clearly exists. With bulky cations, we anticipate obtaining two-dimensional antiferromagnets, with variable values of exchange constants. With smaller cations, linear-chain salts with moderately strong ferromagnetic intrachain interactions are anticipated. The challenge here will be to synthesize similar salts with much smaller interchain interactions ($|J'/J| < 10^{-2}$).

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Registry No. $(BA)_2Cu(ox)_2$, 78307-65-0; $(PDA)Cu(ox)_2$, 78307-66-1.

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Contribution from the Department of Chemistry,
Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

Magnetic Properties of $K_5[(H_2O)_3(SO_4)_6Fe_3O]\cdot 6H_2O$, a Sulfate Analogue of the Trimeric Basic Iron(III) Carboxylates

JOHN A. THICH, BRIAN H. TOBY, DANA A. POWERS, JOSEPH A. POTENZA,* and HARVEY J. SCHUGAR*

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The title complex contains isolated $[(H_2O)_3(SO_4)_6Fe_3O]^{5-}$ clusters with triangular-planar Fe_3O units bridged by sulfate groups. The effective magnetic moment per Fe(III) in this antiferromagnetic complex varies from 3.40 μ_B at 299.6 K to 2.05 μ_B at 85 K and agrees well with that predicted by the triangular cluster model ($H = -2J(S_1\cdot S_2 + S_1\cdot S_3 + S_2\cdot S_3)$) with $g = 2.00$, TIP = 0, $S_1 = S_2 = S_3 = {}^5/_2$, and $J = -26.0$ cm^{-1}. Since significant Fe(III)···Fe(III) magnetic coupling via bridging SO_4^{2-} appears to be small and comparable magnetic behavior ($J \simeq -30$ cm^{-1}) has been reported for several carboxylate-bridged analogues, the antiferromagnetism shown by these clusters originates either exclusively or predominantly in the Fe_3O^{7+} unit. The structural and magnetic features of Fe_3O^{7+}, Fe_2O^{4+}, and $Fe_2(OH)_2^{4+}$ clusters are compared and discussed. The extent of antiferromagnetism in these clusters appears to be related to the length of the Fe–O bond(s) in the bridge(s). Of lesser importance are variations in the Fe–O–Fe or Fe–OH–Fe bridging angles and in the nature of the nonbridging ligands.

Introduction

Oxygen-bridged Fe(III) clusters play an important role in the inorganic and bioinorganic chemistry of Fe(III).[1-3] Consequently, the properties of such species have received considerable attention, and complexes containing both Fe_2O^{4+} (linear[4] and nonlinear[5]) and $Fe_2(OR)_2^{4+}$ (R = H, alkyl)[6] units have been characterized electronically, structurally, and magnetically. The triangular Fe_3O^{7+} unit, found in the trimeric basic Fe(III) carboxylates, has also been characterized structurally.[7,8]

A basic Fe(III) sulfate, known from early work[9] as Maus' salt (synthetic material) or metavoltine (natural material), has been shown to crystallize in the hexagonal system. Synthetic material, formulated as $K_5[(H_2O)_3(SO_4)_6Fe_3O]\cdot 7H_2O$, has been shown[10] to contain crystallographically equivalent Fe(III) ions in $[(H_2O)_3(SO_4)_6Fe_3O]^{5-}$ trimeric units with bridging sulfate groups. Based on its structure, this uniaxial complex appears to be well suited for electronic–structural and magnetic studies, particularly since, relative to carboxylate, bridging SO_4^{2-} is spectroscopically transparent and since Fe(III) superexchange coupling via bridging SO_4^{2-} appears to be modest. We report here the characterization of the $[(H_2O)_3(SO_4)_6Fe_3O]^{5-}$ unit by magnetic susceptibility measurements and by single-crystal electronic spectral studies.

