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Anionic metal dicyanamide networks with paramagnetic counter-cations

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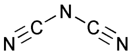
The $M(bipy)_3^{2+}$ cations in the isomorphous structures of $[M(bipy)_3][M'(dca)_3]_2$, [dca = dicyanamide, $N(CN)_2^-$; M = Fe, M′ = Mn 1, Fe 2 or M = Ni, M′ = Mn 3] are contained within hexagonal windows of anionic 2D (6,3) $M(dca)_3^-$ sheets; weak antiferromagnetic coupling is observed between metal centres within the anionic networks of all three compounds.

Our recent work, and that of others, on the topology and magnetism of binary transition metal(II) dicyanamides $M(dca)_2$ [dca = $N(CN)_2^-$] and on neutral adducts of type $M(dca)_2L_x$, where $x = 3$ for L = H_2O, $x = 2$ for L = pyridine, MeOH, EtOH, DMF and $x = 1$ for L = pyrazine, 4,4′-bipyridine, H_2O and 2-aminopyridine, has revealed a fascinating array of structures and magnetic phenomena.[1,2] To date all compounds reported have been homometallic. However, we have recently extended our dicyanamide work to include the anionic coordination polymers $M(dca)_3^-$ and $M(dca)_4^{2-}$ first reported by Köhler *et al.* but without any crystallographic or magnetic characterisation.[3] We have found that the network topology of the anion is dependent on the counter-cation used—the networks are in fact cation templated.[4] We realised that these systems also offered the possibility of making heterometallic systems through the use of paramagnetic metal-containing counter-cations. Thus we report here the structural and magnetic properties of new anionic metal dicyanamide systems containing $M(bipy)_3^{2+}$ (bipy = 2,2′-bipyridine) counter-cations. Future work will involve use of spin-crossover Fe(II) and Co(II) cationic chelates to search for cooperative effects when such centres are dispersed in a 2D host lattice (*vide infra*).

Reaction of sodium dicyanamide, $M(bipy)_3^{2+}$ and the appropriate metal nitrate or perchlorate gave dark red crystals of $[Fe(bipy)_3][M(dca)_3]_2$, M = Mn **1**, Fe **2** and orange/pink crystals of $[Ni(bipy)_3][Mn(dca)_3]_2$ **3**.† The structures were determined by single crystal X-ray crystallography and found to be isomorphous.[5] Bulk sample purities were confirmed by powder X-ray diffraction. The structures consist of infinite hexagonal (6,3) anionic sheets of $M(dca)_3^-$ and $M(bipy)_3^{2+}$ counter-cations (Fig. 1). Each octahedral metal atom in a sheet is bridged by three pairs of dca ligands, coordinating through only the terminal nitrile nitrogen atoms, to three other metal atoms. There are two crystallographically unique metal atoms in the sheets, and within each sheet they are arranged in an alternating fashion [M–N 2.203(3)–2.238(2) Å (**1**), 2.130(2)–2.185(2) Å (**2**) and 2.200(2)–2.242(2) Å (**3**)]. These sheets lie in the *yz* plane, and stack in the *x* direction. The $M(bipy)_3^{2+}$ counter-cations lie inside the hexagonal windows of the sheets (Fig. 2).



dca

There are a number of close contacts between the cations and the anionic networks. The most significant of these are H···C contacts of 2.695 Å (C–H···C = 116.7°), 2.745 Å (148.0°), 2.775 Å (123.6°) for **1**; 2.690 Å (116.6°), 2.674 Å (148.2°), 2.798 Å (121.6°) for **2**; and 2.700 Å (114.0°), 2.714 Å (148.9°), 2.770 Å (126.4°) for **3** and H···N contacts of 2.675 Å (C–H···N = 140.5°), 2.682 Å (121.1°) for **1**; 2.602 Å (140.1°), 2.683 Å (117.0°) for **2**; and 2.663 Å (139.3°), 2.673 Å (119.9°) for **3**. There are also edge-to-face [centroid–centroid = 5.07 Å (**1**), 5.02 Å (**2**) and 5.04 Å (**3**)] and vertex-to-face [centroid–centroid = 4.96 Å (**1**), 4.92 Å (**2**) and 4.91 Å (**3**)] inter-cation interactions between the pyridyl rings of cations in adjoining sheets.

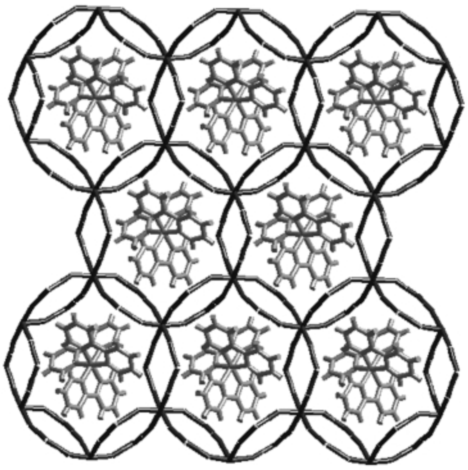


Fig. 1 The sheet structure of **1–3**.

