Inorg. Chem. **1983**, *22*, 1725-1729

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Exchange Coupling in Tris(μ-hydroxo)bis[(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III)] Triperchlorate Trihydrate

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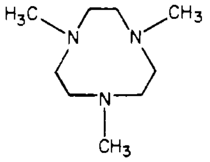
Received July 26, 1982

Magnetic susceptibility data have been collected in the temperature range 1.7–336 K for the tris(μ-hydroxo)-bridged bimetallic chromium complex $[LCr(OH)_3CrL](ClO_4)_3\cdot 3H_2O$. The magnetic susceptibility data reflect antiferromagnetic exchange coupling interactions and may be fit with the assumption of bilinear and biquadratic exchange of the form $-2JS_1\cdot S_2 - j(S_1\cdot S_2)^2$ with the Van Vleck equation. The best fit of the experimental data yields $J = -64$ (1) cm^{-1}, $j = 1.8$ (2) cm^{-1}, and $g = 1.98$ (1) with an estimated impurity percentage of 0.84 (1). The large value of the bilinear exchange coupling constant reflects the number of bridging hydroxo groups as well as structural features of the superexchange pathway. EPR spectra collected as a function of temperature at X- and Q-band have been theoretically simulated with the spin Hamiltonian parameters $D = \pm 0.34$ cm^{-1}, $D_e = \pm 0.18$ cm^{-1}, and $g = 1.98$, with $\Delta H_{pp} = 150$ G.

Introduction

A reasonable body of structural and magnetic data now exists for mono(μ-hydroxo)-[1-16] and bis(μ-hydroxo)-bridged[17-35] bimetallic chromium(III) complexes, and a unified explanation for the effects of chemical and structural variations on exchange coupling processes is emerging. The recent synthesis and structural characterization of $[LCr(OH)_3CrL]I_3\cdot 3H_2O$,[36] the first authentic triply hydroxo-bridged bimetallic complex of chromium(III) reported thus far, provide the opportunity of investigating and comparing magnetic and structural properties in bimetallic chromium(III) complexes with one, two, and three bridges of the same kind. The ligand is the cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane:



We report here the results of our studies of the magnetic properties of an analogue of the compound for which the structure has been determined, that being $[LCr(OH)_3CrL](ClO_4)_3\cdot 3H_2O$. The data are analyzed in terms of molecular orbital theory, and a comparison of the structural and magnetic properties of mono-, bis-, and tris(μ-hydroxo)-bridged chromium(III) complexes is presented.

Experimental Section

Sample Preparation. The sample used for the magnetic susceptibility measurements was prepared by the method given by Wieghardt and co-workers.[36] Analytical data confirmed the formulation $[Cr_2(OH)_3L_2](ClO_4)_3\cdot 3H_2O$.

Magnetic Measurements. Magnetic susceptibility data were collected with a Foner type vibrating-sample magnetometer (VSM). The vibrating-sample magnetometer was operated at 10 kOe for the measurements and was calibrated with $HgCo(NCS)_4$.[37] Diamagnetic corrections for the constituent atoms were made by using Pascal's constants.[38-41] The sample was checked for ferromagnetic contamination at room temperature in the magnetic field range 5–19 kOe. No evidence for ferromagnetic impurities was detected. The absolute accuracy of the data is estimated to be <±3%.

A flow type cryostat with an internal helium reservoir was used for the measurements between 336 and 1.7 K. The temperature was measured with a calibrated Au (0.3% Fe)/chromel thermocouple, and

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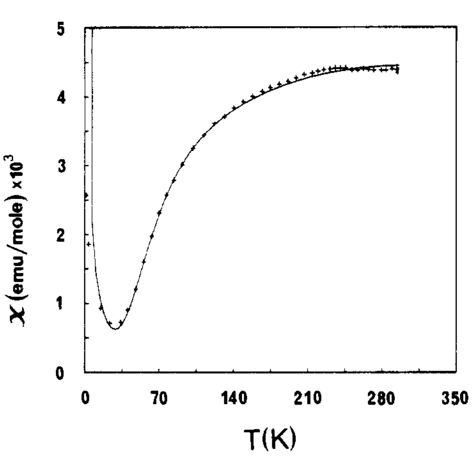

Figure 1. Magnetic susceptibility data for $[LCr(OH)_3CrL]I_3 \cdot 3H_2O$. The solid line is the best fit of the theoretical expression for a pair of exchange-coupled $S = {}^3/_2$ spins, including biquadratic exchange. Best fit parameters are given in the text.

the absolute accuracy of the temperature measurements is $<\pm 1$ K (20–300 K).

