Structural isomers of M(dca)$_2$ molecule-based magnets. Crystal structure of tetrahedrally coordinated sheet-like β-Zn(dca)$_2$ and β-Co/Zn(dca)$_2$, and the octahedrally coordinated rutile-like α-Co(dca)$_2$, where dca$^-$ = dicyanamide, N(CN)$_2^-$, and magnetism of β-Co(dca)$_2$

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β-Zn(dca)$_2$ and 0.12% Co(II) doped β-Zn(dca)$_2$ contain tetrahedrally coordinated metal ions within a corrugated sheet network structure [dca = dicyanamide, N(CN)$_2^-$], β-Co(dca)$_2$ is a spin-canted antiferromagnet (T_N = 9 K), while the rutile-like octahedral α-form is a ferromagnet.

We have recently described an important new class of molecule-based magnets of type M(dca)$_2$ which possess a rutile-like single net structure.[1] In this α-structural type, the metal ions are octahedrally coordinated to six dicyanamide (dca) ligands *via* the nitrile and amide N-donor atoms, each dca therefore being a 3-connector. The Co(II) and Ni(II) compounds are ferromagnets, with T_c = 9 and 20 K respectively, while the Cu(II) compound is a near-paramagnet, with Jahn–Teller distorted Cu–N(amide) bond lengths. α-Mn(dca)$_2$ and α-Fe(dca)$_2$ are spin-canted antiferromagnets with T_N values of 16 and 19 K, respectively.[2] Kepert and Kurmoo[3] and Miller and Epstein and coworkers[4] have subsequently reported some of the same α-type compounds. Here, we describe a structural isomer of the β-type in which the metal ions are each tetrahedrally coordinated to four dca ligands *via* nitrile N-donor atoms to form an infinite sheet structure. This structure has been refined for colourless crystals of β-Zn(dca)$_2$ and for deep blue crystals of Co(II) doped β-Zn(dca)$_2$. As indicated earlier by Köhler,[5] the blue β-Co(dca)$_2$ phase can be prepared by removal of pyridine from Co(dca)$_2$(pyridine)$_2$. We report here antiferromagnetic coupling and magnetic order in β-Co(dca)$_2$ prepared in this way and compare these to the magnetic behaviour observed in the ferromagnetic α-isomer.

β-Zn(dca)$_2$ was prepared by reaction of Zn(NO$_3$)$_2$·6H$_2$O with sodium dicyanamide in water in a 1:2 mole ratio. Colourless crystals were obtained by slowly diffusing the reagents together. The 0.12% Co(II) doped crystals were prepared by mixing hot aqueous solutions of Zn(NO$_3$)$_2$·6H$_2$O and Co(NO$_3$)$_2$·6H$_2$O with one of Na(dca). Deep blue crystals formed from the pink solution. Doubling of some of the C–N bands from coordinated dca occurs in the IR spectrum probably because of the presence of two structurally distinct dca ligands in Zn(dca)$_2$ and in Co/Zn(dca)$_2$.†

The structures of α-Co(dca)$_2$, β-Zn(dca)$_2$ and 0.12% β-Co/Zn(dca)$_2$ were solved by single-crystal X-ray crystallography. The structure of α-Co(dca)$_2$ is isomorphous with the other members of the α-M(dca)$_2$ compounds discussed above.[1–4] It possesses a rutile-like structure with octahedral cobalt ions and three-connecting dca ligands [Co-N(nitrile) 2.092(2) Å, Co–N(amide) 2.150(3) Å].‡ These values are obviously much closer together than in the Jahn–Teller distorted Cu [1.975(1) and 2.478(2) Å, respectively],[1] and are shorter than those found in Mn [2.189(1) and 2.290(2) Å].[2] In all three structures the metal–amide bonds are longer than the metal–nitrile bonds.

