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Spin Canting in the 3D Anionic Dicyanamide Structure $(SPh_3)Mn(dca)_3$ (Ph = Phenyl, dca = Dicyanamide)

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Through use of the SPh_3^+ (Ph = phenyl, C_6H_5) cation as a molecular template, a new three-dimensional $Mn(dca)_3^-$ [dca = dicyanamide, $N(CN)_2^-$] anionic structure has been crystallized. At room temperature, $(SPh_3)Mn(dca)_3$ (**1**) crystallizes in the monoclinic space group $P2_1/c$, with $a = 11.7079(5)$ Å, $b = 12.8554(5)$ Å, $c = 16.8605(6)$ Å, $\beta = 100.666(2)°$, and $V = 2493.8(3)$ Å^3. Magnetic susceptibility measurements indicate that this salt exhibits a spin canted long range antiferromagnetically ordered ground state below 2.5 K.

The coordination polymers formed when divalent first-row transition metals are linked with the multidentate dca [dca is dicyanamide, $N(CN)_2^-$] anion are of current research interest because their structural diversity leads to a variety of bulk magnetic properties. The neutral, binary systems, $M(dca)_2$, form three-dimensional rutile-like structures that exhibit ferromagnetic (M = Co and Ni),[1,2] antiferromagnetic (M = Cr, Mn, and Fe),[2−6] or paramagnetic (M = Cu)[2] ground states. Until recently, the corresponding anionic $M(dca)_3^-$ complexes, which were initially reported nearly 40 years ago,[7,8] have been less studied. Various cations have now been used as molecular templates to form various structural modifications of the $M(dca)_3^-$ anion. Within the past three years, polymeric one-dimensional chains,[9,10] two-dimensional layers,[9−12] and three-dimensional networks[11,13] of $M(dca)_3^-$ (M = Co, Ni, and Mn) have been reported.

Small changes in the cationic molecular template have been shown to have dramatic effects on the topology of the $M(dca)_3^-$ anion. For example, with the EPh_4^+ (E = P or As; Ph = phenyl, C_6H_5) cations, the $M(dca)_3^-$ anion forms a two-dimensional square lattice.[11] However, replacement of one phenyl ring with a methyl group yields the $(MePh_3P)Mn(dca)_3$ (Me = methyl, CH_3) salt which possesses a three-dimensional distorted triple rutile-type structure in which doubly $\mu_{1,5}$-dca$^-$ bridged dimerized manganese units are joined together through single $\mu_{1,5}$-dca$^-$ linkages.[11] Three-dimensional $M(dca)_3^-$ α-polonium (pseudo-cubic) type structures have recently been reported[13] for the $(BzR_3N)M(dca)_3$ (Bz = benzyl, $C_6H_5CH_2$; R = C_4H_9 and C_2H_5; M = Mn, Co, and Fe) salts in which single $\mu_{1,5}$-dca$^-$ bridges connect each metal center to its six nearest neighbors. To date, no long range magnetic ordering has been reported for any of the three-dimensional $M(dca)_3^-$ structures. To further study possible magnetic superexchange interactions in three-dimensional $M(dca)_3^-$ networks, we chose the triphenylsulfonium (SPh_3^+) cation, which is structurally similar to $MePh_3P^+$, as a promising molecular template. Herein, we report the preparation, X-ray structural analysis,[14] and variable-temperature magnetic study of $(SPh_3)Mn(dca)_3$ (**1**), which is the first example of a spin canted antiferromagnetic three-dimensional anionic $M(dca)_3^-$ structure.

Triphenylsulfonium triflate (500 mg, 1.21 mmol, Aldrich) was dissolved in 10 mL of ethanol and combined with a

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(14) Crystallographic analysis for **1**: monoclinic space group $P2_1/c$, with $a = 11.7079(5)$ Å, $b = 12.8554(5)$ Å, $c = 16.8605(6)$ Å, $\beta = 100.666(2)°$, $V = 2493.8(3)$ Å^3, $T = 25$ °C, $Z = 4$, $\mu = 0.64$ mm^{-1}, $R_1(F_o) = 0.0350$ ($I > 2\sigma$; 5788 reflections), $R_w(F_o^2) = 0.1079$ (all data; 7629 reflections).