Experimental Section

1. Preparation and Characterization of the Title Complex (1). The preparation of **1** by concentrating aqueous $Fe_2(SO_4)_3/K_2SO_4$ at 80 °C has been described elsewhere.[9-11] Our procedure employs a lower temperature and the addition of K_2CO_3. All chemicals employed were reagent grade products of the J. T. Baker Co. A hot solution of 27.0 g of hydrated $Fe_2(SO_4)_3$ (71.8% assay as $Fe_2(SO_4)_3$ by standard EDTA

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titration) and 1.35 g of $K_2CO_3\cdot 1.5H_2O$ in 50 mL of distilled H_2O was filtered through a Millipore membrane (pore size = 0.22 μm). A separate solution of 30 g of K_2SO_4 in 150 mL of hot distilled H_2O was then filtered into the above solution. Within several hours after cooling to room temperature, the resulting deep red-brown filtrate began to deposit well-formed hexagonal crystals. Brown crystals up to 1 cm or larger in size could be easily produced. The crystals were slowly efflorescent and cracked after standing in air. Monoclinic modifications of **1** have been described elsewhere.[11]

Crystals of the title complex, prepared as described above, were characterized crystallographically with use of a CAD-3 automated diffractometer. The observed density (2.39 (1) g/cm^3, measured by the gradient method) was slightly lower than that reported by Giacovazzo et al.[10] (2.412 g/cm^3) and is consistent with six rather than seven lattice water molecules per cluster. Unit cell dimensions (a = 9.706(5) Å, c = 18.994(5) Å) measured at 22 ± 1 °C were equivalent within experimental error to those reported previously,[10] while solution of the structure in the centrosymmetric space group $P6_3/m$ (full-matrix refinement of 845 diffraction maxima with $F^2 \geq 3\sigma(F^2)$; final R_F = 0.099) showed that both structures were virtually identical. In particular, none of the coordinates of the $[(H_2O)_3(SO_4)_6Fe_3O]^{5-}$ cluster differed by more than two estimated standard deviations, while both structures showed an unusually small value for β_{33} of the oxide ion, an unusually large value of β_{22} for one sulfate O atom, and a disordered site occupied by K ions and water molecules.[12]

2. Magnetic Measurements. Variable-temperature magnetic susceptibility studies were performed in the laboratory of Professor H. B. Gray with a PAR FM-1 vibrating-sample magnetometer; the apparatus and techniques used to collect the data have been described elsewhere.[13] So that it could be ensured that efflorescence of **1** did not seriously affect the magnetic data, two separate experiments were performed. Crystals of **1** were washed with distilled water and either dried rapidly by blotting or dried in air to the point where they began to crack. Both samples were immediately ground and loaded into separate airtight plastic containers; both gave magnetically identical results. A diamagnetic correction of 156 × 10^{-6} cgsu/Fe(III) was calculated from Pascal's constants.[14]

3. Electronic Spectral Measurements. Spectral measurements were made at 25 °C with a Cary Model 14 spectrometer. A crystal was lightly coated with Vaseline (to prevent dehydration) and mounted so that its c axis was oriented ~45° with respect to the vertical direction in the Cary cell compartment and perpendicular to the direction of the light beam. Polarization measurements were made with matched (230–2000 nm) Glan–Thompson prisms that were joined by silicone fluid; these gave a usable angular polarized field of ~15°. Separate polarizers in the sample reference compartments were rotated in unison by means of a chain-drive mechanism. The maximum and minimum absorbances of a well-resolved band at ~850 nm corresponded to the electric vector of the light being perpendicular and parallel, respectively, to the c axis of the crystal.

Results

1. Magnetic Susceptibility. Magnetic susceptibility data in the temperature range 85–299.6 K, corrected for diamagnetism, are presented as μ_{eff}/Fe(III) in Table I. The data were analyzed from the perspective of the isotropic spin–spin coupling model for a triangular cluster.[14,15] The use of the simplified exchange Hamiltonian $H = -2J(S_1 \cdot S_2 + S_1 \cdot S_3 + S_2 \cdot S_3)$ is justified by the crystallographically imposed equivalency of the Fe(III) ions.[10] If it is assumed that g = 2.00 and TIP = 0, the following relationship may be developed:[14]