EPR Measurements. EPR spectra of powdered samples were obtained at X-band (9 GHz) and Q-band (35 GHz) with a Varian E 15 spectrometer using DPPH as a standard. Spectra were obtained between 50 and 300 K at X-band with use of a helium-flow cryostat (Oxford Instruments) and at fixed temperatures (120, 300 K) at Q-band.

Results

Magnetic susceptibility data for $[LCr(OH)_3CrL](ClO_4)_3 \cdot 3H_2O$ which were collected in the temperature range 1.7–300 K are displayed in Figure 1. There is a Curie-like tail at low temperatures, which arises from a small quantity of paramagnetic impurities, and the high-temperature data reflect antiferromagnetic exchange coupling interactions, which were expected in view of the superexchange pathways provided by the three bridging hydroxo ligands.

Exchange coupling in bimetallic chromium(III) complexes may be described by the Hamiltonian

$$\mathcal{H}_{ex} = -2J_{12}\hat{S}_1 \cdot \hat{S}_2 - j(\hat{S}_1 \cdot \hat{S}_2)^2 \qquad (1)$$

where J is the bilinear exchange coupling constant and j is the biquadratic coupling constant. In bis(μ-hydroxo)-bridged chromium complexes $|j/J|$ ranges from 0 to 0.1, with smaller values being observed most frequently. When the energies of the spin states that result from the application of the exchange Hamiltonian in eq 1 to the spin wave functions are substituted in the Van Vleck equation and an isotropic Zeeman effect is assumed, the temperature dependence of the magnetic susceptibility of a pair of exchange-coupled $S = {}^3/_2$ ions becomes[42]

$$\chi_M = (Ng^2\mu_B{}^2/kT) \times \{2 \exp[(2J - 6.5j)/kT] + 10 \exp[(6J - 13.5j)/kT] + 28 \exp[(12J - 9j)/kT]\}\{1 + 3 \exp[(2J - 6.5j)/kT] + 5 \exp[(6J - 13.5j)/kT] + 7 \exp[(12J - 9j)/kT]\}^{-1} \qquad (2)$$

In view of the small Curie tail in the magnetic susceptibility data at low temperatures, a correction for a small quantity of monomeric impurities was made under the assumptions that $\chi_{Cr} = \chi_{dimer}/2 + \chi_{impurity}$ and that the magnetic susceptibility of the impurity obeys the Curie law. The following equation for the total susceptibility resulted from these assumptions

$$\chi_{Cr} = \{P[Ng^2\mu_B{}^2S(S + 1)]/3kT + (100 - P)\chi_{dimer}/2\}/100 \qquad (3)$$

where S is the spin of the impurity ion (assumed to be ${}^3/_2$ in this case), P is the percent impurity to be determined, and g was taken as a variable (and equal to the dimer g value) in the fitting process.

Equation 2 with the impurity correction in eq 3 was fit to the magnetic susceptibility data with use of a Simplex nonlinear fitting routine.[43–46] The function that was minimized in curve fitting was

$$F = \sum w_i(\chi_i{}^{obsd} - \chi_i{}^{calcd})^2 \qquad (4)$$

with the weights being assigned $w_i = (\chi_i{}^{obsd})^{-1}$. The best fit of eq 1 to the data in the temperature range 1.7–300 K yielded $J = -64$ (1) cm^{-1}, $j = 1.8$ (2) cm^{-1}, $g = 1.98$ (1), and $P = 0.84$ (1).