As both β-isomer structures are isomorphous, we will discuss only the Zn(dca)$_2$ structure in detail.‡ The structure consists of tetrahedral Zn atoms [N–Zn–N 108.05(9)–111.9(2)°] bridged by two-connecting dicyanamide ligands [Zn–N 1.958(4), 1.936(4)

and 1.960(3) Å]. The kinked nature of the dca bridge, aided by some bending at the coordinating nitrogen donors [C–N–Zn 155.3(3), 165.4(4) and 171.9(4)°], allows the tetrahedral ions to be bridged into a corrugated square-grid sheet structure (Fig. 1). The sheets stack in the direction of the *c* axis and are interdigitated. As a result, the shortest Zn···Zn distances (4.447 Å) are between sheets, with the intrasheet Zn···Zn distances (*via* the dca bridges) being 7.584 and 7.606 Å. The structure of the 3D rutile-like α isomer is obviously markedly different to the 2D sheet structure for the β isomer described here. The former contains octahedral metal ions and three-connecting dca ligands, while the latter contains tetrahedral metal ions and two-connecting dca ligands (*i.e.* the amide nitrogens do not coordinate).

The structures described above of β-Zn(dca)$_2$ were determined at 123 K. The room temperature structure was also determined,‡ and found to possess a different space group (*Cmcm, vs Pnma* at 123 K). Further investigation showed a reversible phase change occurring between 210 and 220 K. A second phase change occurred at 120 K which resulted in fragmentation of the crystal. The topology and connectivity of the structure in the room temperature phase is the same as in the 123 K phase. The phase change arises due to ordering of one of the two crystallographically unique dca ligands (dca1). At room temperature dca1 is disordered over two positions, which are related by a mirror plane. The ligand 'leans over', with its mean plane making an angle of 16.6° to this mirror plane (on which lie the metal atoms and nitrile nitrogen atoms of dca1). The mirror plane arises because the lean of dca1 is disordered equally between the two alternative directions. In the 123 K structure, however, this ligand becomes ordered, with all the dca1 ligands in a sheet tilting in the one direction only, and the mirror plane symmetry is lost.

The deep blue β-Co(dca)$_2$ was produced by depyridination under vacuum of Co(dca)$_2$(pyridine)$_2$.[5] Although the powder was largely amorphous and diffracted extremely weakly, the pattern was suggestive of being isomorphous with β-Zn(dca)$_2$. The visible spectra (diffuse reflectance) of neat β-Co(dca)$_2$ and of Co doped Zn(dca)$_2$ are identical thus indicating that the tetrahedral coordination geometry around Co(II) is the same; λ_{max}/nm 602, 565(sh), 483w (sh). Upon exposure to the

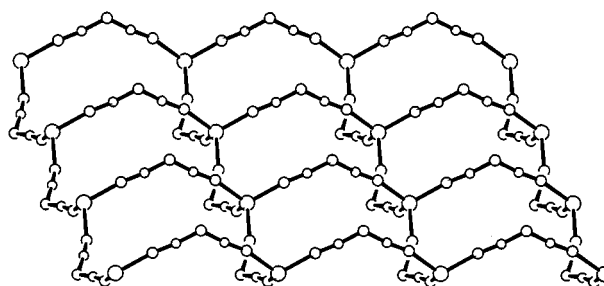**Fig. 1** The puckered, square-grid sheets of β-Zn(dca)$_2$.

atmosphere, the powder turns from blue to pink. Again, although the diffraction was very weak, the X-ray powder diffraction pattern was suggestive of the presence of the rutile-like α-Co(dca)$_2$. The diffuse reflectance visible spectra was also now reminiscent of the α phase; λ_{max}/nm = 1131(br), 510, 481.

