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[6] Single-crystal X-ray diffraction data: **2b** ($C_{100}H_{116}LiN_4O_7P_4Yb$, M_r = 1785.82): STOE-STADI IV, space group $P2_1/c$ (no. 14), a = 1487.97(13), b = 2454.0(2), c = 2606.90(3) pm, β = 103.897(7)°, T = 203 K, Z = 4, $V = 9240(1)\times 10^6\ \text{pm}^3$, $\rho_{calcd} = 1.287\ \text{g cm}^{-3}$, $\theta_{max} = 45°$, 11554 reflections collected, 11554 independent reflections. The structure was solved by Patterson methods (SHELXS-86 and SHELXL-93) and refined by full-matrix least-square techniques using 8262 reflections with $I > 2\sigma(I)$, $R_1 = 0.0610$ and $wR_2 = 0.1369$. **2c** ($C_{100}H_{116}LiLuN_4O_7P_4$, M_r = 1791.76): STOE-STADI IV, space group $P2_1/c$ (no. 14), a = 1487.1(5), b = 2450.9(5), c = 2607.4(4) pm, β = 104.032(8)°, T = 203 K, Z = 4, $V = 9220(4)\times 10^6\ \text{pm}^3$, $\rho_{calcd} = 1.291\ \text{g cm}^{-3}$, $\theta_{max} = 45°$, 12007 reflections collected, 12007 independent reflections. The structure was solved by Patterson methods (SHELXS-86 and SHELXL-93) and refined by full-matrix least-square techniques using 8241 reflections with $I > 2\sigma(I)$, $R_1 = 0.0607$ and $wR_2 = 0.1300$. **3** ($C_{18}H_{16}NP$, M_r = 277.29): STOE-STADI IV, space group $Pca2_1$ (no. 29), a = 930.8(3), b = 1709.2(5), c = 951.5(3) pm, T = 200 K, Z = 4, $V = 1513.8(8)\times 10^6\ \text{pm}^3$, $\rho_{calcd} = 1.217\ \text{g cm}^{-3}$, $\theta_{max} = 48°$, 1274 reflections collected, 1274 independent reflections. The structure was solved by direct methods (SHELXS-86 and SHELXL-93) and refined by full-matrix least-square techniques using 1131 reflections with $I > 2\sigma(I)$, $R_1 = 0.0299$ and $wR_2 = 0.0659$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410439 (**3**), CSD-410440 (**2b**), and CSD-410441 (**2c**).

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[16] Selected atomic distances [pm] and angles [°] of the calculated anions: $[(H_2PNH)_4Y]^-$: a) DFT: Y−N 226.0 and 226.1, Y−P 351.1 and 351.6, N-Y-N 101.9 – 113.4; b) MP2: Y−N 224.4, Y−P 348.1, N-Y-N 102.5 – 113.1; $[(Me_2PNMe)_4Y]^-$: a) DFT: Y−N 228.0 and 228.7, Y−P 321.8 and 325.7, N-Y-N 106.6 – 117.6; b) MP2: Y−N 225.8 and 225.9, Y−P 310.3 and 311.5, N-Y-N 101.2 – 122.5; $[(Ph_2PNPh)_4Y]^-$: a) DFT: Y−N 232.4 and 234.5, Y−P 306.7 and 321.9, N-Y-N 102.5 – 113.0; b) MP2 (extrapolated): Y−N 229.6 and 230.5, Y−P 287.6 and 297.4, N-Y-N 91.8 – 122.9.

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Solvothermal Synthesis of the Canted Antiferromagnet $\{K_2[CoO_3PCH_2N(CH_2CO_2)_2]\}_6\cdot x\,H_2O$**

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Annie K. Powell, and Paul T. Wood*

Derivatives of phosphonic acid have recently been shown to introduce structural diversity into metal oxide based materials produced both solvothermally and by conventional means.[1] We are currently investigating the use of solvothermal reactions to construct metal – ligand frameworks and have found that rigid aromatic carboxylic acid derivatives are excellent structural members around which to form infinite lattices.[2] However, the number of molecular clusters synthesized by using solvothermal techniques is still relatively small[3] and the factors which promote formation of molecular rather than infinite structures are poorly understood. We report herein the results of the extension of our efforts to the synthesis of large molecular species based on flexible chelating ligands.