The EPR spectra for $[LCr(OH)_3CrL](ClO_4)_3 \cdot 3H_2O$ are shown for X- and Q-band at 120 K in Figures 2 and 3, respectively. The spin Hamiltonian[47,48] for strongly exchange-coupled chromium pairs in an axial crystal field can be written separately for each spin state S in the form

$$H_S = \mu_B\hat{H} \cdot g \cdot \hat{S}_i + (3\alpha_S D_c + \beta_S D)[\hat{S}_{iz}{}^2 - {}^1\!/_3 S(S + 1)] \qquad (5)$$

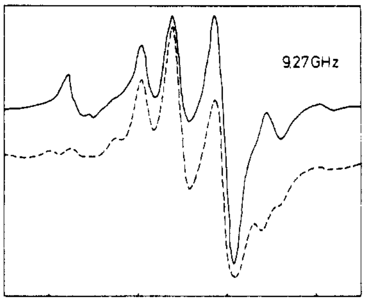

Figure 2. Experimental (solid line) and simulated (dashed line) X-band EPR spectra for a powdered sample of $[LCr(OH)_3CrL](ClO_4)_3 \cdot 3H_2O$ at 120 K. The simulated spectrum was calculated with the parameters given in the text.

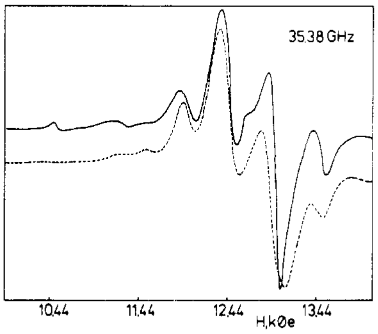

Figure 3. Experimental (solid line) and simulated (dashed line) Q-band EPR spectra for a powdered sample of $[LCr(OH)_3CrL](ClO_4)_3 \cdot 3H_2O$ at 120 K. The simulated spectrum was calculated with the parameters given in the text.

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where the first term in the spin Hamiltonian is the Zeeman term, and the second term is the anisotropic zero-field splitting term. The z axis is taken to be collinear with the chromium–chromium vector. An effective zero-field splitting parameter arises from exchange and dipole–dipole interactions (D_e), and from coupling with the electric crystal field (D), and the effective zero-field splitting parameter is dependent on the spin state. The parameters α_S and β_S are given by

$$\alpha_S = [S(S+1) + 4S'(S'+1)]/[2(2S-1)(2S+3)]$$

$$\beta_S = [3S(S+1) - 3 - 4S'(S'+1)]/[(2S-1)(2S+3)]$$

S' is the single-ion spin, and S denotes the spins of the states arising from exchange coupling. The zero-field splitting in the $S = 2$ state of the exchange-coupled system is independent of the interaction with the crystal field since β_2 is zero. The zero-field splitting of the $^4A_2$ ground state of a single chromium ion is $2D$.

The spin Hamiltonian parameters were obtained by simulating the experimental EPR spectra from the powdered samples with an emphasis on the triplet-state features.[48] The **g** tensors in this preliminary treatment were assumed to be isotropic with $g = 1.98$ in agreement with the magnetic susceptibility data. For the simulation, spectra were calculated for field directions between the z axis and the xy plane, and the calculated Lorentzian curves were folded in to form the line shapes of the powdered sample spectra. The line width, Δ_{pp}, was assumed to be independent of the field direction, and the relative intensities of line arising from resonances in the exchange-coupled levels at $2J$, $6J$, and $12J$ were obtained by a Boltzmann weighting factor to describe the thermal populations at the temperature selected for the simulation calculation.

Comparisons of the X- and Q-band simulated spectra (dashed lines) with the experimental spectra (solid lines) are given in Figures 2 and 3. At 120 K, the best fit of the calculated spectra with the experimental results were obtained for $D = \pm 0.34$ cm^{-1} and $D_e = \pm 0.18$ cm^{-1} with $\Delta H_{pp} = 150$ G. Studies on single crystals will be undertaken, and the details will be presented at a later time. Since the signal in the X-band spectrum at 1.6 kG does not vanish at 4 K, it may be attributed to an impurity. This absorption obscures the half-field transition, which is observed in the Q-band spectrum.

In view of the complexity of the EPR spectra, no attempt was undertaken to independently determine the isotropic exchange coupling constant from intensity measurements as a function of temperature. Except for the impurity at 1.6 kG noted above, all signals in the X-band spectrum disappear between 70 and 60 K. The four main resonances at 120 K may be attributed to the typical $S = 1$ triplet spectrum with the anisotropic g values $g_\parallel \neq g_\perp$ not explicitly considered here.