$$\mu_{eff}^2/\mathrm{Fe(III)} = (340 + 455z^{15} + 429z^{28} + 330z^{39} + 210z^{48} + 105z^{55} + 20z^{60} + z^{63})/(4 + 7z^{15} + 9z^{28} + 10z^{39} + 10z^{48} + 9z^{55} + 4z^{60} + z^{63})$$

where $z = \exp(-J/kT)$. A J value at each temperature (Table I) was obtained from the μ_{eff}^2 vs. T data and from tables of μ_{eff}^2 vs. kT/J calculated by using the above equation. A modest systematic decrease in J with temperature was observed. Magnetic moments that were calculated with J_{av} = −26.0 (3) cm^{-1}, g = 2.00, and TIP = 0 agreed with the experimentally measured moments to within 0.02 μ_B over the entire temperature range. The general pattern of the fit between the observed and calculated moments is similar to that reported for $[(H_2O)_3(OAc)_6Fe_3O]Cl\cdot 5H_2O$(OAc = acetate).[16] Although the experimental data may be better fit by assuming that the TIP term is finite, the significance of such a procedure is not obvious in view of the approximate nature of the spin-spin coupling model.

Table I. Magnetic Susceptibility Results for **1**

T^a	$\mu_{eff}{}^b$	$-J^c$	$\mu_{calcd}{}^d$
299.6	3.41	26.5	3.43
285.9	3.36	26.4	3.38
273.2	3.31	26.4	3.32
260.5	3.26	26.2	3.27
246.5	3.19	26.2	3.20
232.4	3.13	26.1	3.14
217.7	3.06	26.1	3.06
202.2	2.97	26.1	2.98
186.0	2.88	26.0	2.88
168.6	2.77	26.0	2.77
150.0	2.64	26.1	2.64
129.5	2.49	25.7	2.48
106.0	2.28	25.7	2.27
96.0	2.18	25.7	2.16
85.0	2.06	25.5	2.04

[a] T values in K. [b] Calculated in μ_B at each temperature from the corrected molar susceptibility per Fe(III) with use of the formula $\mu_{eff}^2 = 7.998\chi^{cor}[T(K)]$. [c] Calculated in cm^{-1} at each temperature with use of the procedure described in the text. [d] Calculated in μ_B for $J_{av} = -26.0$ cm^{-1}.

Table II. Electronic Spectral Data (25 °C) for **1**

	EV ∥ c		EV ⊥ c		unpolarized	
assignt	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
$^6A_1 \rightarrow {}^4T_1$	~820[a]	0.4	~850	6	~820	1.8
$^6A_1 \rightarrow {}^4T_2$	560 600	~0.25	560 sh	>0.25	560 sh	

[a] All wavelengths given in nm. EV = electric vector.

2. Electronic Spectra. Results of the electronic spectral studies for **1** are shown in Table II. We assign the broad absorptions at ~820 and ~560 nm as the $^6A_1 \rightarrow {}^4T_1$ and $^6A_1 \rightarrow {}^4T_2$ ligand field (LF) transitions, respectively. Not listed is a shoulder at ~490 nm, which was observed in the perpendicular polarization at ~80 K. This shoulder may cor-

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(12) The reciprocal lattice symmetry (6/m) and systematic extinction (000l, $l = 2n + 1$) observed for **1** lead to a second choice of space group, $P6_3$, which is noncentrosymmetric and in which the point symmetry of the cluster would be reduced from 3/m to 3. In $P6_3$, disorder of potassium ions and water molecules is not required, and smaller β values for the sulfate oxygen atoms are possible if the large values in $P6_3/m$ are assumed to arise from symmetry-enforced overlap of sulfate groups related by mirror planes at $z = {}^1/_4$. To test this possibility, refinement was attempted in space group $P6_3$. Temperature factors for the sulfate O atoms were not reduced substantially while coordinate esd's increased to 2–3 times their values in $P6_3/m$, possibly as a result of large correlation coefficients. Thus, there appears to be no strong crystallographic evidence that these crystals are noncentrosymmetric. As a further test of the space group, preliminary circular dichroism spectra were taken with the use of single crystals of **1**. CD bands were observed in the region of 800 and 590 nm, suggesting that the crystals are enantiomorphic; however, these bands may result from loss of water by the crystals, and further work is required to settle this question unambiguously.

