

Structure and molecular magnetism of the rutile-related compounds $M(\text{dca})_2$, $M = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}$, $\text{dca} = \text{dicyanamide}, \text{N}(\text{CN})_2^-$

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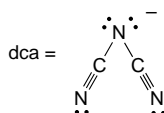
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The isomorphous rutile-related network structures of $\text{Co}(\text{dca})_2$, $\text{Ni}(\text{dca})_2$ and $\text{Cu}(\text{dca})_2$, $\text{dca} = \text{dicyanamide}, \text{N}(\text{CN})_2^-$, are shown to behave as ferromagnets ($T_c = 9$ and 20 K) and a near-paramagnet, respectively.

The deliberate design and construction of coordination polymers with predetermined topology is an area of much current interest.^{1–3} A number of new compounds with interesting properties such as high porosity and catalytic activity has been made following these principles. Here, we describe a series of such compounds which display unusual magnetic properties, including long-range ferromagnetic ordering. A number of existing coordination polymers are already known to display unusual magnetic properties. For instance, $(\text{rad})_2\text{Mn}_2[\text{Cu}(\text{opba})_3(\text{Me}_2\text{SO})_2 \cdot 2\text{H}_2\text{O}]$, $\text{opba} = o$ -phenylenebis(oxamato), $\text{rad}^+ = 2$ -(4-*N*-methylpyridinium)-4,4,5,5-tetramethylimidazole-1-oxyl-3-oxide consists of two sets of 2D hexagonal sheets of $\text{Mn}_2[\text{Cu}(\text{opba})_3]_3^{2-}$ which interpenetrate each other at an angle of 72.7°. Rad⁺ cations connect the sheets, and the solid behaves as a magnet below 22.5 K. The magnetic properties of a large number of bimetallic oxalate structures, $\text{AMM}'(\text{ox})_3$ ($\text{A}^+ = \text{NR}_4^+$), which have a hexagonal sheet structure, have also been studied recently.⁵ There is a great need to explore bridging groups other than these N,O-bonded oxamides and O-bonded oxalates.

The results described herein form part of a study we are undertaking on the binary structures of metal–pseudohalide compounds. The structures of $M(\text{tcm})_2$, $\text{tcm} = \text{tricyanomethanide}, \text{C}(\text{CN})_3^-$, $M = \text{Cr}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}, \text{Hg}^{\text{II}}$, consist of two interpenetrating rutile nets,⁶ and have been found to display weak antiferromagnetic coupling.⁷ The structures and novel magnetochemistry of the binary metal complexes of dicyanamide, $\text{dca}, \text{N}(\text{CN})_2^-$, are now described.



Following the method of Köhler,⁸ combination of aqueous solutions of cobalt nitrate, nickel nitrate or copper nitrate with aqueous solutions of sodium dicyanamide results in small pink rods of $\text{Co}(\text{dca})_2$, a blue microcrystalline powder of $\text{Ni}(\text{dca})_2$, and green rods of $\text{Cu}(\text{dca})_2$, respectively. As in Köhler's original work, there is evidence from IR and microanalytical data† for a small amount of water in $\text{Ni}(\text{dca})_2$ even when we prepared it from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in MeCN using $[\text{N}(\text{PPh}_3)_2](\text{dca})$.

The structure of $\text{Cu}(\text{dca})_2$ was determined by single crystal X-ray crystallography.‡ It was found to consist of a single rutile-related network (Fig. 1). Each dca is coordinated to three metal atoms *via* the two nitrile nitrogens and the central amido nitrogen. Each copper in turn is coordinated to six dca ligands, four *via* the nitrile nitrogens and two *via* the amido nitrogens. The copper shows considerable Jahn–Teller distortion, with the two axial amido nitrogens considerably further from the copper

[2.478(2) Å] than the four equatorial nitrile nitrogens [1.975(1) Å]. There is evidence of π – π interactions between pairs of dca ligands across the square channels seen in Fig. 1, with the closest interactions being $\text{N}_{\text{amido}}-\text{N}_{\text{amido}}$ 3.463 Å, $\text{C}-\text{C}$ 3.513 Å and $\text{N}_{\text{amido}}-\text{C}$ 3.603 Å. The distortions in the framework seen in Fig. 1 may maximise these interactions. The structures of polycrystalline $\text{Co}(\text{dca})_2$ and $\text{Ni}(\text{dca})_2$ have been shown by X-ray powder diffraction to be isomorphous with $\text{Cu}(\text{dca})_2$,§ but with a few very small peaks not indexing and not present in the XRD of $\text{Cu}(\text{dca})_2$.