When Co^{II} nitrate is treated with the potassium salt of the ligand (phosphonomethyl)iminodiacetic acid under hydrothermal conditions only blue-purple solutions are obtained. When the solvent is changed to methanol, the purple crystalline product **1** is formed in good yield. X-ray structure

$\{K_2[CoO_3PCH_2N(CH_2CO_2)_2]\}_6\cdot x\,H_2O$ **1**

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analysis[4] shows the material to be based on a simple structural unit in which the cobalt(II) ions have a trigonal-bipyramidal coordination geometry (Figure 1). The nitrogen atom lies at one apex and the three arms of the ligand coordinate equatorially. This ML unit is the monomer from which hexameric rings are formed. The second apical coordination site is occupied by a phosphonate oxygen from a neighboring monomer such that oligomers are formed in a head-to-tail fashion. This is in contrast to the behavior observed for related tetradentate ligands and ions such as Fe$^{\mathrm{III}}$ where head-to-head bridging generates dimeric six-coordinate species.[5] Hence the backbone of the rings consists of $M_6P_6O_{12}$ rings in which every other atom is an oxygen and the metal and phosphorus alternate in the remaining sites. The six-membered ring is generated by a $\bar{3}$ site and is therefore in the chair conformation. The head-to-tail polymerization can take place in either a clockwise or anticlockwise fashion. The symmetry of the space group results in all of the rings in one layer (parallel to the *ab* plane) having one "handedness", whilst those in the adjacent layers are all of the opposite type. Within each layer the topology of the cobalt atoms is that of a puckered hexagonal sheet which approximates to the gray arsenic[6] structure (Figure 2). The Co–Co distances are 5.516(2) within the rings and 5.507(2) Å between adjacent units. The rings pack together in such a way as to generate infinite channels parallel to the *c* axis.

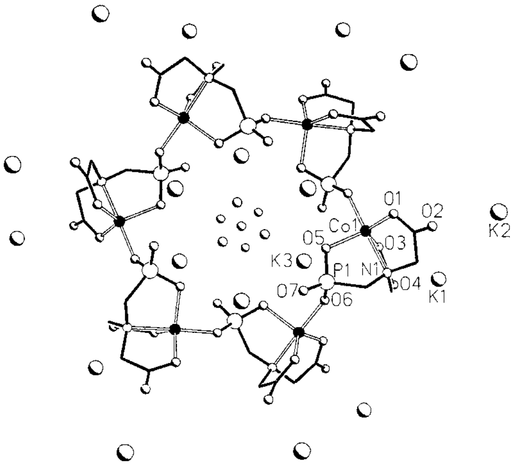

Figure 1. View of a monomeric unit showing the atom numbering scheme. Unlabled shaded spheres in the center of the ring represent the positions of the disordered lattice water molecules. Selected bond lengths [Å] and angles [°]: Co–O1 2.027(6), Co–O3 1.996(7), Co–O5 2.030(6), Co-O6A 1.967(6), Co–N1 2.169(7); O6A-Co-N1 177.6(3), O1-Co-O3 125.8(3), O1-Co-O5 112.9(3), O3-Co-O5 115.8(3).

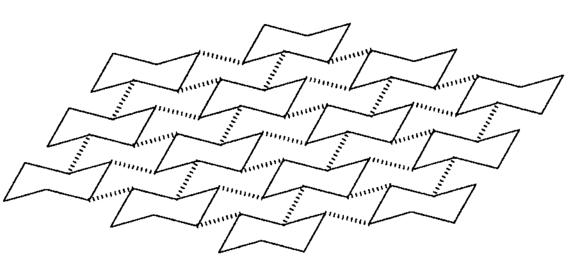

Figure 2. View of the topology of cobalt atoms in a layer parallel to the *ab* plane. Solid lines represent Co–Co vectors within the ring, dashed lines between rings.