The anisotropic contributions from the exchange interaction and the crystal field are represented by D_e and D, respectively. While D simply reflects the zero-field splitting in the $^4A_2$ ground state of the single Cr^{3+} ion, the parameter D_e is a complicated combination of anisotropic interactions with diverse origins.[47] An interpretation of D_e in terms of electronic properties[47] is not possible at this time. Consistent with current practice in the analysis of pair spectra, we report this phenomenological parameter and anticipate that theoretical developments will permit an interpretation subsequently. The rather high D value indicates a very large axial anisotropy of the ligand field or the spin–orbit coupling comparable to that of the trigonally distorted chromium tris(acetylacetonate).[40]

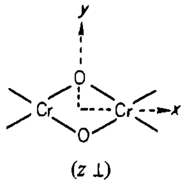
Discussion

These new data now permit an examination of exchange coupling in bimetallic systems in which the number of bridging groups increases from one to three. The structure of the superexchange network as well as the number of bridging groups may be expected to affect the magnitude of exchange coupling, and in the following sections we compare the structural and magnetic data that have been collected for these systems and present a discussion of the superexchange mechanisms in terms of molecular orbital theory. For the latter discussion, we will utilize the procedures described by Hoffmann and co-workers[49] as extended to chromium(III) systems by Scaringe.[23]

Structural and magnetic data now exist for several mono(μ-hydroxo)-bridged chromium(III) complexes; these include two salts of $[(NH_3)_5Cr(OH)Cr(NH_3)_4OH]^{4+}$ ($J \approx -20$ cm^{-1}),[5] $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ ($J \approx -30$ cm^{-1}),[1,2] and $[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]^{5+}$ ($J \approx -33$ cm^{-1}).[16] Cline et al.[16] note that an increase in the angle at the bridging oxygen atom can account in part for the trend in exchange coupling constants and draw attention to the geometry of the bridging hydroxo ligand, especially the relationship of the hydrogen atom on the bridging oxygen to the bridging plane.[34] A possible explanation of this observation is offered in a subsequent section.

Exchange coupling constants in bis(μ-hydroxo)-bridged chromium(III) complexes span a wider range, being +2.2 cm^{-1} in $Na_4[Cr(mal)_2(OH)]_2 \cdot 5H_2O$[25] at one extreme of the range and −55.5 cm^{-1} in $[Cr(phen)_2(OH)]_2Cl_4 \cdot 6H_2O$[20] at the other extreme. The Cr–O–Cr angles in the mono(μ-hydroxo)-bridged chromium(III) systems are on the order of 143–155°,[16] while comparable angles in the bis(μ-hydroxo)-bridged systems range from 97.6 to 103.4°.[32,33] The presence of two bridges dictates the smaller bridging angles in these latter systems. The exchange coupling constant in $[LCr(OH)_3CrL](ClO_4)_3 \cdot 3H_2O$ is the largest yet observed in hydroxo-bridged chromium(III) compounds, and the magnitude of J in $[LCr(OH)_3CrL]^{3+}$ may be understood in terms of the geometrical features and the number of bridges in the superexchange pathway. The Cr–O–Cr angles found in this tris(μ-hydroxo)-bridged system are 84.1°.[36] Since the chromium–bridging oxygen bond distance of 1.972 (6) Å is comparable to those found in the bis(μ-hydroxo)-bridged chromium(III) complexes, the small Cr–O–Cr angles force a very short chromium–chromium separation of 2.642 (2) Å.[36] In view of the arguments by Scaringe,[23] it is unlikely that a direct interaction through space of the unpaired electrons on the two chromium(III) ions dominates the superexchange interaction.

