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Infinite molecular tubes: structure and magnetism of $M(dca)_2(apym)$ [M = Co, Ni, apym = 2-aminopyrimidine, dca = dicyanamide, $N(CN)_2^-$]

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The title compounds have a molecular tube-like structure topologically related to the α-$M(dca)_2$ rutile structure, and display unusual field-dependent magnetic moments at low temperature but without long-range order.

Since our initial report on the unusual molecule-based magnetism of α-$M(dca)_2$ [dca = dicyanamide, $N(CN)_2^-$],[1] a great deal of attention has focussed on the structural and magnetic properties of coordination polymers containing the dca ligand.[2–4] In the α-$M(dca)_2$ series of compounds, M = Co and Ni behave as ferromagnets while M = Cr, Mn and Fe behave as spin-canted antiferromagnets and M = Cu is a paramagnet. All these compounds are isostructural and possess a rutile-like topology, with the octahedral metal ions bridged by dca anions which coordinate through all three nitrogen atoms.

We report here the structural and magnetic properties of a series of polymeric complexes, $M(dca)_2(apym)$ (M = Co **1** or Ni **2**, apym = 2-aminopyrimidine), which form novel 'molecular tubes' that are structurally related to the rutile networks formed by the α-$M(dca)_2$ compounds, and which contain both two- and three-connecting dca ligands.

Reaction of apym, sodium dicyanamide and the corresponding metal nitrate in water resulted in formation of **1** or **2**.† These compounds are formed from the 1 : 2 adducts $M(dca)_2(apym)_2$, (M = Co, Ni). The $M(dca)_2(apym)_2$ compounds exhibit chain structures similar to those of $M(dca)_2L_2$, (L = MeOH, pyridine, DMF)[2,4b,c] full details of which will be published elsewhere.‡ Single crystals of **1** or **2** suitable for X-ray diffraction were grown by slow transformation of $M(dca)_2(apym)_2$ left in the reaction mixture for several months, and their structures were determined by X-ray crystallography.§ The IR spectra of **1** and **2** indicated the presence of both bidentate and tridentate dca ligands. X-Ray powder diffraction was used to prove that the bulk samples of **1** and **2** had the same structure as the single crystals, and were free from contamination.

Both structures are isomorphous (identical space groups), and the structure of **1** is shown in Fig. 1(a). It consists of infinite 1D 'molecular tubes' of square cross-section, with metal atoms occupying the edges and three-connecting dca ligands forming the sides of the tube. The octahedral coordination of the metal atoms is completed by chains of two-connecting dca ligands (with the amide nitrogens uncoordinated) which occupy the outside of each edge, and monodentate apym ligands. The sides of the tubes are 4.864 Å wide (4.821 Å in **2**).

The structure of the square tubes can be related back to the rutile-like structures of α-$M(dca)_2$. Fig. 1(b) shows the (distorted) rutile-like net of α-$Co(dca)_2$, with one of the channels of the structure highlighted. This highlighted channel has the same topology as the tubes. In effect, we have isolated a polymeric 1D section of the rutile-like network of α-$M(dca)_2$. Interestingly, while the channels in α-$M(dca)_2$ are buckled, the molecular tubes are not.

The tubes (all of which are crystallographically equivalent) pack in the crystal structure with extensive hydrogen bonding between the tubes *via* the apym ligands, as shown in Fig. 2. The apym groups form dimeric hydrogen bonded pairs with apym ligands in adjoining tubes, such that the amino group of one ligand hydrogen bonds to the pyrimidine nitrogen of the adjoining ligand, and *vice versa*. These hydrogen bonding interactions (N(7)–H(1)···N(6) 178.6(3)° for**1** [177.4(5)° for **2**], H(1)···N(6) 2.200(3) Å [2.227(5) Å]) connect every alternate tube in the structure (black tube to black tube and white tube to white tube in Fig. 2), giving two separate sets of tubes. The two

