Cation-templated construction of three-dimensional α-Po cubic-type $[M(dca)_3]^-$ networks. Syntheses, structures and magnetic properties of $A[M(dca)_3]$ (dca = dicyanamide; for A = benzyltributylammonium, M = Mn^{2+}, Co^{2+}; for A = benzyltriethylammonium, M = Mn^{2+}, Fe^{2+})

Letter

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A new family of three-dimensional cubic-like $[M(dca)_3]^-$ networks (dca = dicyanamide) templated by appropriate cations has been constructed and structurally characterized by X-ray crystallography.

The crystal engineering of coordination polymers is highly influenced by the judicious choice of ligand, metal coordination geometry, template, and other subtle factors, such as counterion, solvent choice and reaction temperature.[1] Metal dicyanamide (dca) coordination polymers are currently of great interest because of their interesting magnetic properties as well as their varied topologies due to versatile coordination modes.[2] So far, a number of one-, two- and three-dimensional (3D) neutral coordination polymers have been reported with different structural features, such as 1D $[M(dca)_2L]$ chains (L = neutral terminal or chelate ligand),[3] 3D α-Po-like $[M(dca)_2(L)]$ (L = *N*,*N*′-bridging spacers),[4] 2D sheet-like β-$M(dca)_2$[5] and 3D rutile-like α-$M(dca)_2$[6] networks, as well as other types.[7] Recently, the anionic networks formulated as $[M(dca)_3]^-$ have been isolated and some different structural topologies have been shown, namely, 2D square-like (4,4) layers in $(Ph_4E)[M(dca)_3]$ (E = P or As, M = Mn or Co),[8] 2D honeycomb-like (6,3) layers in $[M(2,2'\text{-bpy})_3][M(dca)_3]_2$ (M = Fe or Ni; M′ = Mn)[9] and a 3D network with hexagonal windows in $(MePPh_3)[Mn(dca)_3]$.[8a]

The $[M(dca)_3]^-$ networks with cubic-like α-Po structural type are one of the simplest but most important ones, necessary to understand the magnetic interaction pathways in the three-dimensional $[M(dca)_3]^-$ or $[M(dca)_2L]$ networks (L = neutral bridging ligands); however, no cubic-like $[M(dca)_3]^-$ hypothetical frame has, as yet, been isolated although some exploratory work and the above-mentioned[6–8] anionic $[M(dca)_3]^-$ networks formed through large cation templating have been reported. Working towards this target, we have tried to utilize the templating of cations with suitable and matchable sizes to generate cubic $[M(dca)_3]^-$ networks. In this communication we report the preparation, crystal structures and preliminary magnetic properties of new three-dimensional networks in the $[M(dca)_3]^-$ family, namely, cubic-like $A[M(dca)_3]$ (for A = benzyltributylammonium, M = Mn^{2+} **1**; Co^{2+} **2**; for A = benzyltriethylammonium, M = Mn^{2+} **3**; Fe^{2+} **4**).

All complexes were synthesised by assembly of the metal chloride salts, Na(dca) and benzyltributylammonium chloride or benzyltriethylammonium chloride. The elemental analysis confirmed the formula of **1**–**4**.

X-Ray crystallography has established that **1** and **2** are isomorphous. Each is made up of an anionic three-dimensional cubic network with $M_8(dca)_{12}$ units and benzyltributylammonium cations. As illustrated in Fig. 1, each octahedral M^{II} is bonded to six different dca ligands. Each dca is μ-bonded to two M^{II} atoms through the terminal CN groups. The M^{II} octahedron is slightly distorted from an O_h symmetry with M–N distances of 2.241(2)–2.285(2) and 2.159(3)–2.194(3) Å, averaging to 2.268 and 2.179 Å for **1** and **2**, respectively, while *cis*-N–M–N bond angles range from 89.08° to 90.92°. The dca ligand displays nearly ideal C_{2v} symmetry with C–N bond distances averaging 1.150 Å, which is typical for this ligand.[3–9] The C–N–M bond angles are virtually linear, ranging from 175.1° to 179.6°. The adjacent M···M separations are 8.825–8.909 and 8.740–8.806 Å for **1** and **2**, respectively.

3 and **4** are also isomorphous. Each is made up of an anionic three-dimensional cubic network with $M_8(dca)_{12}$ units and benzyltriethylammonium cations (Fig. 2). The anionic networks of **3** and **4** are similar to those of **1** and **2**. The M–N distances are in the range of 2.183(2)–2.2447(18) and 2.1213(17)–2.1797(16) Å (average 2.217 and 2.153 Å) for **3** and **4**, respectively, while *cis*-N–M–N bond angles range from 88.27(7)° to 91.73(7)°. The C–N bond distances of the dca ligand average to 1.142 Å, similar to those in **1** and **2** and other reported M–dca compounds.[4–9] The C–N–M bond angles deviate appreciably from linearity and range from 169.86(19)° to 175.20(16)°. The intra-network M···M separations are 8.176–8.369 and 8.115–8.302 Å for **3** and **4**, respectively, which are significantly shorter than those found in **1** and **2**.

