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A Study of the Variable-Temperature Magnetic Susceptibility of Two Ti(III) Oxalate Complexes

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Variable-temperature magnetic susceptibility data have been obtained for polycrystalline samples of two Ti(III) oxalate complexes, $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$ and $Ti_2(C_2O_4)_3(H_2O)_5$. The bridging oxalate dianion in the former complex (a seven-coordinate dimer with D_{5h} symmetry) provides an effective path for magnetic exchange between the two Ti(III) ions as evidenced by a rather large intramolecular exchange parameter $J = -60$ cm^{-1}. The partially dehydrated complex, by contrast, exhibits weak intradimer magnetic exchange interactions. Indeed, the variable-temperature magnetic susceptibility data for $Ti_2(C_2O_4)_3(H_2O)_5$ were fit to a distorted-octahedral, single-ion, spin–orbit coupling magnetic model with Δ (ground term splitting) = 300 cm^{-1} and k (orbital reduction factor) = 0.7 with $\lambda' = 155$ cm^{-1}. Room-temperature optical spectra of $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$ and $Ti_2(C_2O_4)_3(H_2O)_5$ were recorded and the resulting band assignments are consistent with D_{5h} and distorted octahedral ligand-field symmetries, respectively.

Introduction

Study of the magnetic properties of ligand-bridged Ti(III) complexes could potentially provide a wealth of information about the mechanism of super-exchange in paramagnetic oligomers. Unfortunately the coordination chemistry of this d^1 ion is not fully developed, principally because of the marked ease of aerial oxidation of many Ti(III) complexes. However, the Ti(III) ion is stabilized by a number of ligands, including halides, and this stabilization is reflected in the types of Ti(III) complexes which have been studied by variable-temperature magnetic susceptibility. For example, several ionic hexahalide complexes of Ti(III) exhibit Curie–Weiss behavior above ~100 K with Weiss constants which range from –50 to –100 K. Some specific examples are $K_3[TiF_6]$ ($\mu_{eff}^{RT} = 1.70\ \mu_B$, $\theta = -50$ K) [1], $(pyH)_3[TiCl_6]$ ($\mu_{eff}^{RT} = 1.58\ \mu_B$, $\theta = -80$ K) [2], and $(pyH)_3[TiBr_6]$ ($\mu_{eff}^{RT} = 1.83\ \mu_B$, $\theta = -94$ K) [3]. Unfortunately, there seems to be little agreement on details of the magnetic susceptibility of these compounds as evidenced by the range of room temperature values of μ_{eff} for $(pyH)_3[TiCl_6]$ [2–5]. Several other Ti(III) complexes with donors other than halides have also been studied by magnetic susceptibility measurements. These include $[Ti(H_2O)_6]Cl_3$ ($\mu_{eff}^{RT} = 1.79\ \mu_B$, $\theta = -22$ K) [6], $[Ti(urea)_6]Cl_3$ ($\mu_{eff}^{RT} = 1.79\ \mu_B$, $\theta = -38$ K) [3], $Ti(acac)_3$ ($\mu_{eff}^{RT} = 1.73\ \mu_B$, $\theta = -34$ K) [6], and $CsTi(SO_4)_2 \cdot 12H_2O$ ($\mu_{eff}^{RT} = 1.80\ \mu_B$, $\theta = -10$ K) [7].

A smaller number of dimeric Ti(III) complexes has been characterized by magnetic susceptibility. Among these are the antiferromagnetic organometallic compounds $(Cp_2TiCl)_2$ [8], $(Cp_2Ti)_2SO_4$ [9], and $(Cp_2Ti)_2CO_3$ [9] and salts of the $(Ti_2Cl_9)^{3-}$ complex anion [10, 11]. The room temperature magnetic moment of $Cs_3[Ti_2Cl_9]$, for example, is reported to be 1.2–1.4 μ_B/Ti [12].

As part of our research effort in the area of the coordination chemistry of oxalate, squarate, and dihydroxybenzoquinone complexes [13–15] we have recently determined the variable-temperature magnetic susceptibility of $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$ and $Ti_2(C_2O_4)_3(H_2O)_5$. Results of these determinations are reported in this paper.

Experimental

μ-Oxalatobis(oxalato)hexaquodittanium(III) tetrahydrate, $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$, was prepared from oxalic acid (Aldrich) and a 20% aqueous solution of $TiCl_3$ (Baker) according to the procedure of Eve and Fowles [16] which is based on the preparation of Stähler [17]. The X-ray powder pattern of this brown complex was consistent with the pattern expected for the published crystal data for $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$ [18]. This material was dehydrated at room temperature under a dynamic vacuum to yield an orange product with formula $Ti_2(C_2O_4)_3(H_2O)_5$. This partial dehydration

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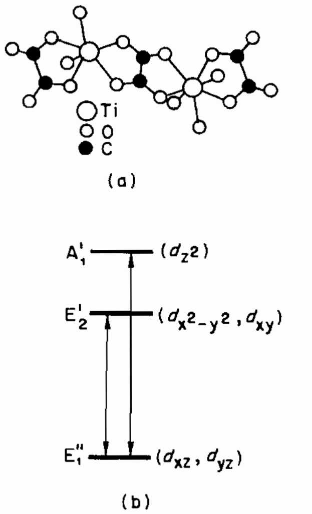

Fig. 1. (a) Dimeric structure of $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$ [18]. Lattice waters are omitted. (b) Term level diagram for weak-field, ligand-field terms in D_{5h} symmetry.