An investigation of the magnetic behavior of **1** (Figure 3) revealed that the room temperature moment is consistent with noninteracting $S = 3/2$ centers and the sample obeys the Curie–Weiss law above 100 K with $\theta = -14$ K. At 14 K there is a magnetic phase transition marked by a sharp increase in the magnetization to a maximum value at 2 K of 115 G cm^3 mol^{-1} (for a field of 100 G). This is equivalent to 0.7 % of that expected for ferromagnetic ordering. This behavior is characteristic of canted antiferromagnetism[7, 8] in which a predominantly antiferromagnetic phase possesses a small spontaneous magnetization due to a small deviation from a strictly antiparallel arrangement. A series of temperature scans in various fields (Figure 3) shows a pronounced field dependence of the low-temperature phase confirming our assignment. Furthermore a hysteresis is observed below T_c (Figure 4), from which we can directly obtain values (at 5 K) for the coercive field of 370 G and remnant magnetization of

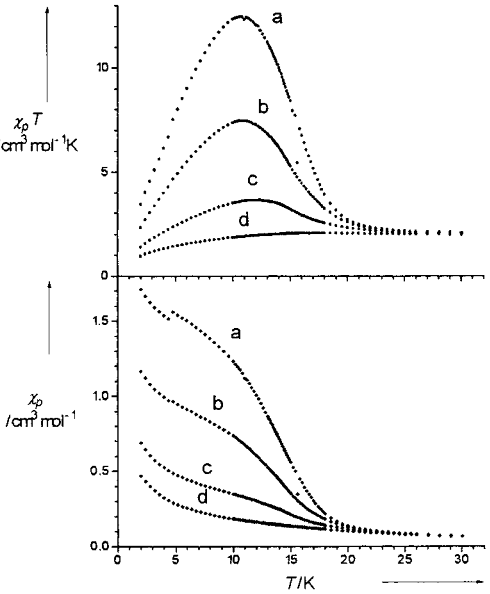

Figure 3. Plot of the temperature dependence of χT (top) and χ (bottom) versus magnetization in fields of a) 10, b) 100, c) 1000, and d)10000 G.

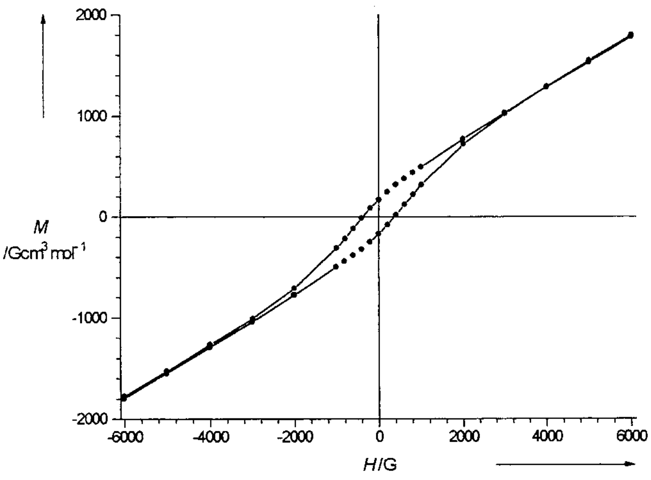

Figure 4. Hysteresis at 5 K.