It is noteworthy that **1**–**4** are the first examples of three-dimensional $[M(dca)_3]^-$ open networks with a cubic-like

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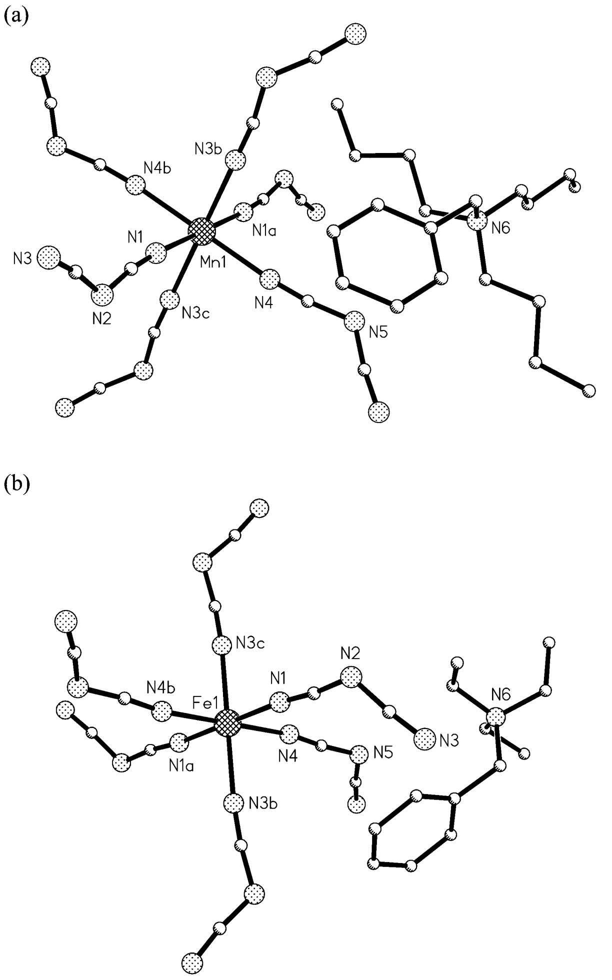

Fig. 1 Co-ordination environments of the metal atoms in **1** (a) and **4** (b).

α-Po structural type constructed by μ-dca. The benzyltributylammonium or benzyltriethylammonium cations are located in these cavities and are in close contact with the anionic framework around them through extensive supramolecular interactions. Of the reported metal–dca networks, only some related compounds with a α-Po-type framework, such as [Mn(dca)$_2$(pyrazine)] and [M(dca)$_2$(4,4′-bpy)] (M = Fe, Co, Ni) have been documented.[4] Another most striking feature is that the shapes and sizes of the cations evidently influence the construction of the three-dimensional networks of **1**–**4**. There are remarkable N-π(phenyl) interactions between the uncoordinated N of dca and the phenyl moieties of the cations. The distances between the N atom and the centroid of the phenyl ring are 3.227–3.237 Å, while the C(phenyl)–centroid–N(dca) angle is 88.9–90.6° for the 6 ring C atoms (Fig. 3). The M···M distances within each cubic M$_8$(dca)$_{12}$ unit are dependent on the size of the templating cation. Moreover, the three ethyl or butyl groups of the cation are oriented with no structural disorder, which can be attributed to the formation of C–H···N hydrogen bonds with adjacent dca N atoms (C···N 3.484–3.896 Å).

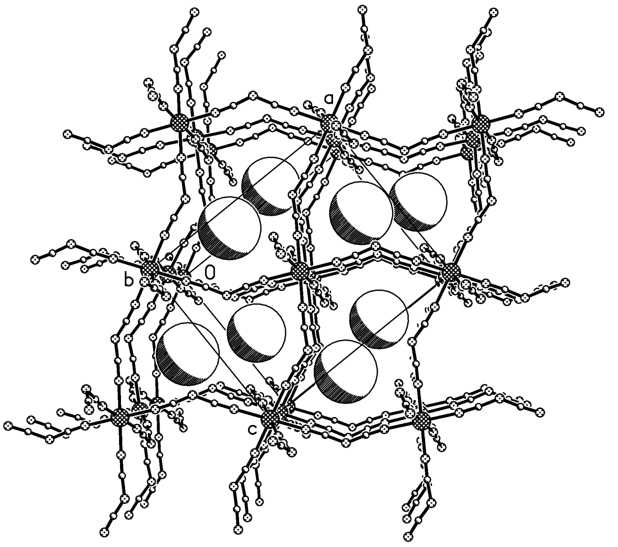

Fig. 2 Perspective view showing 3-D network in **4** along the *b* axis direction. Large open balls represent the cations.