It is interesting to compare the structures of $M(\text{dca})_2$ and $M(\text{tcm})_2$. In both cases the networks have a rutile-like topology with six-connected metal centres and three-connected ligands. In $M(\text{tcm})_2$, all three connections between the trigonal centres and the octahedral centres of the rutile networks are $\text{C}-\text{CN}-\text{M}$ (*ca.* 4.50–4.99 Å), and the structures are composed of two interpenetrating networks. The interpenetration produces a tightly packed structure in which each of the nets is considerably distorted to accommodate the other. In $M(\text{dca})_2$, two of these connections are $\text{N}-\text{CN}-\text{M}$ (4.368 Å), which are comparable with those in $M(\text{tcm})_2$. The third connection between trigonal and octahedral nodes, however, is a direct $\text{N}-\text{M}$ bond [2.478(2) Å], and there is no longer enough room within the structure for a second rutile-related net to be accommodated. Indeed, the packing efficiency of $\text{Cu}(\text{dca})_2$ is very similar to that of $\text{Cu}(\text{tcm})_2$ ($D_c = 2.01$ and 1.918 g cm^{-3} , volume/atom = 14.7 and 14.1 Å^3 , respectively.)

While Hvastijova *et al.*⁹ have made many studies of the magnetism of chain-like compounds of type $M(\text{tcm})_2\text{L}_2$ and $M(\text{dca})_2\text{L}_2$, where $\text{L} = \text{pyridine}, \text{imidazole}, \text{pyrazole}$, there have been no detailed studies until now on the parent

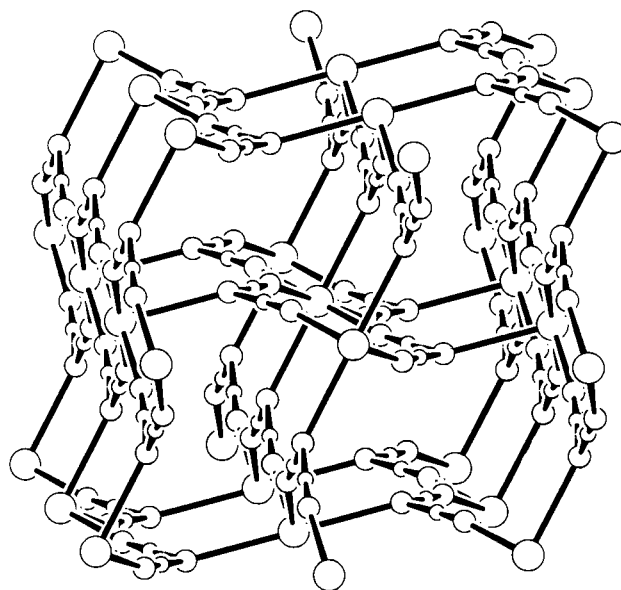


Fig. 1 The rutile-related structure of $\text{Cu}(\text{dca})_2$. The circles represent in order of decreasing size Cu, N and C.

compounds. We find that $\text{Cu}(\text{dca})_2$ shows near-Curie behaviour in a field of 1 T ($C = 0.438 \text{ cm}^3 \text{ K mol}^{-1}$, $\theta = -1.8 \text{ K}$) indicative of extremely weak antiferromagnetic coupling. The μ_{eff} values decrease a little from $1.87 \mu_{\text{B}}$ at 300 K to $1.77 \mu_{\text{B}}$ at 4.2 K. Magnetization studies in a field of 5 Oe show that long-range ordering is not occurring above 2 K. Chain-like $\text{Cu}^{\text{II}}(\text{dca})_2\text{L}_2$ adducts also display very weak coupling and long-range ordering at low temperatures has occasionally been claimed but without proof.⁹

In contrast, the $\text{Co}(\text{dca})_2$ and $\text{Ni}(\text{dca})_2$ samples both display well behaved long-range ferromagnetic ordering with T_{c} values, respectively, of 9 and 20 K. The first evidence of ferromagnetism is given in the Curie–Weiss susceptibility plots obtained in fields of 1 T. Positive Weiss constants are noted with best-fit parameters of $C = 2.074$, $\theta = +6.1 \text{ K}$ (Co) and $C = 1.086$, $\theta = +21.4 \text{ K}$ (Ni). In small applied fields of 5 Oe, the χT values increase sharply at T_{c} reaching values much higher than anticipated for short-range order. Plots of field-cooled (FCM), zero-field cooled (ZFCM) and remanent magnetization (RM), shown in Fig. 2 for $\text{Ni}(\text{dca})_2$, are typical of those expected for a magnetically ordered system.¹⁰ The very sharp increase in the magnetization isotherms at small field values, followed by a gradual increase towards a saturation magnetization value of $2N\mu_{\text{B}}$ [for $\text{Ni}(\text{dca})_2$] in high fields (Fig. 2), lends further support for a ferromagnetic phase transition. Hysteresis loops are observed with the value of the coercive field for $\text{Ni}(\text{dca})_2$ being 191 Oe.