Molecular Orbital Formalism. In an extension of the treatment of superexchange interactions in exchange-coupled transition-metal clusters by Hoffmann and co-workers[49] to pairs of interacting chromium(III) ions, Scaringe[23] constructed two center molecular orbitals from localized molecular orbitals on the chromium(III) ions. These orbitals on chromium(III) that contain the unpaired electrons involved in the superexchange interactions are mainly t_{2g}-like orbitals. With use of the coordinate system



the localized molecular orbitals are defined as

$$\phi_a{}^A \approx d_{x^2-y^2}{}^A \qquad \phi_d{}^B \approx d_{x^2-y^2}{}^B$$

$$\phi_b{}^A \approx d_{xz}{}^A \qquad \phi_e{}^B \approx d_{xz}{}^B$$

$$\phi_c{}^A \approx d_{yz}{}^A \qquad \phi_f{}^B \approx d_{yz}{}^B$$

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where A and B designate the two chromium(III) ions in the exchange-coupled pair, and although not written explicitly, some ligand character is implied. The two-center molecular orbitals are defined as the symmetric and antisymmetric combinations

$$\Phi_1 = 1/2^{1/2}(\phi_a{}^A + \phi_d{}^B) \qquad \Phi_2 = 1/2^{1/2}(\phi_a{}^A - \phi_d{}^B)$$

$$\Phi_3 = 1/2^{1/2}(\phi_b{}^A + \phi_e{}^B) \qquad \Phi_4 = 1/2^{1/2}(\phi_b{}^A - \phi_e{}^B)$$

$$\Phi_5 = 1/2^{1/2}(\phi_c{}^A + \phi_f{}^B) \qquad \Phi_6 = 1/2^{1/2}(\phi_c{}^A - \phi_f{}^B)$$

The exchange coupling constant J_{12} may now be expressed in terms of the Coulomb integrals J_{ij}, the potential exchange integrals K_{ij}, and the one-electron molecular orbital energies E_i of the system. There are two terms in J, those being the ferromagnetic contribution J_F and the antiferromagnetic contribution J_{AF}, that is

$$J_{12} = J_F + J_{AF} \tag{6}$$

where

$$J_F = {}^2\!/_9[K_{ad} + K_{ae} + K_{af} + K_{bd} + K_{be} + K_{bf} + K_{cd} + K_{ce} + K_{cf}] \tag{7}$$

and

$$J_{AF} = -{}^1\!/_{18}[(E_2 - E_1)^2/(J_{aa} - J_{ad}) + (E_4 - D_3)^2/(J_{bb} - J_{bc}) + (E_6 - E_5)^2/(J_{cc} - J_{cf})] \tag{8}$$

Since J_F is the sum of all possible potential exchange integrals between orbitals localized on different metal centers, this contribution to J_{12} is always positive. By the same token, J_{AF} is always negative. The numerators and denominators in the three terms of eq 8 are always positive and the overall expression is negative. The numerators are positive because they are the differences between real numbers and they are squared, and the denominators are always positive because electron–electron repulsion terms J_{ii} between electrons on the same metal center are larger than those between electrons on two metal centers J_{ij}. Hoffmann and co-workers[49] have noted that J_{ij} and K_{ij} are relatively insensitive to subtle structural changes such as those seen in these hydroxo-bridged complexes.

Effects of Structure on Exchange Coupling. It follows from the discussion in the previous section that the effect of structural changes on the exchange coupling constant is determined by the numerators of the J_{AF} term. These are one-electron orbital energy differences between the symmetric and antisymmetric combinations of the same functions, and in this discussion the energies will be considered to be proportional to overlap.

To rationalize the relative magnitudes of the exchange coupling constants, the overlap of the symmetric and antisymmetric combinations of the metal-based orbitals with those of the ligand bridge must be examined, where it may be expected that the p_x, p_y, and p_z orbitals of the bridging hydroxo oxygen atoms are the most important bridge orbitals involved in the superexchange mechanism, although s orbitals are important in case of hydroxo-bridged copper(II) complexes.[49] We will examine the bis(μ-hydroxo)-bridged case first and consider the in-plane orbitals: these include the symmetric and antisymmetric combinations of the $d_{x^2-y^2}$ orbitals and like combinations of oxygen p_x and p_y orbitals. Scaringe[23] concluded that these orbitals made the dominant contribution to J_{AF} based on spectroscopic evidence for an exchange-coupled pair of chromium ions reported by van Gorkom, Henning, and van Stapele.[50] Molecular orbitals involving interactions with the out-of-plane oxygen p_z orbitals are π type overlaps, and these have been shown by van Gorkom, Henning, and van Stapele[50] to be about 5 times less than those of the in-plane contribution to J_{AF}. This would appear to be the key factor in the differences noted in the magnitude of the exchange coupling constants for the bis(μ-hydroxo)-bridged systems and the tris(μ-hydroxo)-bridged systems. There is no clear differentiation between in-plane and out-of-plane orbitals in the latter case, and as a result, all three p orbitals on all three bridging oxygen atoms may contribute nearly equally as effectively in the superexchange mechanism. By group-theoretical methods, it may be shown that the oxygen p orbitals form bases for the representations $A_1' + A_2' + A_2'' + 2\,E' + E''$, while the metal d orbitals transform as $A_1' + A_2'' + 2\,E' + 2\,E''$. Only one linear combination of oxygen p orbitals, that being the A_2' combination, cannot interact with the metal orbitals.