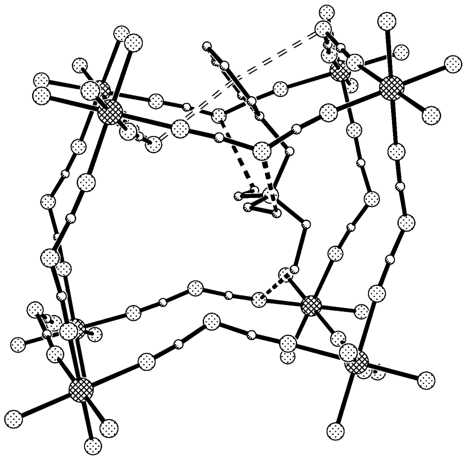

Fig. 3 Perspective view showing the interactions between the cation and the cubic framework in **4**.

Complexes **1**–**4** crystallize in the same space group and the lengths of the *a* axises are similar; however the lengths of the *b* and *c* axes of **1** and **2** are distinctly longer than those of **3** and **4**, which obviously results from the different sizes of the templating cations. It should be noted that the attempt to prepare such a product featuring a α-Po type framework failed even though reaction parameters such as reaction time, temperature, pH value, and molar ratio of reactants were changed when smaller cations such as Me_4N^+, Et_4N^+, were adopted. Particularly, another three-dimensional network with different structural features was isolated when n-Bu_4N^+ was used.[10] Considering the reported results that larger cations (such as Ph_4P^+, Ph_4As^+, $MePh_3P^+$ or $[M(2,2'\text{-bpy})_3]^{2+}$) have templated the formation of two-dimensional square- and honeycomb-like networks and three-dimensional coordination architectures,[8,9] the cations seem to be highly size- and shape-selective in the templated formation of the $[M(dca)_3]^-$ network with cubic-like α-Po structural type.

The 2 to 300 K temperature dependence of the magnetic susceptibility, χ, of **1**, **2** and **3** was measured. The $\chi(T)$ can be fitted to the Curie–Weiss equation with $C = 4.10$ cm^3 mol^{-1} K and $\theta = -2.17$ K for **1**, and $C = 4.47$ cm^3 mol^{-1} K and $\theta = -3.74$ K for **3**. The small θ values reflect weak anti-ferromagnetic couplings between the Mn^{II} ions within the 3D networks of **1** and **3**. Moreover, **3** has a comparatively larger $|\theta|$ value than that for **1**, which is consistent with the results of the X-ray structural analysis. At room temperature, the effective moments, μ_{eff}, have values of 5.69 and 5.99 μ_B for **1** and **3**, respectively, which are comparable with the expected spin-only value of 5.92 μ_B for paramagnetic $S = 5/2$ spins. Upon cooling, $\mu_{eff}(T)$ remains invariant down to *ca.* 55 K, where it then begins to decrease more rapidly owing to increasing antiferromagnetic correlations, similar to those found in recently

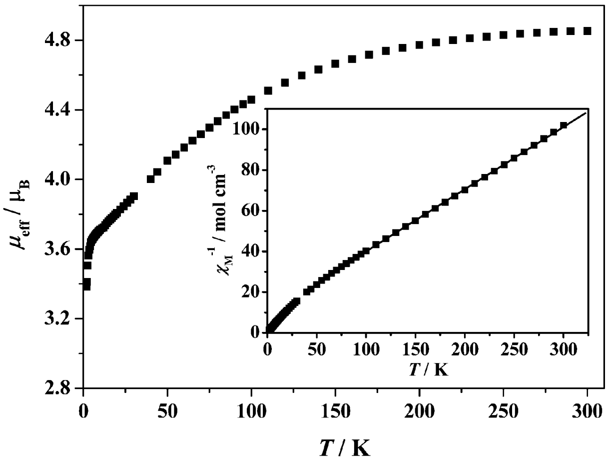

Fig. 4 Temperature-dependent magnetic susceptibility plotted as μ_{eff} *versus* T and $\chi_M{}^{-1}$ *versus* T (insert) at 2 K for a powdered sample of **2**.

reported materials having μ-dca bridges, such as (cation) $[Mn(dca)_3]$[8] (cation = Ph_4P^+ or $MePh_3P^+$) and $Mn(dca)_2(L)$[4,5] (L = pyrazine or 4,4′-bipyridine). For **2**, the data showing a linear dependence of the inverse susceptibility with temperature (75–300 K) were analysed by fitting to the Curie–Weiss law, with $C = 3.27$ cm^3 mol^{-1} K and $\theta = -30.8$ K (Fig. 4). At room temperature, the effective moment, μ_{eff}, has a value of 4.85 μ_B, which is significantly larger than the expected spin-only value of 3.87 μ_B per paramagnetic $S = 3/2$ spin, indicating that the orbital contribution is incompletely quenched. Upon cooling, $\mu_{eff}(T)$ gradually decreases from 4.85 μ_B at 300 K to 3.38 μ_B at 2.0 K owing to the contribution of single-ion behavior of high-spin Co(II) ions and also to antiferromagnetic exchange between the Co centers. Further studies on the magnetic properties of **1**–**4** and the assembly of other $[M(dca)_3]^-$ networks templated by other cations are in progress.