170 G cm^3 mol^{-1}. Fitting the data in the range ±(2000–10000) G to Equation (1) yields a value for the saturated canted moment of $M_s(5\,K) = 288$ G cm^3 mol^{-1} which corresponds to a canting angle ϕ of 0.98(2)°. The positions of

$$M(H,T) = M_s(T) + \chi_{\parallel}(T)H \tag{1}$$

spins within the unit cell shows that the stringent symmetry requirements[7] for canted antiferromagnetism (e.g. no inversion center between coupled spins) are met. That a phase change from paramagnet to canted antiferromagnet occurs without an intermediate antiferromagnetic phase is indicative of the predominant influence of D, the single ion anisotropy over J, the exchange coupling which would have been expected from structural considerations. It is becoming evident that canted antiferromagnetism is surprisingly common in materials with extended structures[8] but there are few examples of this behavior for molecular materials with the exception of some purely organic radicals.[9] Hence we believe this to be the first observation of canting for an inorganic molecular compound.

In the last few years solvothermal synthesis has found new applications in coordination chemistry. Despite a great deal of interest and activity, control of product architecture is still elusive. It has been observed that the use of nonaqueous solvothermal conditions encourages the formation of molecular species[3a] which has also been observed in this work. The ability of Co^{II} to tolerate a range of coordination environments makes it ideal for exploratory studies of this type. Clearly an entirely different lattice would have been observed for a metal requiring octahedral coordination. We have only observed similar structures for Zn^{II}, which also tolerates trigonal-bipyramidal coordination, whilst other divalent metal ions give entirely different structures. In addition the large single-ion anisotropy for trigonal-bipyramidal Co^{II} promotes the formation of the canted magnetic phase.

Experimental Section

A solution of $Co(NO_3)_2 \cdot 6\,H_2O$ (0.435 g, 1.5 mmol) in methanol (2 mL) was added to a stirred solution of $H_2O_3PCH_2N(CH_2CO_2H)_2$ (0.341, 1.5 mmol) and KOH (0.337 g, 6 mmol) in methanol (8 mL). The resulting blue slurry was transferred into a 23 mL Teflon-lined autoclave and heated at 200 °C for two days and allowed to cool to room temperature over a period of three hours. The product was filtered and washed with methanol and dried in air. Inspection of the final solid under an optical microscope, revealed that it consisted of blue-purple hexagonal crystals of **1** (yield 0.65 g, 90% based on Co) and colorless crystals of KNO_3 (ca. 10%), which was identified by IR spectroscopy and elemental analysis.

A KNO_3-free sample of **1** was obtained from an identical reaction with $Co(OAc)_2 \cdot 4\,H_2O$ (0.375 g, 1.5 mmol), $H_2O_3PCH_2N(CH_2CO_2H)_2$ (0.341, 1.5 mmol), and KOH (0.112 g, 2 mmol).

Elemental analysis calcd for $C_5CoH_6K_2NO_7P$ (%): C 16.25, H 1.89, N 3.97; found: C 15.98, H 1.80, N 3.97.

Magnetic measurements were performed on polycrystalline samples using a SQUID magnetometer in the range 2–300 K.

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[4] Crystal data for $C_{30}H_{36}N_6O_{45.5}Co_6K_{12}P_6$: $M_r = 2225.25$, trigonal, $a = 16.269(2)$, $c = 46.597(9)$ Å, $V = 10680(3)$ Å^3, $T = 293$ K, space group $R\bar{3}c$, $Z = 6$, ρcalcd = 2.076 g cm^{-3}, 1882 unique reflections were collected, $2\theta_{max} = 48°$, graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz and polarization factors and an empirical absorption correction applied using Texsan software, $\mu(Mo_{K\alpha}) = 2.3$ mm^{-1}, min/max transmission factors 0.540–1.000, ω scans. The structure was solved by direct methods (SHELXTL-PLUS) the ligand hydrogen atoms were placed on calculated positions and allowed to ride on their parent atoms with fixed isotropic temperature factors, all other atoms were refined anisotropically except for the lattice water oxygens which were refined isotropically. Full-matrix least-squares refinement on $|F^2|$ using SHELX-93 software. 160 parameters refined, $R1 = 0.0566$ for $F > 4\sigma(F)$, $wR2 = 0.1670$ for all data, $S = 1.008$, maximum residual electron density (largest electron hole) = 1.031 (−0.789) e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-106139. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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