Effect of Chromium–Oxygen (Bridge) Bond Distance. The relatively large negative values of the exchange coupling constants in the mono(μ-hydroxo)-bridged chromium dimers appears to arise from effective overlap of the orbitals containing the unpaired electrons with the orbitals of the bridging oxygen as a result of their relative spatial orientations. Differences in chromium–oxygen bond distances cannot account for these larger values of J relative to those for the bis(μ-hydroxo)-bridged systems, since, for example, the chromium–oxygen bond distance in $[(NH_3)_4(H_2O)Cr(OH)Cr(NH_3)_5]Cl_5 \cdot 3H_2O$ is 1.983 (1) Å[16] while the range of chromium–oxygen bond distances in the bis(μ-hydroxo)-bridged systems is 1.919 (7) Å ($J = -43.8$ cm^{-1}) to 1.988 (2) Å ($J = +2.2$ cm^{-1}),[32,33] and the chromium–oxygen bond distance in $[LCr(OH)_3CrL]I_3 \cdot 3H_2O$ is 1.972 (6) Å.[36] The chromium–oxygen bond distance in the perchlorate analogue is not expected to differ markedly from that observed in the iodide salt.

The effect of changing the chromium–oxygen bond distance may also be understood in terms of the contributions to antiferromagnetic and ferromagnetic parts of the exchange coupling constant as gauged by overlap. A decrease in bond distance increases overlap in all cases in which there is overlap. We expect that, for any given angle, a decrease in metal–oxygen separation results in an enhancement of the antiferromagnetic contribution to the exchange coupling constant.

Effect of Bond Distance and Bridge Angle. We now examine the magnetic results for $[LCr(OH)_3CrL](ClO_4)_3 \cdot 3H_2O$ in view of the structural results for the iodide salt and the correlation noted by Scaringe[23] and others[33] between the singlet–triplet splitting ΔE and the geometrical features of the Cr_2O_2 bridging network in thirteen bis(μ-hydroxo)-bridged chromium(III) complexes. Here, ΔE is calculated including bilinear and biquadratic effects to be $2J - 6.5j$, and the geometrical features to be considered are the Cr–O–Cr bridge angle ϕ and the chromium–oxygen (bridge) bond distance R_O. The singlet–triplet splitting increases as the quotient ϕ/R_O increases, reaches a maximum at ϕ/R_O of about 50 cm^{-1}/Å, and then decreases as ϕ/R_O continues to increase. Recognizing that the number of bridges significantly affects the magnitude of the exchange coupling, it is nevertheless gratifying to note that the small ϕ/R_O value of 42.6 cm^{-1}/Å in $[LCr(OH)_3CrL]I_3 \cdot 3H_2O$ (which should be a reasonable approximation for ϕ/R_O in the perchlorate salt) leads to the prediction of a large negative ΔE value. The ΔE value deduced here from the magnetic susceptibility data for $[LCr(OH)_3CrL](ClO_4)_3 \cdot 3H_2O$ is the largest yet observed for bimetallic hydroxo-bridged chromium(III) complexes. Similar correlations between singlet–triplet splittings and ϕ/R have been observed in halide- and sulfur-bridged copper(II) systems.[51]

Effects of Other Structural and Electronic Features. Michelsen and Pedersen[34] have noted the existence of a correlation

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between the exchange coupling constant and the angle between the O–H vector and the bridging Cr_2O_2 plane. In all cases where J is large, the angle is small and vice versa. Basically, as the angle increases, the lone pair on oxygen is shifted out and away from the Cr_2O_2 exchange-coupled unit, and in this manner, the lone pair is less effective in transmitting the superexchange interaction. This interesting observation can be precisely examined in the case of alkoxo-bridged complexes, as can the effect of electron density on the bridging oxygen atom since this latter quantity is governed by the hydrocarbon substituent and may be varied over a limited range at least. While major structural and chemical factors that affect exchange coupling may be determined from systematic studies[52] of which this work forms an integral part, there are a number of features that give rise to subtle changes, and these may prove to be very difficult to detect. In addition, the exchange coupling constant is slightly temperature dependent in some of these compounds,[53] and this property may tend to complicate a highly refined treatment.