It is of interest to compare these structures to a number of closely related oxalate networks reported. Numerous hexagonal 2D (6,3) sheet structures have been reported for metal oxalate $[M_2(ox)_3]^{n-}$ networks with a variety of counter-cations,[6] including paramagnetic ones such as $[(Cp^*)_2M]^+$.[7] In contrast to the structures reported here, however, the counter-cations lie *between* the sheets rather than *within* the planes of the sheets. This is due to the smaller size of the hexagonal windows in the oxalate sheets compared to the dca sheets. Interestingly, when oxalate networks are crystallised with $M(bipy)_3^{n+}$ counter-cations, chiral 3D (10,3)-a networks are formed.[6b,c] Each crystal contains cations of only one handedness, and all $M(ox)_3^{n-}$ centres are also of a single hand. In contrast, the structures described here contain cations of both handedness, with each anionic sheet containing counter-cations of only one hand but successive anionic sheets containing counter-cations of alternating hands. As for the oxalate analogues, each (6,3) $M(dca)_3^-$ sheet contains $M(dca)_6^{4-}$ centres of alternating hands. The structure is nonetheless non-centrosymmetric (space group *Fdd*2) as layers of opposite cation chirality are related by glide planes rather than inversion centres. The alternating layers stack

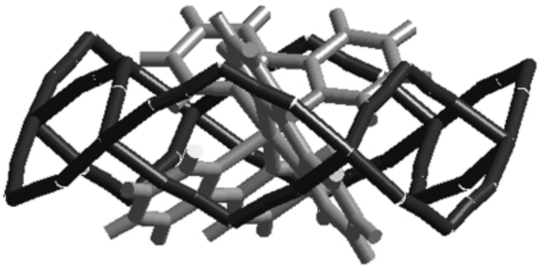


Fig. 2 Location of a $M(bipy)_3^{2+}$ cation inside a hexagonal window of a $M(dca)_3^-$ sheet.

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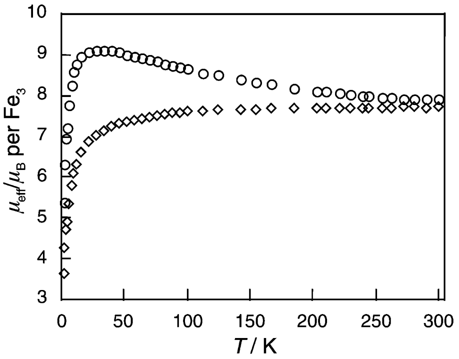

Fig. 3 Plots of μ_{eff} (per Fe_3) *vs.* temperature for $[Fe(bipy)_3][Fe(dca)_3]_2$ **2** measured in a field of 1 T as a neat powder (○) and dispersed in vaseline (◇).

such that successive layers are offset from each other, and hexagonal channels are not formed.

Since it contains a diamagnetic cation, $Fe(bipy)_3^{2+}$, the μ_{eff} value at room temperature of 8.04 μ_B for **1** is that due to $Mn(dca)_3^-$ alone. The variation in temperature mirrors that found for salts such as $PPh_4[Mn(dca)_3]$, which contain a 2D sheet structure, different to that of **1**. μ_{eff} values in **1** remain constant down to 50 K then decrease rapidly below this due to weak antiferromagnetic coupling. In an applied field of 1 T, **2** shows a μ_{eff} value at 300 K of 7.7 μ_B, per Fe_3, which, when the sample is dispersed in a vaseline mull to prevent crystallite torquing, remains constant down to 50 K and then decreases rapidly to 3.6 μ_B at 2 K because of weak antiferromagnetic coupling combined with zero field splitting effects (Fig. 3). Since the $Fe(bipy)_3^{2+}$ group is d^6 low spin the expected μ_{eff} value for uncoupled ($S = 0, S = 2, S = 2$) centres, with $g = 2.0$, is 48 = 6.93 μ_B, excluding orbital contribution/spin–orbit coupling effects on the high spin $Fe^{II}(dca)_3^-$ centre and second order Zeeman effects (TIP) on the $Fe(bipy)_3^{2+}$. An interesting feature, and one possibly overlooked in high-spin Fe(II) systems, including crossover studies, is the field induced torquing which occurs when a neat solid sample was used (Fig. 3). It can be seen that, as the temperature is raised from 2 K, in $H = 1$ T, a ferromagnetic like plot is obtained with a broad maximum in μ_{eff}, the room temperature value being similar to that in the mull sample. This effect arises from anisotropy in the susceptibility of high spin Fe(II), as was also found in Mn(III).[8] It is possible, therefore, to draw wrong conclusions, particularly in extended systems of the present type and caution is warranted.