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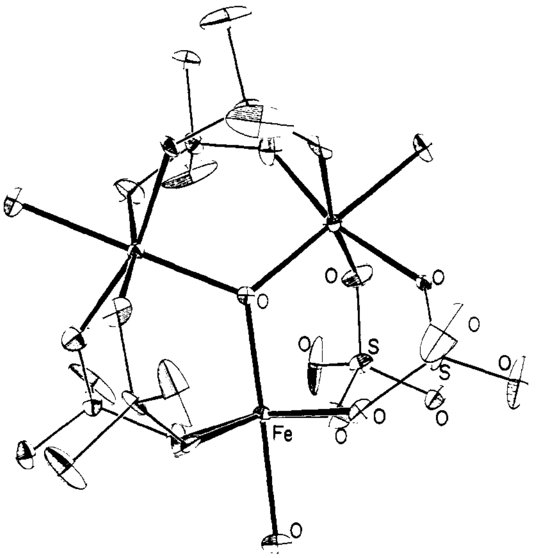

Figure 1. The $[(H_2O)_3(SO_4)_6Fe_3O]^{5-}$ unit in **1** viewed approximately along the *c* axis (perpendicular to the Fe_3O^{7+} plane).

respond to the third LF band ($^6A_1 \rightarrow {}^4A_1, {}^4E$). In the parallel polarization, the second LF band appeared as two overlapping bands at ~560 and ~600 nm. The splitting of the first and particularly the second LF band of Fe(III) and Mn(II) ions situated in noncubic six-coordinate ligand environments has been observed for a number of other systems.[17] The LF absorptions at ~820 and ~560 nm show maximum intensity in the perpendicular polarization (i.e., in the Fe_3O plane). Relative to the spectra of typical magnetically dilute Fe(III) chromophores, the LF bands of **1** are enhanced approximately 100-fold. For example, the first and second LF bands of the $Fe(H_2O)_6^{3+}$ chromophore in $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ have ϵ's of 0.05 and 0.01, respectively.[18] Thus, the energies, polarizations, and intensities of the LF bands are those expected for $S = {}^5/_2$ Fe(III) ions exhibiting substantial spin–spin coupling localized predominantly within the Fe_3O plane.

Discussion

The crystal structure of **1**[10] shows that it consists of isolated $[(H_2O)_3(SO_4)_6Fe_3O]^{5-}$ clusters (Figure 1) surrounded by K^+ ions and lattice H_2O molecules. Each cluster has $3/m$ crystallographic symmetry with the Fe_3O units in mirror planes and each pair of Fe atoms bridged by two SO_4^{2+} groups, one above and one below the Fe_3O plane. The $(H_2OFe)_3O^{7+}$ geometry found in **1** is common to several structures[10,11] and does not vary appreciably when ligation is completed by bridging SO_4^{2-}, acetate,[8] or the carboxylate portion of alanine.[7]

Highly condensed Fe(III) sulfates such as $NH_4Fe(SO_4)_2$ and $Fe_2(SO_4)_3$ exhibit Weiss temperatures of −12 and −80 K, respectively.[19a,b] A recent magnetochemical study of monoclinic $Fe_2(SO_4)_3$ revealed Curie–Weiss behavior over the temperature range 38–298 K with the calculated magnetic moment per Fe(III) falling in the range 5.81–6.02 μ_B.[19b] It is clear that superexchange interactions of Fe(III) ions via bridging SO_4^{2-} groups cannot contribute to the antiferromagnetic behavior of **1** to any large degree and that the antiferromagnetism ($J = -26.0\ (3)\ cm^{-1}$) observed for **1** arises primarily from spin–spin coupling within the Fe_3O^{7+} unit.