The magnetic moment, per mol of Co, of the 0.12% Co(II) doped Zn(dca)$_2$ sample remains constant at 4.6 μ_B over the range 300–15 K. This was anticipated for a magnetically dilute tetrahedral d^7 ion having a $^4A_2$ ground state influenced by spin–orbit coupling. Together with the lack of any observed long-range order under small applied-fields, the data are consistent with random doping of the diamagnetic Zn(II) sites by Co(II), much like traditional doping into zinc oxide hosts. In contrast, the magnetic properties of neat β-Co(dca)$_2$ are indicative of antiferromagnetic coupling and a magnetic phase change occurring at *ca.* 9 K, due to spin canted antiferromagnetism (weak ferromagnetism). This contrasts markedly with α-Co(dca)$_2$ which displays a ferromagnetic transition, also at 9 K.[1] In a magnetic field of 1 T, the effective magnetic moment, per Co, of the β-isomer decreases a little from 4.55 μ_B at 300 K to 4.3 μ_B at 22 K before increasing sharply to reach a maximum of 4.45 μ_B, then decreasing rapidly towards 2.39 μ_B at 2 K (Fig. 2). The corresponding χ values show small deviation from Curie-Weiss behaviour above 25 K with θ = −4.5 K [*cf.* α-Co(dca)$_2$, θ = +6.1 K]. Long range magnetic order is clearly evident in the magnetisation data measured in small applied fields. It can be seen in Fig. 2 that the field-cooled (FCM) and zero-field cooled (ZFCM) magnetisation values increase rapidly below 9.5 K
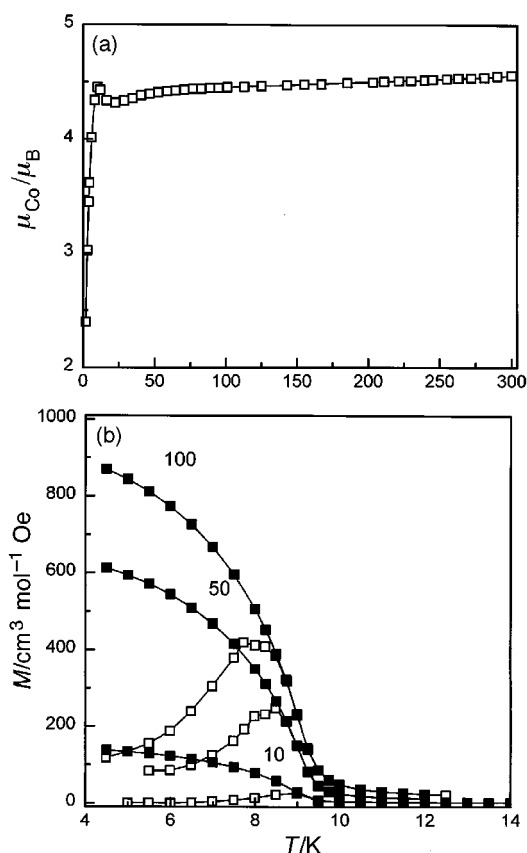
under fields of 10, 50 and 100 Oe. The temperature at which the FCM and ZFCM data diverge changes a little with field *viz.* 9.0 K (10 Oe), 8.83 K (50 Oe), 8.65 K (100 Oe). The ZFCM data likewise pass through a field-dependant maximum.

A powder sample of β-Co(dca)$_2$ displays hysteresis in magnetisation with a coercive field of 538 Oe and remanent magnetisation of 0.22 $N\mu_B$ at 2 K. High field magnetisation data in fields of up to 5 T show small diversions from linearity without reaching saturation and with a small value of only 2.37 $N\mu_B$ at 5 T. This contrasts markedly with the rapid saturation behaviour noted in the ferromagnetic α-isomer and is indicative of antiferromagnetic coupling. The nature of the ordered state is therefore one of a spin-canted antiferromagnet as was also found in α-Mn(dca)$_2$ and α-Fe(dca)$_2$. Such ordering is becoming increasingly common in homometallic molecular magnets.[2–4,6]

Notes and references

† IR (cm^{-1}, Nujol) Zn(dca)$_2$: ν_{as}(C≡N) 2298m, 2280m; ν_s(C≡N) 2209s; ν_{as}(C–N) 1417(sh), 1408s, ν_s(C–N) 964 vw.