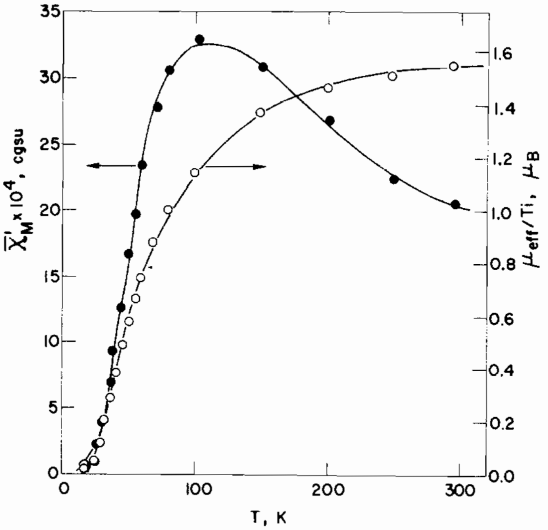

Fig. 2. Molar magnetic susceptibility (○) and effective magnetic moment per Ti (●) *vs.* T for $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$. The solid line is a fit to the HDVV $S_1 = S_2 = ½$ dimer model with g = 1.95 and J = -60 cm^{-1}.

required approximately 48 hours. C and H analyses were performed by Integral Microanalytical Laboratories, Raleigh, N.C. with the following results. Calcd for $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$: C, 13.35; H, 3.73. Found: C, 13.40; H, 3.69. Calcd for $Ti_2(C_2O_4)_3(H_2O)_5$: C, 16.02; H, 2.24. Found: C, 16.13; H, 2.37.

Magnetic susceptibility data were obtained with a conventional Faraday balance which has been described [13–15]. This balance was calibrated with $Hg[Co(NCS)_4]$ [19]. Experimental magnetic susceptibilities were fit to theoretical expressions by using the Simplex minimization algorithm [20]. Ligand diamagnetism was calculated from a table of Pascal's constants [21]. The underlying diamagnetism of Ti^{3+} was taken as -9×10^{-6} cgsu [22]. Optical spectra were recorded on a Cary 14 spectrophotometer. X-ray powder diffraction data were obtained with the Straumanis technique [CuKα, $\lambda_{mean} = 1.5423$ Å].

Results and Discussion

The Ti(III) oxalate complexes prepared as above are slowly oxidized in air to give a white, diamagnetic product of undetermined composition. The partially-dehydrated product, $Ti_2(C_2O_4)_3(H_2O)_5$, is somewhat less stable than $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$, but both materials are sufficiently stable to permit their transfer in air. The mull optical spectrum of $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$, taken at room temperature consists of a strong absorption in the visible at 23800 cm^{-1} and two weak, near infrared bands at 12200 and 9600 cm^{-1}. These transitions may be assigned upon examination of the structure of $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$ [18] which is shown in Fig. 1a. The effective microsymmetry about the seven-coordinate Ti(III) ion is D_{5h}. The corresponding weak-field terms for a ligand field of D_{5h} symmetry are illustrated in Fig. 1b. On the basis of this structure the absorptions at 9600 and 12200 cm^{-1} may be assigned to the ligand-field transitions $E_1'' \rightarrow E_2'$ and $E_1'' \rightarrow A_1'$, respectively. These assignments are identical with those previously made [18] for the diffuse reflectance spectrum of this complex. Because of the high intensity of the 23800 cm^{-1} band, it seems likely that this absorption corresponds to an intramolecular charge transfer transition.

The mull optical spectrum of $Ti_2(C_2O_4)_3(H_2O)_5$ consists of an asymmetric absorption in the near infrared, centered at approximately 10500 cm^{-1}, and a relatively intense band in the visible at 23000 cm^{-1}. The former band is most likely a ligand-field transition whereas the latter is probably of the charge transfer type. Lack of a single-crystal structure of this material precludes a detailed assignment of this spectrum.