Conclusion. The major conclusion to be drawn from this work is that exchange coupling in the tris(μ-hydroxo)-bridged chromium(III) complex $[LCr(OH)_3CrL](ClO_4)_3 \cdot 3H_2O$ results in the largest exchange coupling constant yet observed in hydroxo-bridged chromium(III) complexes, probably as a result of the symmetry and number of bridging ligands.

Acknowledgment. We wish to thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the National Science Foundation (Grant No. CHE 80 09685) for support of this research. Helpful discussions with Dr. S. K. Hoffmann are gratefully acknowledged.

Registry No. $[Cr_2(OH)_3L_2](ClO_4)_3$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), 81915-52-8.

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Single-Crystal Magnetic Study on Ferromagnetic Manganese(II) Phthalocyaninate

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Received August 31, 1982

A magnetic study has been carried out in the temperature range 1.2–25 K and magnetic field range 0–50 kOe on single crystals of manganese(II) phthalocyaninate. At higher temperatures the magnetic properties of manganese(II) phthalocyaninate exhibit chainlike characteristics, which may be understood in terms of ferromagnetic intrachain exchange of $S = {}^3/_2$ ions with a weak antiferromagnetic interchain interaction. In the ordered state, T_C = 8.3 K, MnPc is a canted ferromagnet with easy axes of magnetization being along χ_1 and χ_3 directions. A zero-field splitting of the single-ion ${}^4A_2$ state of the manganese(II) ion gives rise to canted ferromagnetism, which does not show complete saturation at the high-field range of these experiments (50 kOe). The spin structure of manganese(II) phthalocyaninate at low temperature is discussed.

Introduction

Manganese(II) phthalocyaninate (MnPc) is a planar molecule and is known to be isostructural with other divalent metal phthalocyaninates.[2,3] The stacking of the planar MnPc molecules in the crystal lattice is shown in Figure 1. The figure shows that the two pyrrole nitrogen atoms of each molecule lie exactly above or below the Mn belonging to nearest neighbors. The distance between these axially located nitrogen atoms and the Mn atom is 3.4 Å and thus may provide a possible pathway for magnetic exchange interactions. The Mn(II) ions lie on linear arrays parallel to the b axis of the molecule such that MnPc may be considered as containing magnetic linear chains along the b axis of the crystal.

Magnetic susceptibility and magnetization measurements on MnPc down to 1.4 K have established that the Mn(II) ion in MnPc is in an $S = {}^3/_2$ spin state and that MnPc behaves as a molecular ferromagnet at low temperatures.[4] A qualitative explanation for the ferromagnetism was given in terms of the overlap of d orbitals of the Mn(II) ion and the π-system of the phthalocyanine ring.[4] The data were later quantitatively explained in terms of a model for an $S = {}^3/_2$ linear chain exhibiting ferromagnetic interactions, and a value for the exchange energy of $J = +7.6$ cm^{-1} was deduced.[5] Existence of ferromagnetism in MnPc was subsequently confirmed by Miyoshi et al.,[6,7] who also determined the Curie temperature to be 8.6 K.

To determine the easy axis of magnetization in MnPc, Miyoshi[8] measured the single-crystal magnetization at 4.2 K. MnPc belongs to the monoclinic system with two crystallographically inequivalent molecules in the unit cell, and crystals generally grow as long flat needles elongated along the b axis. Crystals used by Miyoshi were very small, weighing less than 10^{-2} mg. The "single-crystal" magnetization measurements were therefore made on a bundle of single crystals oriented along the long b axis of the crystals. Miyoshi measured magnetization along the perpendicular to the long axis (i.e., b axis) of this bundle and concluded that the easy axis of magnetization lies along the b axis of the crystals.

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