rearrangement. Moreover, contrary to the claim[3] that "oxygen bond formation cannot significantly precede silicon-carbon bond breaking" based on the Hammett ρ value, it is now found that the Si-O bond formation is indeed the driving force of the reaction.

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Structure and Magnetic Properties of a Unique Cobalt(II) Hippurate Complex: a Canted, Oxygen Bridged, Metamagnet

Sir:

Interest in the low temperature magnetic properties of multinuclear transition metal complexes has accelerated in the past few years as adequate experimental systems and theoretical models have been developed for data collection and interpretation.[1] Many examples of ferromagnetic and antiferromagnetic long-range ordering have been observed, particularly in carboxylate and halide complexes of the first-row transition metals.[2,3] However, few magnetically ordered compounds have been characterized which exhibit metamagnetic phase transitions. Most of the reported cases of metamagnet behavior involve linear chain molecules with metal centers bridged by halides[4-6] although the phenomenon has been observed in neptunium(V) oxalate, $(NpO_2)_2C_2O_4 \cdot 4H_2O$.[7] This communication reports the preparation and characterization of the first example of an apparent metamagnet which has water molecules bridging the metal centers.

A compound of empirical formula, $Co[(C_6H_5)CONHCH_2COO]_2 \cdot 5H_2O$, was prepared by adding 1.82 g of $Co(ClO_4)_2 \cdot 6H_2O$ in 20 ml of distilled water to 2.01 g of sodium hippurate (sodium *N*-benzoylglycinate) in 50 ml of distilled water. Pink needles began to form after 4-5 h. The product was filtered and recrystallized from a 1:1 water/ethanol mixture. The stoichiometry was established by elemental analysis with the number of water molecules verified from the initial weight loss in the thermal gravimetric curves obtained on a Perkin-Elmer differential scanning calorimeter DSC-1B (values were reproducible to ±0.1% H_2O).[8]

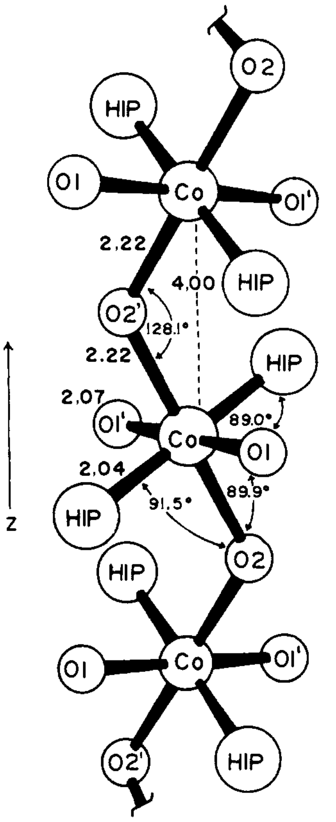

Figure 1: Projection view of the site symmetry about the Co(II) ions.

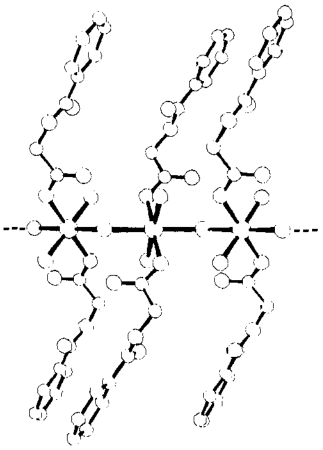

Figure 2: Projection view of the $Co[(C_6H_5)CONHCH_2COO]_2 \cdot 5H_2O$ molecule.

The compound crystallizes in the monoclinic space group $C2/c$ with four formula weights in a unit cell of dimensions a = 40.82, b = 6.90, c = 7.99 ± 0.01 Å and β = 91.9 ± 0.1°. Intensity data were collected out to a 2θ limit of 100° on a G.E. XRD-490 fully automated diffractometer system using Cu $K\alpha$ radiation. A total of 715 reflections were considered statistically significant and used in the subsequent refinement. At the present stage of refinement using anisotropic temperature factors and fixed hydrogens calculated from predicted geometry, the structure calculation has progressed to the point where the reliability index has a value of $R = 0.094_4$.[9]

The backbone of the structure, shown in Figure 1, is made up of cobalt ions linked in infinite chains along the z cell axis. Each cobalt is bonded to two hippurate molecules and two water molecules in the central plane. These planes are then connected by a water bridge having a longer bond than the other cobalt-oxygen distances, forming a tetragonally distorted octahedron. The closest cobalt-cobalt distance is 4.00 Å across