Unfortunately, $[(H_2O)_3(ala)_6Fe_3O] \cdot 7ClO_4$ (ala = alanine) is the only carboxylate analogue for which both structural (R = 15%) and magnetic ($J = -31\ cm^{-1}$) data are available;[7] only structural data (R = 11.1%) have been reported for $[(H_2O)_3(OAc)_6Fe_3O] \cdot ClO_4$.[8] It appears, however, that the $[(H_2O)_3(RCO_2^-)_6Fe_3O]^+$ structure (R = CH_3, H, $ClCH_2$, and C_6H_5) is present in several salts that have been characterized by detailed susceptibility studies. Depending on the extent to which the susceptibility data have been fit by a single J value, the Fe(III) ions in these latter complexes have been considered as either equivalent or nearly equivalent. It thus appears that there are a number of basic Fe(III) carboxylates whose magnetic behavior[16,20,21] is essentially that predicted by the triangular cluster model with $J = -30 \pm 3\ cm^{-1}$. A comparison of these observations with the above results for **1** suggests that the bulk of the antiferromagnetism exhibited by these trimers also is attributable to spin–spin coupling within the Fe_3O^{7+} unit. While exchange via the bridging carboxylates cannot be excluded, it must be small relative to exchange via the bridging oxide ion. This simplification allows the magnetic and structural aspects of the Fe_3O^{7+} clusters to be compared with those previously reported for clusters in which the exchange paths are restricted to those resulting from single-oxide or double-hydroxide bridges.

The available magnetic and structural data for $Fe_2(OH)_2^{4+}$, $Fe_2(OPr)_2^{4+}$ (OPr = propoxide) and Fe_3O^{7+} clusters along with representative results for the well-known Fe_2O^{4+} clusters are summarized in Table III. The distance between Fe(III) ions in these clusters has been included for convenience; as pointed out elsewhere,[15] magnetic exchange via the direct overlap of the metal ion d orbitals is expected to be insignificant. We adopt the model in which magnetic exchange originates from the interaction of the d orbitals on different Fe(III) ions via their mutual overlap with the appropriate filled valence orbitals of intervening diamagnetic ligands. Salient features of this model include the number and nature of the dominant antiparallel exchange paths involving σ and/or π bonding. Magnetic coupling is related to the extent of net three-center overlap in the Fe–O–Fe and Fe–OH(R)–Fe linkages and may be represented as a matrix element or "transfer integral" weighted by coulombic repulsion considerations.[25]

For the approximately linear Fe_2O^{4+} clusters, the following symmetry-allowed exchange paths for antiparallel coupling may be constructed (internuclear direction = y axis): $e_g||p_y||e_g'$, $e_g||s||e_g'$, $d_{yz}||p_z||d_{yz}'$, and $d_{xy}||p_x||d_{xy}'$ (notation from ref 25). Magnetic coupling via the σ-bonding framework (e.g., the first two pathways) is expected to predominate. As is seen in Table III, comparable exchange coupling ($J \simeq -100\ cm^{-1}$) is observed despite variations in the following: (a) nature of the nonbridging ligands; (b) four-, five-, six-, and seven-coordination of the Fe(III) ions; (c) Fe–O–Fe bridging angles of 139–180°. A relatively short Fe–O bond distance of ~1.8 Å has been observed in all structurally characterized Fe_2O^{4+} clusters.[4,5,24]

Relative to the Fe_2O^{4+} clusters, the Fe_3O^{7+} clusters exhibit smaller Fe–O–Fe angles (120°), longer Fe–O distances (1.92–1.96 Å), and a 3-fold reduction in magnetic coupling ($J \simeq -30\ cm^{-1}$). Since both the nature of the nonbridging