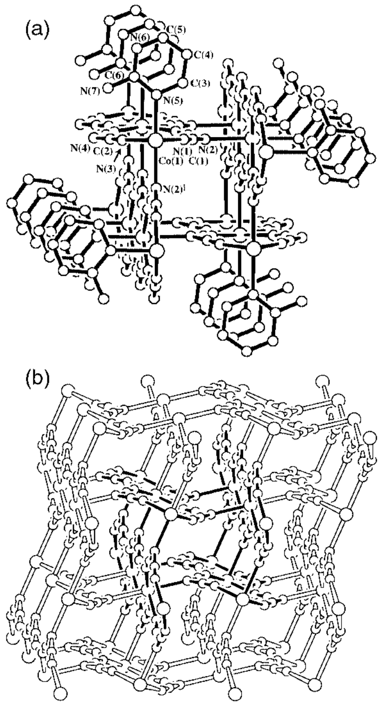

Fig. 1 (a) Structure of a single molecular tube in $Co(dca)_2(apym)$ **1**. Selected bond lengths (Å) for **1** (**2** in parentheses): Co(1)–N(1) 2.110(1) (2.074(3)), Co(1)–N(3) 2.089(1) (2.048(3)), Co(1)–N(5) 2.149(2) (2.126(4)), Co(1)–N(2)^i 2.224(2) (2.201(4)). (b) The rutile-like network of α-$Co(dca)_2$ with a single channel with the same topology as the tubes highlighted.

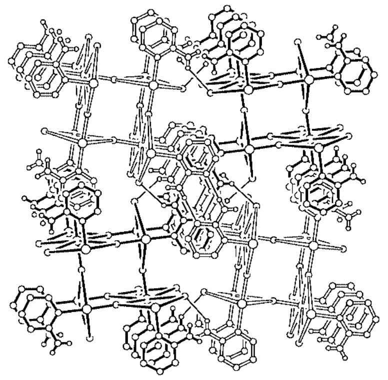

Fig. 2 Hydrogen bonding interactions between four tubes in the crystal lattice. For clarity, only the amino protons are shown. Hydrogen bonding interactions are shown by thin lines.

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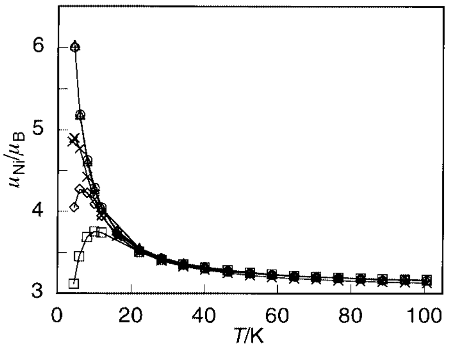

Fig. 3 Plots of the effective magnetic moment μ_{eff}, per Ni, *vs.* temperature for Ni(dca)$_2$(apym) **2**. Applied-field values are 20 Oe (Δ), 200 Oe (+), 10000 Oe (×), 20000 Oe (◇) and 40000 Oe (□). The μ_{eff} values are independent of field and essentially constant between 100 and 300 K.

sets of tubes are then connected by weaker hydrogen bonding interactions between the amino group of the apym ligands and the amide nitrogens of the two-connecting dca anions (N(7)–H(2)··N(4) 136.1(3)° for **1** [135.8(5)° for **2**], H(2)··N(4) 2.539(3) Å [2.517(5) Å]), white tubes to black tubes in Fig. 2.

Another feature of the packing is the interdigitation of the apym ligands of adjoining tubes into infinite π-stacked columns (Fig. 2). The mean planes of the ligands are separated by $c/2$ = 3.691 (for **1**) and 3.655 (for **2**) Å.

The magnetic data for **2** will be emphasised briefly here. The samples measured were shown to be free from any contaminant by checking the powder X-ray diffraction patterns. It can be seen in Fig. 3 that μ_{eff}, per Ni, remains constant at 3.1 μ_B between 300 and 100K in a field of 1 T as expected for octahedral Ni(II) centres. A gradual increase then occurs before reaching a maximum of 4.9 μ_B at 3.6K, behaviour indicative of ferromagnetic coupling. The corresponding χ^{-1}_{Ni} *vs.* temperature data are Curie–Weiss like, with $\theta = +3.1$K. As the applied field is increased to 4 T, the μ_{max} region becomes broader in shape, with μ_{max} values lower and moving to higher temperatures. Magnetisation isotherms (M *vs.* H; 2–10 K) show rapid increases in M at low H and are indicative of ferromagnetic coupling, with a saturation value M_{sat} of 2.1 $N\beta$ noted at 2 K. Since μ_{eff} is a derived quantity ($\mu_{eff}{}^2 = 7.997\ MT/H$) the unusual shape of μ_{eff} at high fields and low temperatures to some extent will reflect this derivation since M is not linear with H. The shapes are also reminiscent of Zeeman level (M_S) depopulation effects noted in ferromagnetically coupled clusters.[6]

Measurements in low applied fields also lead to unusual behaviour. In Fig. 3 it can be seen that μ_{eff} increases sharply as H is decreased, then attenuates to a value of 6 μ_B for H = 200 or 20 Oe. The corresponding M *vs.* temperature plots are Curie–Weiss like with no sharp rise which would be indicative of a transition to long-range order. Other tests for long-range order such as measuring ac susceptibilities, χ' and χ'' (2–20 K), where χ'' was found to be zero at all temperatures between 4 and 20 K, or dc magnetisation in field-cooled or zero-field cooled modes, proved negative. In contrast to these puzzling features observed for **2**, the magnetic behaviour of the linear chain precursor, Ni(dca)$_2$(apym)$_2$, gives quite normal S = 1 behaviour with very weak antiferromagnetic coupling and/or zero-field splitting evident at low temperatures, and independent of H.

