraces between Ph_4E^+ and RPh_3E^+ cations has been studied in detail by Dance and co-workers.[9] These embraces are regularly occurring supramolecular motifs that involve concerted C−H···π and π···π contacts between the phenyl rings of adjoining cations. The cations in **1** and **2** show orthogonal 4-fold phenyl embrace (O4PE) interactions[9] between neighbors that involve four separate edge-to-face C−H···π interactions. These embraces create linear infinite chains of translational 4-fold phenyl embraces (LIT4PE)[9] in the (010) direction (vertical direction in Figure 1b; E···E separation = b = 7.5742(1) Å (**1**), 7.5841(1) Å (**2**)). These chains are cross-linked in the (101) direction by offset face-to-face π···π interactions (horizontal direction in Figure 1b; closest non-hydrogen contact = 3.315 Å (**1**), 3.322 Å (**2**); E···E separation = 9.56 Å (**1**), 9.52 Å (**2**)). The E···E separation is longer than the Mn···Mn separation in this direction because the E atoms are not collinear but zigzag.

These cation−cation interactions, however, play only a part in determining the overall structure. The cation layers need to be commensurate in both charge and separation with the repeat unit of the $Mn(dca)_3^-$ layers; indeed, the geometry of the anionic layers to a large extent dictates the E···E separation in the cation layers. There are also a number of weak supramolecular interactions between the cations and the anionic layers. The most significant of these are H···N contacts of 2.519 Å (C−H···N = 136.8°) and 2.617 Å (136.2°) for **1** (2.513 Å (136.6°) and 2.635 Å (135.2°) for **2**) and a H···C contact of 2.715 Å (120.9°) for **1** (2.729 Å (120.7°) for **2**).

Given the subtle balance of supramolecular forces in **1** and **2** discussed above, we were interested in exploring the effect of altering the nature of the cation. Use of $MePh_3P^+$ in place of Ph_4E^+ has a number of potential effects. There is insufficient structural flexibility in the $Mn(dca)_3^-$ layers in **1** and **2** to accommodate the smaller cations without a corresponding reduction in the packing efficiency of the cation layer. The replacement of a phenyl group with a methyl group will also disrupt the numerous subtle cation−cation and cation−anion supramolecular interactions discussed above.

Reaction of $MePh_3PBr$, sodium dicyanamide, and $Mn(NO_3)_2 \cdot 4H_2O$ in methanol/water resulted in precipitation of large colorless crystals of $(MePh_3P)Mn(dca)_3$ (**3**). The structure was determined by X-ray crystallography. The structure is vastly different from that seen in **1** and **2**. It now contains a 3D $Mn(dca)_3^-$ network. The cations are no longer in discrete layers but occur in pairs contained within cavities in the $Mn(dca)_3^-$ network.

The network can be described in terms of sheets lying in the xz plane cross-linked in the y direction into a 3D net. The sheets consist of Mn atoms connected by single dca bridges and double dca bridges (in the ratio 2:1) into a (6,3) hexagonal network. The double dca bridges occur on opposite sides of the hexagonal windows. Although all sheets are crystallographically equivalent, they display two different orientations. Each sheet is then connected to sheets above and below by single dca bridges, giving the overall 3D network with hexagonal channels (Figure 2a).

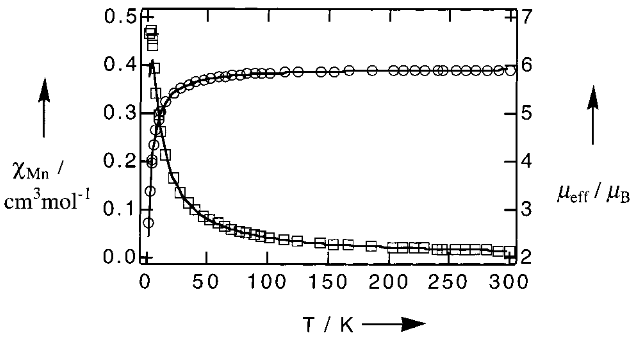

Figure 3. Plot of χ_{Mn} (□) and μ_{Mn} (○) vs temperature for **3**. The solid lines were calculated using a 2D model for $S = {}^5/_2$ [5k,12a] with $g = 2.01$, $J = -0.13$ cm^{-1}.

The anionic network contains cavities defined by one hexagonal window each from two adjoining hexagonal sheets and the six dca bridges connecting the two windows. Each of these cavities contains two $MePh_3P^+$ cations (Figure 2b). These two cations, which are crystallographically distinct, make a number of close contacts with the anionic framework around them. The cation centered on P1 interacts with the framework more strongly than that centered on P2, although both cations each make 11 separate C−H···C/N interactions that are less than the sum of the van der Waals radii. The most significant interactions for the P1 cation are H···N contacts of 2.539 Å (C−H···N = 167.5°) and 2.563 Å (145.3°) and H···C contacts of 2.645 Å (170.9°), 2.666 Å (141.1°), and 2.674 Å (164.0°). The most significant interaction for the P2 cation is a H···C contact of 2.735 Å (161.7°). The two cations within each cavity also engage in a moderate pseudo-6-fold phenyl embrace (pseudo-6PE),[10] which in fact involves three phenyl groups from the P1 cation and two phenyl groups and the methyl group from the P2 cation (P1···P2 = 6.81 Å). By use of the Dance notation, this would be a 5P1Y interaction.[10] The phenyl rings of the cations also display intercavity edge-to-face and vertex-to-face interactions.