Compound **3** also displays Curie-like susceptibilities with a value of μ_{eff} (per mol) of 8.7 μ_B at 300 K, which decreases gradually to reach 8.2 μ_B at 50 K then rapidly to 4.9 μ_B at 2 K. The data are again compatible with essentially isolated cationic and extended anionic sublattices, the latter showing weak antiferromagnetism [μ(uncoupled) = 8.83 μ_B for $S = 1 + S = 5/2 + S = 5/2$]. Despite this lack of cation (paramagnet)–anion interaction, the prospect of obtaining unusual magnetic effects when spin-crossover cations are incorporated remains positive since it is well known that weak intermolecular perturbations (*e.g.* solvate, H-bonding, π–π stacking) can sensitively influence the crossover and cooperative behavior in crystals.[9]

Notes and references

† **1**: an ethanol–water solution (5 ml) of Na(dca) (270 mg, 3.0 mmol) and $Mn(ClO_4)_2 \cdot 4H_2O$ (360 mg, 1.1 mmol) was added to an ethanol–water solution (10 ml) of $[Fe(bipy)_3](ClO_4)_2$ (360 mg, 0.50 mmol). Dark red crystals of **1** were obtained after 24 h (400 mg, 0.39 mmol, 77%). Found: C, 48.73; H, 2.31; N, 32.65. Calc. for $C_{42}H_{24}FeMn_2N_{24}$: C, 48.95; H, 2.33; N, 32.63%. Selected IR (2100–2300) (cm^{-1}, Nujol): 2291m, 2232m, 2169s.

2: an ethanol–water solution (10 ml) of Na(dca) (103 mg, 1.16 mmol) and $Fe(BF_4)_2 \cdot 6H_2O$ (129 mg, 0.382 mmol) was added to an ethanol–water solution (25 ml) of $[Fe(bipy)_3](ClO_4)_2$ (135 mg, 0.187 mmol). Dark red crystals of **2** formed after 2 days (25 mg, 0.024 mmol, 13%). Found: C, 49.11; H, 2.32; N, 32.49. Calc. for $C_{42}H_{24}Fe_3N_{24}$: C, 48.86; H, 2.34; N, 32.56%. Selected IR (2100–2300) (cm^{-1}, Nujol): 2288m, 2235m, 2172s.

3: an ethanol–water solution (10 ml) of $Ni(bipy)_3(NO_3)_2$ (162 mg, 0.249 mmol) and Na(dca) (140 mg, 1.57 mmol) was allowed to diffuse slowly into an ethanol–water solution (10 ml) of $Mn(NO_3)_2 \cdot 4H_2O$ (125 mg, 0.498 mmol). After 2 days large orange/pink crystals of **3** were collected (126 mg, 0.122 mmol, 49%). Found: C, 48.98; H, 2.26; N, 32.13. Calc. for $C_{42}H_{24}NiMn_2N_{24}$: C, 48.88; H, 2.32; N, 32.54%. Selected IR (2100–2300) (cm^{-1}, Nujol): 2290m, 2231m, 2165s.

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5 *Crystal data*: for $C_{42}H_{24}FeMn_2N_{24}$ **1**: $M = 1030.58$, orthorhombic, space group *Fdd*2 (no. 43), $a = 28.7821(7)$, $b = 12.5280(3)$, $c = 23.7374(4)$ Å, $U = 8559.3(3)$ Å^3, $T = 123$ K, $Z = 8$, $D_c = 1.600$ g cm^{-3}, $F(000) = 4160$, μ(Mo-Kα) = 0.981 mm^{-1}, dark red crystal, 28565 reflections measured, 5287 unique ($R_{int} = 0.0635$), 313 parameters, $R_1 = 0.0424$ for 4323 reflections with $I > 2\sigma(I)$, $wR_2 = 0.0699$ (all data). For $C_{42}H_{24}Fe_3N_{24}$ **2**: $M = 1032.40$, orthorhombic, space group *Fdd*2 (no. 43), $a = 28.8799(6)$, $b = 12.4011(3)$, $c = 23.5140(3)$ Å, $U = 8421.4(3)$ Å^3, $T = 123$ K, $Z = 8$, $D_c = 1.629$ g cm^{-3}, $F(000) = 4176$, μ(Mo-Kα) = 1.087 mm^{-1}, dark red crystal, 28083 reflections measured, 4983 unique ($R_{int} = 0.0398$), 313 parameters, $R_1 = 0.0290$ for 4487 reflections with $I > 2\sigma(I)$, $wR_2 = 0.0608$ (all data). For $C_{42}H_{24}Mn_2N_{24}Ni$ **3**: $M = 1033.44$, orthorhombic, space group *Fdd*2 (no. 43), $a = 28.8625(5)$, $b = 12.5231(2)$, $c = 23.9239(3)$ Å, $U = 8647.2(2)$ Å^3, $T = 123$ K, $Z = 8$, $D_c = 1.588$ g cm^{-3}, $F(000) = 4176$, μ(Mo-Kα) = 1.071 mm^{-1}, orange/pink crystal, 28783 reflections measured, 5323 unique ($R_{int} = 0.0334$), 313 parameters, $R_1 = 0.0259$ for 4791 reflections with $I > 2\sigma(I)$, $wR_2 = 0.0564$ (all data). For all structures hydrogens were included at calculated positions (C–H = 0.95 Å) but not refined; H···C/N distances in the text are calculated using these C–H distances. CCDC 182/1821. See http://www.rsc.org/suppdata/cc/b0/b007080g/ for crystallographic files in .cif format.

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