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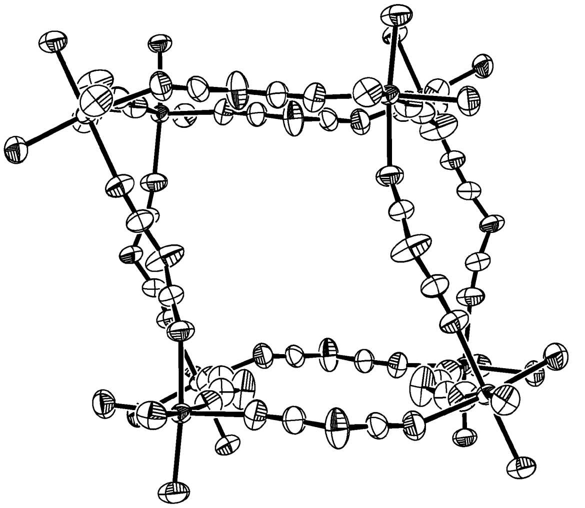

Figure 1. The distorted cubelike anion framework observed in **1**. Thermal ellipsoids are drawn at the 50% probability level.

solution of sodium dicyanamide (323 mg, 3.63 mmol, Lonza) in 10 mL of water. This mixture was layered on top of a solution of manganese(II) nitrate hydrate (217 mg, 1.21 mmol, Aldrich) in 10 mL of water. After 2 months, colorless blocky crystals were collected by filtration. Mp: 210 °C. Selected IR $\nu_{C\equiv N}$ (KBr, cm^{-1}): 2299 (s), 2286 (s), 2240 (s), 2175 (vs). Anal. Calcd (%) for $C_{24}H_{15}MnN_9S$: C, 55.81; H, 2.93; N, 24.41. Found: C, 55.47; H, 3.09; N, 24.13. μ_{Mn} (250 K) = 5.8 μ_B.

As illustrated in Figure 1, the polymeric $M(dca)_3^-$ network in the crystal structure of **1** is closely related to the three-dimensional α-polonium-type structures previously reported.[13] However, the previously known three-dimensional $M(dca)_3^-$ structures are orthorhombic [the space group of $(MePh_3P)Mn(dca)_3$ is $P2_12_12_1$,[11] and in the $(BzR_3N)M(dca)_3$ salts it is *Pnma*[13]], while **1** is monoclinic ($P2_1/c$). As illustrated in Figure 1, the manganese atoms in **1** are joined to six equivalent manganese centers through single $\mu_{1,5}$-dca$^-$ bridges. The Mn···Mn separations within the *ab*-plane are 8.7555(4) and 8.6914(4) Å, whereas parallel to the *c*-axis it is 8.4436(3) Å. The manganese atom lies on a general position with the octahedral coordination sphere consisting of the nitrile nitrogen atoms of six dicyanamide anions. The Mn−N distances within the *ab*-plane are 2.214(2), 2.216(1), 2.225(1), and 2.270(1) Å, while along the *c*-axis, the lengths are 2.207(2) and 2.254(1) Å. The C≡N bond distances, which average 1.139(5) Å, are typical for dca. The Mn−N−C bond angles range from 150.8(1)° to 173.8(2)°, and the *cis*-N−Mn−N bond angles are between 83.55(6)° and 96.18(6)°.