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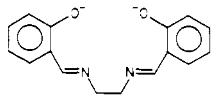
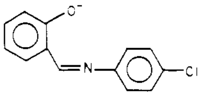
Table III. Magnetic Structural Aspects of Oxygen-Bridged Fe(III) Clusters

complex	Fe–O(R)–Fe angle, deg	Fe–O(R) dist, Å	Fe–Fe sepn, Å	J, cm^{-1}	ref
$[Dipic(H_2O)FeOH]_2$[a]	103.6	1.938, 1.993	3.089	−11.4	22
$[Chel(H_2O)FeOH]_2\cdot4H_2O$[b]	103.2	1.938, 1.989	3.078	−7.3	22
$[(CH_3)_2NC_7H_2NO_4(H_2O)FeOH]_2\cdot2H_2O$	105.3	1.937, 1.986	3.118	−11.7	6
$[Fe_2(OPr)_2]^{4+}$[c]	108.2	1.926, 1.988	3.217	−17.1	23
	110.6	2.001, 1.972			
$K_5[(H_2O)_3(SO_4)_6Fe_3O]\cdot6H_2O$	120.0	1.956, 1.962	3.332	−26.0	10, this work
$[(H_2O)_3(ala)_6Fe_3O]\cdot7ClO_4$	120(?)	1.92	3.32	−31	7
$[Cl\text{-}C_7H_2NO_4(H_2O)_2Fe]_2O\cdot4H_2O$	180	1.773, 1.772	3.545	−115	4
$(SalenFe)_2O$[d,e]	144	1.77	3.39	−95	5
$(SalenFe)_2O\cdot2py$[d,e]	139	1.82	3.36	−90	5
$[(Sal\text{-}N\text{-}p\text{-}ClC_6H_4)_2Fe]_2O$[e,f]	175	1.76	3.53	−90 to −100	5
$enH_2[(HEDTAFe)_2O]\cdot6H_2O$[g]	165	1.79	3.56	−95	5
$[(B)(H_2O)Fe]_2O\cdot4ClO_4$[h,i]	178	1.8	3.6	−100	5
$[pyH]_2[Cl_3Fe]_2O\cdot py$[j]	155.6	1.755	3.431	−92	24

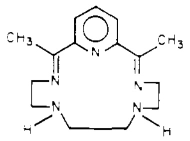
[a] Dipic = 2,6-pyridinedicarboxylate. [b] Chel = 4-hydroxo-2,6-pyridinedicarboxylate. [c] Six-coordination completed by Schiff base. [d] The coordination number of Fe(III) is 5. [e] Salen =



[f] Ligand =



[g] $enH_2 = H_3\overset{+}{N}CH_2CH_2\overset{+}{N}H_3$; $HEDTA = [(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)(CH_2CH_2OH)]^{3-}$. [h] B =



[i] The coordination number of Fe(III) is 7. [j] The coordination number of Fe(III) is 4.

ligands and the variation in the Fe–O–Fe bridging angles do not affect the magnetic properties of the Fe_2O^{4+} clusters to any large extent, we suggest that the reduced antiferromagnetic coupling of the Fe_3O^{7+} clusters is due predominantly to the lengthened Fe–O–Fe exchange path (reduced transfer integral). This effect may be extrapolated to the $Fe_2(OH)_2^{4+}$ and $Fe_2(OR)^{4+}$ (OR = alkoxo) clusters, which exhibit a further lengthening of the exchange path (asymmetric bridges with Fe–O distances ranging from 1.93 to 2.00 Å) and a further reduction in antiferromagnetic interaction ($J \simeq -10$ cm^{-1}). For bridging angles in the 90–180° range, considerations of the symmetry-allowed exchange paths for bridged d^5 ions lead to the prediction of net antiferromagnetic coupling.[25] However, within this context, the relative importance of specific exchange paths and thus the extent of antiferromagnetic coupling possibly may exhibit an angular dependency. The data in Table III indicate simply that the angular dependence of antiferromagnetic coupling between d^5 ions appears to be less important than its variations with the exchange path length. These results are in contrast to those obtained for $Cu_2(OH)_2^{2+}$ dimers in which both the magnitude and mode of spin–spin coupling (parallel or antiparallel) exhibit a large dependency on the Cu–OH–Cu angles.[26] Unlike the d^5 dimers, those of d^9 ions are expected to exhibit a crossover from antiferromagnetic to ferromagnetic coupling as the bridging angles decrease to 90°.[25]

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