Further experimental and theoretical work is in progress on these novel tube-like materials to try and explain these magnetic anomalies, which are also present in the Co complex. Preliminary Heisenberg-type calculations made in collaboration with Kurmoo,[7] using a Ni$_8$ fraction of a tube, reproduce the 20 Oe data very well.

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Notes and references

† *Preparative details*: **1**: an aqueous solution (7 ml) of Co(NO$_3$)$_2$·6H$_2$O (368 mg, 1.26 mmol) was added to an aqueous solution (3 ml) of Na(dca) (200 mg, 2.25 mmol) and apym (107 mg, 1.13 mmol) at room temperature yielding an instant pale pink precipitate [Co(dca)$_2$(apym)$_2$]. 10 ml H$_2$O was added and the reaction mixture boiled to dissolve the pink precipitate. Boiling was continued and the volume of the solution reduced to *ca.* 10 ml. A pink–purple microcrystalline powder formed and was filtered off (255 mg, 0.891 mmol, 79%). Found: C, 33.7; H, 1.5; N, 44.2. Calc. for C$_8$H$_5$CoN$_9$: C, 33.6; H, 1.8; N, 44.1%. Selected IR (dca) (cm^{-1}, Nujol): ν_{as}(C≡N) 2268m, 2260m; ν_s(C≡N) 2192s, 2182s(sh); ν_{as}(C–N) 1356, 1317. Crystals suitable for X-ray study were obtained by allowing the initial pink precipitate to transform in solution over several months.

2: a hot aqueous solution (10 ml) of Ni(NO$_3$)$_2$·6H$_2$O (375 mg, 1.29 mmol) was added to a hot aqueous solution (10 ml) of Na(dca) (200 mg, 2.25 mmol) and apym (110 mg, 1.16 mmol). The solution was boiled and the volume reduced to *ca.* 15 ml yielding a blue microcrystalline powder (245 mg, 0.857 mmol, 76%). Found: C, 33.6; H, 1.6; N, 43.9. Calc. for C$_8$H$_5$NiN$_9$: C, 33.6; H, 1.8; N, 44.1%. Selected IR (dca) (cm^{-1}, Nujol): ν_{as}(C≡N) 2274m, 2268m; ν_s(C≡N) 2198s; ν_{as}(C–N) 1354, 1314.

‡ Reedijk and coworkers[5] have just reported the crystal structure of Cu(dca)$_2$(apym)$_2$. It is the same as those of Ni and Co except for small symmetry differences owing to Jahn–Teller distortions.

§ *Crystal data*: **1**: C$_8$H$_5$CoN$_9$, M = 286.14, tetragonal, space group $P4_2/mbc$, a = 17.1243(2), c = 7.3816(1) Å, U = 2164.59(5) Å^3, T = 123 K, F(000) = 1144, Z = 8, D_c = 1.756 g cm^{-3}, μ(Mo-Kα) = 1.582 mm^{-1}, red needle, 31921 reflections measured, 1695 unique (R_{int} = 0.050), 102 parameters, R_1 = 0.0279 for 1471 reflections with $I > 2\sigma(I)$, wR_2 = 0.0626 (all data), S = 1.099. The structure of **1** was also solved at 295 K.

2: C$_8$H$_5$NiN$_9$, M = 285.92, a = 17.0863(6), c = 7.3099(2) Å, U = 2134.1(1) Å^3, T = 297 K, F(000) = 1152, D_c = 1.780 g cm^{-3}, μ(Mo-Kα) = 1.815 mm^{-1}, blue needle, 15738 reflections measured, 1653 unique (R_{int} = 0.113), 97 parameters, R_1 = 0.0530 for 1127 reflections with $I > 2\sigma(I)$, wR_2 = 0.1010 (all data), S = 1.092. CCDC 182/1585. See http://www.rsc.org/suppdata/cc/a9/a909067c/ for crystallographic files in .cif format.

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