Similar to that previously reported for the SPh_3 BF_4 salt,[15] the triphenylsulfonium cation in **1** has a slightly distorted trigonal pyramidal geometry, with a mean S−C distance of 1.783(5) Å and C−S−C angles ranging from 102.6(1)° to 106.5(1)°. The distance of the sulfur atom from the trigonal plane formed by the three bonded carbon atoms is 0.731(1) Å. A weak intermolecular contact of 3.321(2) Å, shorter than the sum of the van der Waals radii (3.35 Å),[16] is observed between the sulfur atom and one of the amide nitrogen atoms. The shortest S···S separations are 7.9446(5) Å, which occur as zigzag chains along the (010) direction between the open faces of the triphenylsulfonium cations. The second shortest S···S separations are 8.4391(3) Å, which occur along chains in the (001) direction. Whereas multiple phenyl embraces between Ph_4E^+ (E = P or As) cations have been well documented as structure directing entities,[17,18] such interactions seem to be less important in this case with greater importance given to the formation of the three-dimensional anionic structure and cation−anion interactions.

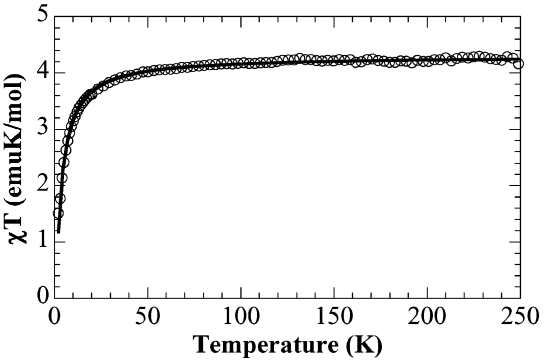

Figure 2. Temperature dependence of χT measured in a dc field of 1 KOe for a polycrystalline sample of **1**. The solid line illustrates the fit of the data to a Heisenberg 3D AFM model.

The temperature dependence of χT is shown in Figure 2. Near room temperature, χT has a value of 4.246 emu K/mol that is slightly reduced from the expected value of 4.375 emu K/mol for high-spin Mn^{2+} ions. As the temperature is lowered, χT remains essentially unchanged until ~50 K. Due to increasing antiferromagnetic (AFM) correlations, χT decreases rapidly down to 2 K, where it reaches a final value of 1.508 emu K/mol. A Curie−Weiss fit to the data yields excellent agreement for $g = 1.954(1)$ and $\theta = -3.7(2)$ K, the θ-value being consistent with near-neighbor AFM interactions mediated via Mn−NCNCN−Mn pathways.

The structure of $SPh_3[Mn(dca)_3]$ can be approximated to a simple cubic network where each Mn^{2+} ion is equally surrounded by six others. Accordingly, we employed a Heisenberg 3D AFM model for classical spins developed by Rushbrooke and Wood[19] ($H = -J\sum_{i,j}S_iS_j$) that gave $g = 1.961(1)$ and $J/k_B = -0.140(2)$ K. The fitted *J*-value is consistent with this type of magnetic interaction.

The zero field ac susceptibility, measured at 125 Hz (Figure 3), suggests that **1** is a noncollinear antiferromagnet as evidenced by a sharp peak at 2.5 K in both the real and imaginary components. This sharp feature superimposes a broader cusplike maximum and is most likely due to the presence of a small uncompensated magnetic moment manifested by a weak single-ion anisotropy of the Mn^{2+} site. We define the three-dimensional ordering temperature, T_N, as the position of this peak.[20] Further, ac susceptibility

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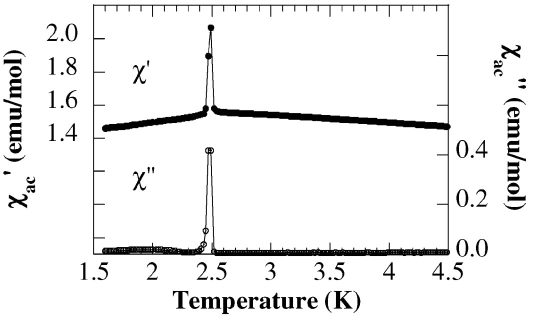

Figure 3. Real or in-phase (χ') and imaginary or out-of-phase (χ'') components of the ac susceptibility of a polycrystalline sample of **1** as a function of temperature, measured in an oscillating field of amplitude H_{ac} = 2 Oe and frequency f = 125 Hz.