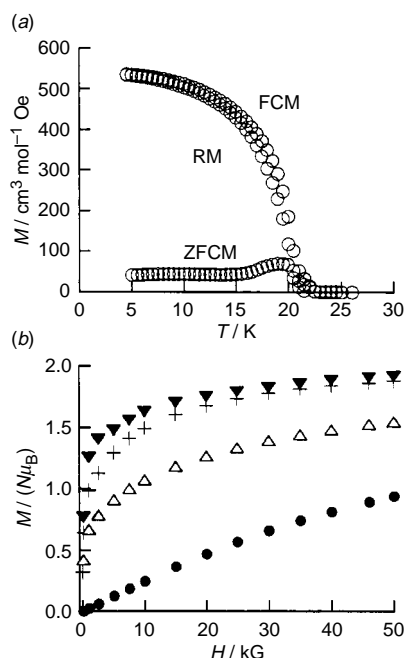


Fig. 2 (a) Plots of field-cooled (FCM), zero field-cooled (ZFCM) and remanent magnetization (RM) vs. temperature for $\text{Ni}(\text{dca})_2 \cdot x\text{H}_2\text{O}$ and (b) plots of magnetization, M (in units $N\mu_{\text{B}}$) vs. applied field at various temperatures for $\text{Ni}(\text{dca})_2 \cdot x\text{H}_2\text{O}$: (●) 30 K, (△) 20 K, (+) 10 K, (▼) 5 K

The origin of ferromagnetic ordering in the Co^{II} and Ni^{II} dca compounds and the lack thereof in the structurally characterized Cu^{II} species is intriguing and is being vigorously pursued. If we assume that the majority $Pnmm$ phase in all three samples (*vide supra*) is responsible for the magnetic behaviour then Jahn–Teller distortions in $\text{Cu}(\text{dca})_2$, along the Cu–N(amido) links, may prevent magnetic interactions between $\text{Cu}(\text{dca})_2$ chains in the crystal, while such interchain interactions can occur in the Co and Ni derivatives. This contrasts with the situation in one of

the few known homometallic ferromagnetic systems $(\text{NH}_3\text{R})_2[\text{MX}_4]$, ($\text{Mn}^{\text{II}} = \text{Cu}, \text{Cr}$; $\text{X} = \text{Cl}, \text{Br}$), in which Jahn–Teller elongated M–X bonds within metal–halide layers are orthogonal from one MX_6 octahedron to the next,^{10,11} thus giving the required orthogonality of neighbouring magnetic orbitals. Orthogonality relationships are not obvious from Fig. 1 but presumably must involve the M–N≡C–N–M pathways otherwise $\text{Cu}(\text{dca})_2$ should behave likewise. In conclusion, it is clear that some of these d-blocks pseudohalide species provide new and fascinating examples of molecular magnets.

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Notes and References

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† Analyses: $\text{Cu}(\text{dca})_2$. Found: C, 24.9; H, 0; N, 43.1. Calc. C, 24.6; H, 0; N, 43.0%. $\text{Ni}(\text{dca})_2 \cdot 0.5\text{H}_2\text{O}$. Found: C, 24.1; H < 0.2; N, 41.9. Calc. C, 24.0; H, 0.5; N, 42.0%. $\nu(\text{OH})$ 3400 cm^{-1} (br), $\delta(\text{OH})$ 1636 cm^{-1} . $\text{Co}(\text{dca})_2$. Found: C, 25.2; H, 0; N, 44.2. Calc. C, 25.1; H, 0; N, 44.0%.

‡ Crystal data for $\text{Cu}(\text{dca})_2$: C_4CuN_6 , $M = 195.63$, orthorhombic, space group $Pnmm$ (no. 58), $a = 7.340(1)$, $b = 6.1218(8)$, $c = 7.1815(6) \text{ \AA}$, $U = 322.69(7) \text{ \AA}^3$, $T = 293 \text{ K}$, $Z = 2$, $F(000) = 190$, $D_{\text{c}} = 2.013 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 3.312 \text{ mm}^{-1}$, $2\theta_{\text{max}} = 37.5^\circ$. A green rod ($0.09 \times 0.09 \times 0.4 \text{ mm}$). Absorption corrections applied ($T_{\text{min}} 0.9639$, $T_{\text{max}} 0.9817$). 1426 total reflections, 905 independent reflections ($R_{\text{int}} = 0.0579$), of which 765 were observed [$I > 2\sigma(I)$]. At final convergence R_1 [$I > 2\sigma(I)$] = 0.0260, wR_2 (all data) = 0.0802 for 29 parameters, $S = 1.162$. CCDC 182/723.

§ Common space group $Pnmm$: $\text{Co}(\text{dca})_2$: $a = 7.301(7)$, $b = 6.014(4)$, $c = 7.073(5) \text{ \AA}$; $\text{Ni}(\text{dca})_2$: $a = 7.294(2)$, $b = 6.024(4)$, $c = 7.023(2) \text{ \AA}$; $\text{Cu}(\text{dca})_2$: $a = 7.352(2)$, $b = 6.126(1)$, $c = 7.180(1) \text{ \AA}$.

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