Interpenetrating three-dimensional rutile-like frameworks. Crystal structure and magnetic properties of $Mn^{II}[C(CN)_3]_2$

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The interpenetrating double-density rutile-like structure and magnetic properties of $Mn^{II}[C(CN)_3]_2$ are determined.

Molecule-based magnetic materials have been the focus of intense investigations since the ferromagnetic electron transfer salt $[FeCp^*_2]^{\cdot+}[TCNE]^{\cdot-}$[1,2] and the ferrimagnetic $Mn^{II}Cu^{II}$ chains[2,3] were discovered to magnetically order.[1,2] In the meantime, numerous one-, two-, and three-dimensional coordination polymers comprising paramagnetic transition metal cations and diamagnetic organic ligands exhibiting a wide variety of cooperative phenomena have been reported.[2,4] Furthermore, several diamagnetic examples of molecular materials that mimic three-dimensional inorganic network solids (*e.g.* α Po, diamond, α-$ThSi_2$, *etc.*) have also been described including systems in which interpenetration of two or more identical lattices occurs.[5] The majority of these polymeric frameworks are comprised of Ag^+ cations because of their propensity to afford multiple coordination geometries. Notable examples where Ag^+ possesses octahedral, tetrahedral, and trigonal planar geometries include $[Ag(pyz)_3]SbF_6$ (pyz = pyrazine),[6] $[Ag(DCPA)_2]ClO_4{\cdot}H_2O$ (DCPA = 3,3′-dicyanodiphenylacetylene),[7] and $[Ag_2(pyz)_3](BF_4)_2$,[8] respectively.

In order to construct new molecule-based magnetic materials it is important to assemble solid state structures analogous to those just described. To do this, appropriate paramagnetic transition metal ions and organic bridging ligands capable of significant spin coupling are required. Conjugated bridging ligands, such as cyanide and oxalato, have been shown to provide spin coupling between metals sites and extension to other classes of ligands are sought.[4] We selected tricyanomethanide, $[C(CN)_3]^-$, due to its ability to bind to three metal sites, and the aqueous reaction of $Mn^{II}(NO_3)_2$ and $[C(CN)_3]^-$ leads to the formation of $Mn[C(CN)_3]_2$.‡ The tricoordinate $[C(CN)_3]^-$ could lead to geometrical spin frustration.[10]

$Mn[C(CN)_3]_2$ has a complex interpenetrating network structure.‡ Each Mn^{II} bonds to six $[C(CN)_3]^-$ anions, Fig. 1, and each $[C(CN)_3]^-$ is μ_3-bonded to three Mn^{II} ions, Fig. 2, forming a rutile-like (TiO_2) lattice and is isomorphous to $Zn[C(CN)_3]_2$.[11] $[C(CN)_3]^-$ is planar with C(1)–C(3) and C(2)–C(3) bond distances of 1.404(2) and 1.412(2) Å (av. 1.408 Å), and C(1)–N(1) and C(2)–N(2) distances of 1.151(2) and 1.149(2) Å (av. 1.150 Å), respectively, as is typical of $[C(CN)_3]^-$.[11,12] The Mn^{II} cation occupies a 2/*m* special position while C(2) and N(2) reside on mirror planes, all on the crystallographic *a*-axis. Each Mn^{II} center is slightly elongated from octahedral symmetry with Mn–N(1) and Mn–N(2) bond distances of 2.222(1) and 2.272(2) Å, respectively, and averaging 2.247 Å. These Mn–N distances compare favorably to those found in related materials.[13] This distortion is significantly less than that observed for $Zn[C(CN)_3]_2$ with Zn–N(1) and Zn–N(2) distances of 2.120(2) and 2.211(2) Å,[11] respectively. Hence, the distortion is not a consequence of ligand-field effects, but is imposed by steric constraints. Likewise, owing to crystal packing forces the *cis*-N–M–N′ bond angles demonstrate a marked distortion from 90° and range from 88.9 to 96.7° for $Mn[C(CN)_3]_2$ and 84.4 to 95.6° for $Zn[C(CN)_3]_2$,[11] respectively. Additionally, the large $Mn\cdots C_{centroid}$ separations (*ca.* 4.8 Å) provide cavities of sufficient size for interpenetration of a second identical lattice, Fig. 2. Furthermore, the shortest intra- and inter-network Mn···Mn separations are 7.679 and 5.383 Å, respectively.

The rutile structure is a fundamental solid state structure-type and is one way to connect octahedral centers with trigonal planar ligands to form three-dimensional networks for spin coupling. Antiferromagnetic coupling between spin sites coupled *via* the D_{3h} μ_3-bridging $[C(CN)_3]^-$ ligand should lead to geometrical spin frustration akin to a Kagomé lattice.[10] Additionally, the interpenetrating rutile-like frameworks may lead to enhanced or unusual magnetic properties that may arise if communication between them is sufficient, thus leading to effective dipolar exchange.