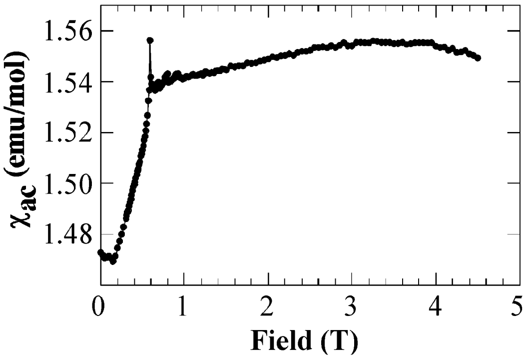

Figure 4. Real or in-phase (χ') component of the ac susceptibility of a polycrystalline sample of **1** as a function of magnetic field, measured in an oscillating field of amplitude H_{ac} = 2 Oe and frequency f = 125 Hz at 1.75 K.

measurementsat 10 and 1000 Hz (Supplementary Figure 3, Supporting Information) yielded similar results with no shift in the peak position. Using the J-value calculated above and $z = 6$, we calculate $T_N = 2.45$ K from the mean-field result, $T_N = zJS(S + 1)/3k_B$, which is in excellent agreement with the observed value. Similar behavior has previously been reported for the neutral Mn(dca)$_2$ complex (T_N = 15.9 K)[4,5] as well as (n-$C_3H_7NH_3)_2MnCl_4$ (T_N = 39.2 K).[21] Because Mn^{2+} has a weak anisotropy, we expect the spin canting angle to be <0.1° as observed in the aforementioned examples.

As illustrated in Figure 4, the real component of the ac susceptibility was measured as a function of applied magnetic field at 1.75 K. A sharp peak is observed at 0.6 T, which is identified as the spin-flop field, H_{SF}. This value is comparable to those reported for the related Mn(dca)$_2$[4] and Mn(dca)$_2$(pyz)[22] complexes. Although not observed up to 4.5 T, a second spin transition to a paramagnetic (or field-induced ferromagnetic-like) state, H_c, should occur at much higher fields. With our knowledge of H_{SF}, we can estimate the critical field values, i.e., H_E and H_A, from eqs 1 and 2.[23] We

$$H_E = z|J|S/g\mu_B \tag{1}$$

$$H_{SF} = (2H_EH_A - H_A^{\,2})^{1/2} \tag{2}$$

obtain H_E = 1.6 T and H_A = 0.12 T, which are comparable to those obtained for Mn(dca)$_2$(pyz).[22] The upper critical field can be estimated from the relation $H_c \approx 2H_E$,[23] from which we obtain $H_c \approx 3.2$ T. This value is consistent with the observed gradual downward curvature in $\chi'(H)$. The dc magnetization at 2 K reaches a value of 27100 emu Oe/mol at 9 T (Supplementary Figure 4, Supporting Information), which is 97% of the saturation value.

In conclusion, when the triphenylsulfonium cation is used as the molecular template, the Mn(dca)$_3^-$ anion adopts a cube-type polymeric structure in which each metal center is connected to six equivalent metal centers through single $\mu_{1,5}$-dca bridges. Ac susceptibility measurements indicate that this salt is a spin canted antiferromagnet below T_N = 2.5 K with H_{SF} = 0.6 T. We are currently investigating the use of other molecular cationic templates in an attempt to control the supramolecular architecture of M(dca)$_3^-$ salts and hence any cooperative magnetic behavior.

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Supporting Information Available: Experimental details (X-ray crystallography, magnetic measurements, infrared spectroscopy, and elemental analysis), bond lengths and angles (CIF format), thermal ellipsoid plots with atom labeling for (SPh$_3$)Mn(dca)$_3$, and plots of the ac susceptibility as a function of temperature at various frequencies and dc magnetization as a function of magnetic field at 2 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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