‡ *Crystal data* for α-Co(dca)$_2$: C$_4$N$_6$Co, M = 191.02, orthorhombic, *Pnnm* (no. 58), a = 7.0433(2), b = 5.9748(3), c = 7.4039(4) Å, U = 311.57(2) Å^3, T = 123 K, Z = 2, F(000) = 186, D_c = 2.036 g cm^{-3}, μ(Mo-Kα) = 26.81 cm^{-1}, pink acicular crystal (0.10 × 0.03 × 0.03 mm), 4200 total reflections ($2\theta_{max}$ = 56.5°), 473 independent reflections (R_{int} = 0.047), 336 observed [$I > 3\sigma(I)$], refined against F, 29 parameters, R_1 [$I > 3\sigma(I)$] = 0.0281, R_w = 0.0285, goodness of fit = 2.57.

For β-Zn(dca)$_2$ at 123 K: C$_4$N$_6$Zn, M = 197.46, orthorhombic, *Pnma* (no. 62), a = 7.6060(3), b = 7.5844(3), c = 11.8422(4) Å, U = 683.14(8) Å^3, Z = 4, F(000) = 384, D_c = 1.920 g cm^{-3}, μ(Mo-Kα) = 35.28 cm^{-1}, colourless tablet (0.20 × 0.16 × 0.08 mm), 9157 total reflections ($2\theta_{max}$ = 56.4°), 1019 independent reflections (R_{int} = 0.048), 700 observed [$I > 3\sigma(I)$], refined against F, 61 parameters, R_1 [$I > 3\sigma(I)$] = 0.0225, R_w = 0.0226, goodness of fit = 2.24.

For 0.12% Co doped β-Zn(dca)$_2$: structure refined assuming 100% Zn, C$_4$N$_6$Zn, M = 197.46, orthorhombic, *Pnma* (no. 62), a = 7.6070(3), b = 7.5828(4), c = 11.8468(6) Å, U = 683.35(10) Å^3, T = 123 K, Z = 4, F(000) = 384, D_c = 1.919 g cm^{-3}, μ(Mo-Kα) = 35.27 cm^{-1}, blue tablet (0.20 × 0.20 × 0.07 mm), 8876 total reflections ($2\theta_{max}$ = 56.5°), 1020 independent reflections (R_{int} = 0.059), 667 observed [$I > 3\sigma(I)$], refined against F, 61 parameters, R_1 [$I > 3\sigma(I)$] = 0.0273, R_w = 0.0244, goodness of fit = 2.25.

For β-Zn(dca)$_2$ at 293 K: orthorhombic, *Cmcm* (no. 63), a = 7.5526(3), b = 12.2167(8), c = 7.5882(4) Å, U = 700.15(7) Å^3, Z = 4, F(000) = 384, D_c = 1.873 g cm^{-3}, μ(Mo-Kα) = 34.41 cm^{-1}, colourless prism (0.3 × 0.2 × 0.1 mm), 2534 total reflections ($2\theta_{max}$ = 60°), 567 independent reflections (R_{int} = 0.036), 512 observed [$I > 2\sigma(I)$], refined against F^2, 39 parameters, R_1 [$I > 2\sigma(I)$] = 0.0390, wR_2 (all data) = 0.1246, goodness of fit = 1.217.

CCDC 182/1120. See http://www.rsc.org/supp.data/cc/1999/177/for crystallographic files in .cif format.

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Fig. 2 (a) Plot of μ(per Co) *vs* temperature for β-Co(dca)$_2$ in a field of 1 T. (b) Plots of field-cooled (FCM) (■) and zero-field cooled (ZFCM) (□) magnetisation *vs* temperature for β-Co(dca)$_2$ in fields of 10, 50 and 100 Oe.