The temperature dependence (2–300 K) of the magnetic susceptibility of $Mn[C(CN)_3]_2$ was measured and can be fit by the Curie–Weiss expression, $\chi \propto (T - \theta)^{-1}$, with $\theta = -5.1$ K indicative of finite antiferromagnetic coupling between the Mn^{II}

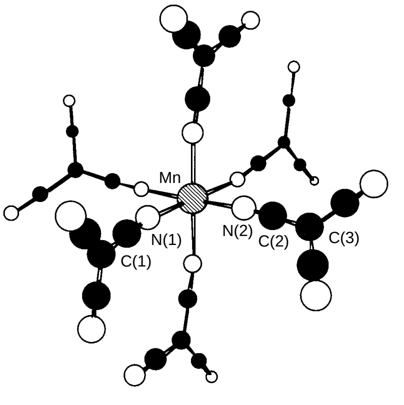

Fig. 1 Illustration showing only the first coordination sphere of the Mn^{II} cation (shaded). Filled and unfilled spheres represent C and N atoms, respectively. Bound nitriles do not coordinate linearly as can be seen clearly here in this view: Mn–N(1)–C(1) 170.03(10), Mn–N(2)–C(2) 166.4(2)°.

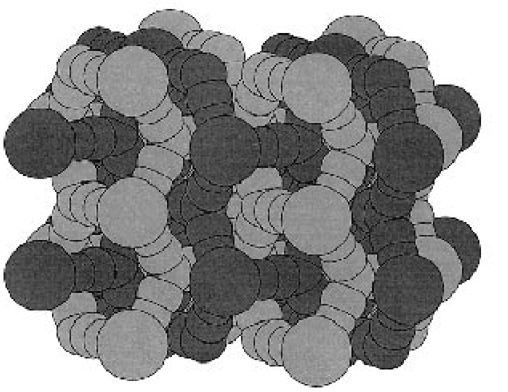

Fig. 2 Space filling model of $Mn^{II}[C(CN)_3]_2$ emphasizing the interpenetrating nature of the two identical rutile-like frameworks

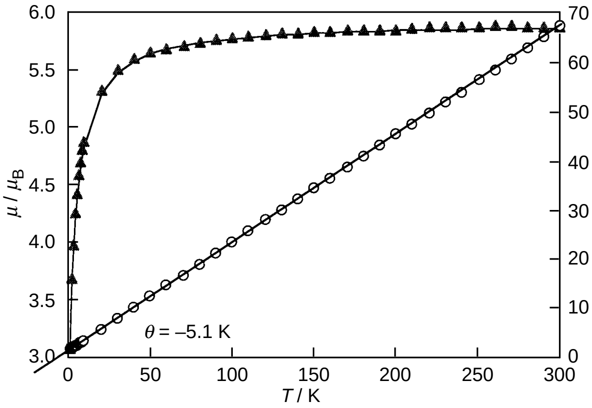

Fig. 3. Temperature dependence of the moment and the reciprocal molar magnetic susceptibility for $Mn^{II}[C(CN)_3]_2$. The data were fitted to the Curie–Weiss law (—) using the following parameters: $S = 5/2$, $g = 2.00$ and $\theta = -5.1$ K.

metal centers, Fig. 3. At 300 K the effective moment is 5.86 μ_B, in good agreement with the expected value (5.92 μ_B) for isolated $S = 5/2$ Mn^{II} ions and decreases at lower temperatures owing to antiferromagnetic coupling. The -5.1 K θ-value is larger than expected for isolated Mn^{II} ions and suggests that (*a*) the diamagnetic $[C(CN)_3]^-$ ligand mediates a superexchange interaction between the Mn^{II} ions, and/or (*b*) owing to shorter internetwork Mn···Mn separation with respect to intranetwork separation, through-space (dipolar) antiferromagnetic coupling between the interpenetrating rutile networks may dominate and lead to bulk antiferromagnetic coupling. Both mechanisms are expected to contribute as the internetwork Mn···Mn separations leading to dipolar interactions are shorter than the intranetwork Mn···Mn separations leading to superexchange.

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Footnotes and References

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† A 20 ml aqueous solution of $Mn(NO_3)_2{\cdot}4H_2O$ (0.1 mmol, 2.51 g) was mixed with an aqueous solution (20 ml) of $K[C(CN)_3]$ (0.2 mmol, 2.59 g). The final yellow solution was allowed to stand at room temp. for several months and small colorless crystals were obtained. ν_{CN} (Nujol): 2256w, 2195vs and 2152 (sh) cm^{-1}. The synthesis and room temp. effective moment of $Mn^{II}[C(CN)_3]_2{\cdot}0.25H_2O$ have been reported previously.[9]

‡ *Crystal data* for C_8MnN_6: $M = 235.07$, orthorhombic, space group *Pmna*, $a = 7.6791(3)$, $b = 5.3837(2)$, $c = 10.6230(4)$ Å, $U = 439.18(3)$ Å^3, $Z = 2$, $D_c = 1.778$ Mg m^{-3}, $\lambda = 0.710\,73$ Å, $T = 273$ °C, $2\theta_{max} = 65.5°$, $R_1 = 0.0259$, $wR_2 = 0.0685$, and a goodness of fit of 1.114, and the largest peak on the final difference map was 0.347 e$^-$ Å^{-3} are based upon the refinement of the *XYZ*-centroids of 2646 reflections above 20σ(I). The data was collected on a standard Siemens SMART™ CCD-based X-ray diffractometer system operated at 2000 W power. The detector was placed at a distance of 4.032 cm from the crystal and 1321 frames were collected with a scan width of 0.3° in ω and an exposure time of 30 s frame^{-1}. The frames were integrated with the Siemens SAINT© software package using a narrow-frame integration algorithm. The structure was solved and refined using the Siemens SHELXTL© (Version 5.0) Software Package. CCDC 182/703.

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