In summary, we have obtained a new family of three-dimensional $[M(dca)_3]^-$ networks with cubic $[M_8(dca)_{12}]$ building units. Our results also suggest effective routes to constructing desired cationic or anionic frameworks *via* the templating of suitable counterions.

Experimental

Synthesis

An aqueous solution (5 cm^3) of Na(dca) (0.270 g, 3.0 mmol) was added dropwise to a stirred MeOH solution (10 cm^3) of MCl_2 (1.0 mmol) and benzyltriethylammonium chloride (1.0 mmol) or benzyltributylammonium chloride (1.0 mmol) at 50 °C for 30 min. The resulting solution was filtered and allowed to stand in air at room temperature for 2 weeks, yielding well-shaped crystals (*ca.* 70–90% yields for **1**–**4**). Anal. calcd for $C_{25}H_{34}MnN_{10}$ (**1**): C, 56.69; H, 6.47; N, 26.46%; found: C, 56.56; H, 6.44; N, 26.28%. Calcd for $C_{25}H_{34}CoN_{10}$ (**2**): C, 56.26; H, 6.43; N, 26.26%; found: C, 56.12; H, 6.35; N, 26.20%. Calcd for $C_{19}H_{22}MnN_{10}$ (**3**): C, 51.22; H, 4.98; N, 31.46%; found: C, 51.10; H, 4.85; N, 31.32%. Calcd for $C_{19}H_{22}FeN_{10}$ (**4**): C, 51.11; H, 4.97; N, 31.39%; found: C, 51.02; H, 4.95; N, 31.26%.

X-Ray crystallography

Data collections were performed at 293 K on a Siemens R3m or Rigaku CCD diffractometer (Mo-Kα, $\lambda = 0.71073$ Å). The structures were solved with direct methods and refined with full-matrix least-squares technique (SHELXL-97),[11] giving a final R_1 value of 0.0597 for 179 parameters and 2516 unique reflections with $I \geq 2\sigma(I)$ and wR_2 of 0.1785 for all 3493 reflections for **1**, a final R_1 value of 0.0578 for 179 parameters and 1958 unique reflections with $I \geq 2\sigma(I)$ and wR_2 of 0.1812 for all 3050 reflections for **2**, a final R_1 value of 0.0412 for 149 parameters and 2077 unique reflections with $I \geq 2\sigma(I)$ and wR_2 of 0.1133 for all 2609 reflections for **3**, a final R_1 value of 0.0329 for 149 parameters and 1907 unique reflections with $I \geq 2\sigma(I)$ and wR_2 of 0.0891 for all 2582 reflections for **4**.

Complexes **1**–**4** crystallize in the orthorhombic system, space group *Pnma* (no. 62).

Crystal data for **1**: $C_{25}H_{34}MnN_{10}$, $M_r = 529.56$, $a = 12.654(6)$, $b = 17.650(7)$, $c = 12.543(6)$ Ma, $U = 2801(2)$ Å^3, $Z = 4$, $D_c = 1.256$ g·cm^{-1}, $\mu = 5.03$ cm^{-1}.

Crystal data for **2**: $C_{25}H_{34}CoN_{10}$, $M_r = 533.55$, $a = 12.536(8)$, $b = 17.480(1)$, $c = 12.372(6)$ Å, $U = 2711(2)$ Å^3, $Z = 4$, $D_c = 1.307$ g·cm^{-1}, $\mu = 6.66$ cm^{-1}.

Crystal data for **3**: $C_{19}H_{22}MnN_{10}$, $M_r = 445.41$, $a = 12.932(6)$, $b = 16.352(7)$, $c = 10.625(5)$ Å, $U = 2246.9(16)$ Å^3, $Z = 4$, $D_c = 1.317$ g cm^{-3}, $\mu = 6.14$ cm^{-1}.

Crystal data for **4**: $C_{19}H_{22}FeN_{10}$, $M_r = 446.32$, $a = 12.799(5)$, $b = 16.229(7)$, $c = 10.577(5)$ Å, $U = 2197.0(16)$ Å^3, $Z = 4$, $D_c = 1.349$ g cm^{-3}, $\mu = 7.13$ cm^{-1}.

CCDC reference numbers 205621–205624. See http://www.rsc.org/suppdata/nj/b3/b300760j/ for crystallographic files in CIF or other electronic format.

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