The magnetic properties of compounds **1**−**3** are generally similar and indicative of very weak antiferromagnetic coupling occurring between the Mn^{II} ($^6A_{1g}$) centers, combined with single-ion zero-field splitting effects. In a field of 1 T, the μ_{Mn} values remain essentially constant at ca. 5.9 μ_B between 300 and 50 K, then decrease rapidly toward 3.0 μ_B at 2 K, in a manner similar to that noted for polymeric adducts of type $Mn(dca)_2L_2$ (where L = pyridine, $(pyrazine)_{1/2}$, CH_3OH), which contain Mn−NCNCN−Mn bridges.[5d,k] Taking complex **3** as an example, we see in Figure 3 that in a field of 1 T the susceptibilities, χ_{Mn}, pass through a maximum at 3 K. Since the irregular 3D network in **3** is made up of cross-linked sheets (vide infra), two models for a Heisenberg ($-2JS_1S_2$) antiferromagnet were used to fit the data, a 2D[5k] and a 3D (simple cubic)[11] high-temperature series expansion model, first developed by Rushbrooke and Wood.[12] Zero-field splitting was not included and was expected to be very small in size. The best-

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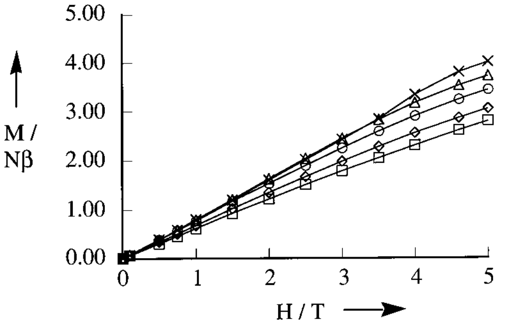

Figure 4. Magnetization isotherms for **3** measured at 2 (×), 3 (△), 4 (○), 5.5 (◇), and 7 K (□).

fit values were 2D: $g = 2.01$, $J = -0.13$ cm^{-1}; 3D, $g = 2.02$, $J = -0.08$ cm^{-1}. While neither model is expected to reproduce the χ_{max} region,[12] the 2D model was better below 10 K and both yielded good and similar fits above 10 K. Calculation of J using Line's[13] 2D equation for $S = {}^5/_2$ involving the temperature of χ_{max} gave -0.11 cm^{-1}, in good agreement with the best-fit value. The 2D model also gave best-fit values of $J = -0.08$ cm^{-1} for **1** and **2**.

Measurements of magnetization of **3**, in zero-field (ZFCM) or field-cooled (FCM) modes (5 Oe) gave no bifurcation of M, which does occur in ordered canted-spin antiferromagnets such as α-Mn(dca)$_2$.[5d] High-field magnetization isotherms for **3**, shown in Figure 4 (2−7 K and $H = 0$−5 T), give close to linear M vs H behavior up to $H \approx 3$ T, then a gentle downward curvature, reaching values at 5 T below the saturation value for $S = {}^5/_2$ of 5 Nβ, and indicative of antiferromagnetic coupling.[5a,d] The 2 K data show an unusual S shape at around 3 T. Further work is in progress to confirm whether 3D antiferromagnetic ordering is occurring in **3**. Similar situations arose recently in a structurally more regular 3D network system, $(Me_4N)Mn(N_3)_3$,[11] for which χ_{max} occurred at 70 K and J was -1.7 cm^{-1}, and in an interpenetrating double-net system Mn(dca)$_2$(pyrazine),[5k] for which χ_{max} was at 2.7 K and J was -0.12 cm^{-1}.

In summary, we have reported interesting new examples of cation templation of anionic coordination polymers. It appears that subtle and comparatively weak interactions between the cations and the anionic networks, and between the cations themselves, have a dramatic effect on the structure of the coordination polymer networks. We are currently exploring the effect of variation of cation size, shape, and charge on the topology of anionic dicyanamide networks. Structures isomorphous to those reported here have been found with M = Fe, Co, Ni,[8,14] while hexagonal 2D networks are formed when paramagnetic M(2,2′-bipy)$_3^{2+}$ cations are used.[15] A number of solvated anionic networks has also been discovered.[14]

Acknowledgment. This work was supported by grants from the Australian Research Council (ARC Large and Small Grants) to K.S.M. The receipt of an ARC Postdoctoral Fellowship (to S.R.B.) is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic details, in CIF format, tables of selected bond lengths and angles, and thermal ellipsoid plots with atom labeling for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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