The temperature dependence of the magnetic susceptibility and effective magnetic moment per Ti of $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$ are illustrated in Fig. 2 [23]. The value of μ_{eff}/Ti at 295 K is 1.54 μ_B, in good agreement with the value of 1.59 μ_B reported by Eve and Fowles [16]. The temperature dependence of the susceptibility of this compound is typical of an antiferromagnetically-coupled dimer in that the susceptibility shows a broad maximum in the vicinity of 100 K and decreases to a very small value at 15 K. This susceptibility behavior may be modeled by using eq. 1 which is the HDVV parti-

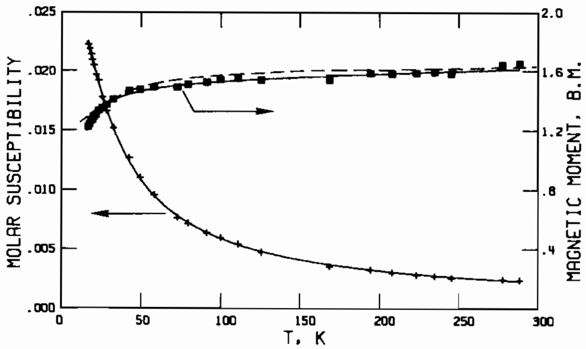

Fig. 3. Molar magnetic susceptibility (+) and effective magnetic moment per Ti (■) *vs.* T for $Ti_2(C_2O_4)_3(H_2O)_5$. The solid line is a fit to the HDVV $S_1 = S_2 = ½$ dimer model with $g = 1.78$, $J = -7.2$ cm^{-1}, and $N\alpha = 238 \times 10^{-6}$ cgsu. The dashed line represents a fit to the low-symmetry model of ref. 25, $\Delta = 300$ cm^{-1} and $K = 0.7$.

tion function for an $S_1 = S_2 = ½$ dimer. In eq. 1 the symbols have their usual meanings

$$\chi_M = (N\beta^2 g^2/3kT)[6x(1 + 3x)^{-1}] \qquad (1)$$

and $x = \exp(2J/kT)$. In fitting eq. 1 to the data of Fig. 2, the values $J = -60$ cm^{-1} and $g = 1.95$ are obtained. These values were used in calculating the theoretical χ_M *vs.* T curve shown as the solid line in Fig. 2. The substantial value of J found for $Ti_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$ indicates that the bridging oxalate ligand provides an effective pathway for magnetic exchange in this compound. This value of the exchange parameter is significantly larger than that observed for Cu(II) and Ni(II) dimers which contain bridging oxalate dianions [24].

The temperature dependence of the magnetic susceptibility and effective magnetic moment of $Ti_2(C_2O_4)_3(H_2O)_5$ is as illustrated in Fig. 3 [23]. The value of μ_{eff}/Ti drops from 1.65 μ_B at 290 K to 1.22 μ_B at 17 K. Application of the $S_1 = S_2 = ½$ dimer expression (eq. 2) results in an acceptable fit to the data only if a large temperature-independent paramagnetic correction, $N\alpha$, is applied. This fit is shown as the solid curve in Fig. 3 with $J = 7.2$ cm^{-1}, $g = 1.78$, and $N\alpha = 238 \times 10^{-6}$ cgsu. This 'forced-fit' is clearly unrealistic in view of the untypical values of g and $N\alpha$. We therefore sought to apply the appropriate low-symmetry magnetic model of Figgis [25] to these data. The result of fitting this model to the data for $Ti_2(C_2O_4)_3(H_2O)_5$ is illustrated as the dashed line in Fig. 3 and yields Δ (ground term splitting) = 300 cm^{-1} and k (orbital reduction factor) = 0.7. (These values were calculated by assuming that the term spin–orbit coupling constant λ' was equal to the free ion value of 155 cm^{-1} [26]. See reference 25 for a more detailed discussion of these parameters.) These low-symmetry ligand-field parameters which were obtained for $Ti_2(C_2O_4)_3(H_2O)_5$ are similar to those found for similar distorted octahedral Ti(III) complexes. For example, magnetic susceptibility data for $[Ti(urea)_6]I_3$ were fit [26] to this model [25] with $\Delta = 480$ cm^{-1}, $k = 0.65$, and $\lambda = 160$ cm^{-1}.

Conclusions

Magnetic susceptibility and optical spectroscopic data for $Ti_2(C_2O_4)_3(H_2O) \cdot 4H_2O$ are consistent with the observed seven-coordinate (D_{5h}) structure of this complex. The bridging oxalate dianion provides an effective pathway for magnetic superexchange in this complex as evidenced by the value of J (= -60 cm^{-1}). In contrast, the partially-dehydrated material, $Ti_2(C_2O_4)_3(H_2O)_5$, appears to be structurally characterized as a distorted octahedral complex, *i.e.* J is small. The large difference in the magnitude of J for these two complexes is a surprising result, given the presence of bridging oxalate in both materials. This difference is undoubtedly due to a major structural difference between the two compounds. It is conceivable that $Ti_2(C_2O_4)_3(H_2O)_5$, is a polymeric material with a solid-state structure similar to that of $Sc_2(C_2O_4)_3 \cdot 6H_2O$ [27]. Although our data are consistent with this possibility, a single-crystal diffraction study will be required for final structure determination.

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