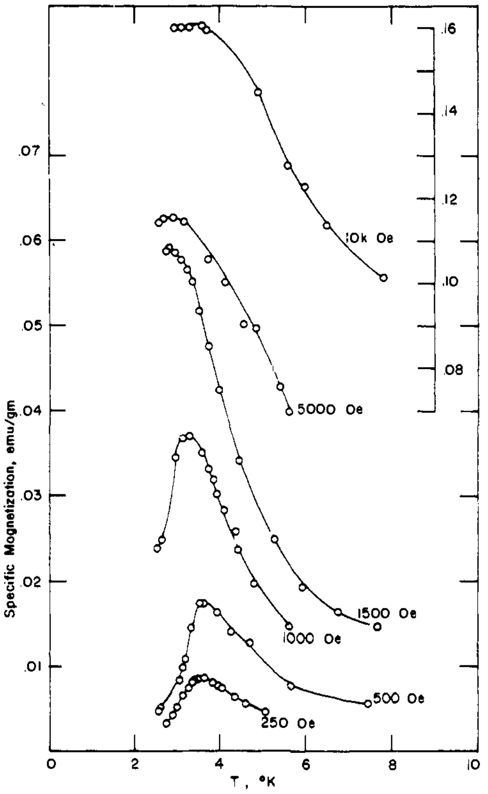

Figure 3: Specific magnetization vs. temperature for several values of applied magnetic field for a powdered sample of Co[(C_6H_5)-$CONHCH_2COO]_2 \cdot 5H_2O$. (Right hand ordinate is for the curves at 10 kOe and 5000 Oe. Left hand ordinate is for the curves at 250, 500, 1000, and 1500 Oe.)

the bridge. The chains show no close contact distances to each other with the closest cobalt-cobalt contact distance across two chains, of 6.90 Å along the *y* cell axis.

The hippurate molecules are bonded to the cobalt through the carboxyl oxygen atoms as has been previously observed in the case of the copper hippurate.[10,11] Figure 2 shows how these molecules fan out from the backbone like alternating rungs of a ladder. The two remaining water molecules in the structure lie between the hippurate steps and have no close contact with the cobalt ions.

Zero field magnetic susceptibility data for the powdered complex were obtained from 2.5 to 80 K. The plot of $1/\chi_M$ vs. T (not shown) was indicative of Curie-Weiss law behavior above 40 K (with $\theta = 32°$ and $C = 0.46$). Between 40 and 10 K a broad minimum, typical of an antiferromagnet, was observed, followed by a sharp, essentially linear decrease in $1/\chi_M$ as the temperature was lowered below 10 K. Susceptibility behavior of this type is expected for a metamagnet. However, the metamagnetic character of the compound is more convincingly exhibited by the temperature dependent magnetization data taken with magnetic fields in the range of 0–10 kOe. Field dependent isothermal magnetization curves (not shown) were obtained from 2.59 to 5.62 K in fields up to 10 kOe. Below 3.14 K S-shaped curves characteristic of metamagnets were observed. Curves of specific magnetization vs. T at constant applied fields are shown in Figure 3. Note that the specific magnetization maximum shifts to lower temperatures as the external field strength is increased, again indicating that the complex exhibits metamagnet behavior rather than a "spin-flop" transition. At an applied field of approximately 1500 Oe, the antiferromagnetic transition disappears and ferromagnetic saturation is observed. These magnetic data are analogous to those reported for the $Co(pyr)_2Cl_2$ system[4-6] which has been interpreted in terms of strong ferromagnetic exchange interactions along the chains and weak antiferromagnetic exchange between chains. Work is presently underway to model the magnetic data via equations developed for Ising linear chains[4] and to relate the exchange phenomena to the observed low temperature optical spectra.

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Reductive Coupling of Adjacent Ligands in a Seven-Coordinate Molybdenum(II) Isocyanide Complex[1]

Sir:

Recently we have synthesized and structurally characterized the seven-coordinate molybdenum(II) complexes $[MoL_7]^{2+}$ and $[MoL_6X]^+$, where L is *tert*-butyl isocyanide and X = Cl, Br, I.[2-5] The structures consist of a capped trigonal prism with either halide or isocyanide as the capping ligand (Figure 1). The short nonbonded contacts between coordinated carbon atoms suggested that ligand migration or coupling reactions, known to occur for other metal isocyanide complexes,[6-9] might be especially facile for these heptacoordinate molybdenum(II) cations.

A suspension containing 3 mmol of red-orange $[(RNC)_6MoI]I$,[3] R = *tert*-butyl, and 10 mmol of zinc dust in tetrahydrofuran was allowed to reflux under nitrogen for 2 h. The final, deep red solution was filtered and the solvent removed in vacuo. Red, air-stable crystals were obtained in 90% yield upon recrystallization from acetone or benezene and diethyl ether. Analytical data were consistent with the empirical formula $(RNC)_6MoI_2H_2$.[10] The infrared spectrum of the compound mulled in carbon tetrachloride had absorptions at 2128 cm^{-1} (br, mult), assigned to terminal isocyanide stretching modes, bands at 1593 and ~1400 cm^{-1} in the C=C and C=N stretching region, two N—H stretching frequencies at 3102 and 3160 cm^{-1}, and an N—H deformation band at 1513 cm^{-1}. The assignment of the N—H stretching bands was verified by a deuterium exchange experiment. They shifted to 2309 and 2359 cm^{-1}, respectively, when the complex was deuterated by shaking a solution of it in chloroform with D_2O for 1 h, separating the layers, and precipitating the product