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Magnetic Properties of Tetra-n-butylammonium Bis(maleonitriledithiolato)iron(III)

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The magnetic susceptibility of tetra-n-butylammonium bis(maleonitriledithiolato)iron(III) has been measured in the temperature range 77 - 371° K. The compound was found to be antiferromagnetic, and the data are interpreted in terms of coupling of pairs of ferric ions of spin 5/2 or 3/2 to form a singlet (S = 0) ground state and a manifold thermally acessible excited states.

Introduction

Recently there has been a considerable amount of interest in the preparation and properties of transition metal complexes of cis-dithiolates. Gray[1] and Schauzer[2,3] have written review articles which describe the general character of these substances. A summary of the available structural data has been reported by Sartain and Truter[4] and by Forrester, Zalkin, and Templeton.[5] The crystal and molecular structures of tetra-n-butylammonium bis(maleonitriledithiolato)-iron(III) $(n\text{-}C_4H_9)_4NFe(MNT)_2$ have been determined.[6] The anions are binuclear as illustrated in Figure 1. The coordination about each iron is approximately that of a square pyramid. Our interest in the $Fe(MNT)_2^-$ ion is attributed largely to the various reports regarding its magnetic states. The triphenylmethylarsonium salt of $Fe(MNT)_2^-$ was reported[7] to have a spin of 3/2 for the Fe^{3+}, for measurements taken on an acetone solution of the complex. Weiher and associates[8] made a χ versus T study of the tetraethylammonium salt of the complex and although only the room temperature magnetic moment of 1.62 B.M. was reported, the authors indicated that their results deviated significantly from that expected for a spin of 1/2 per Fe^{3+}. However, Hamilon, and Bernal[6] stated that their magnetic susceptibility data for the tetra-n-butylammonium salt could be reasonably fitted to a system of two S = 1/2 components.

Because of the disagreement between these measurements, we have determined the magnetic susceptibility of $(n\text{-}C_4H_9)_4NFe(MNT)_2$ over the temperature range 77 - 371° K with the objectives of providing accurate quantitative parameters describing the extent of spin-spin coupling and of determining the mechanism of coupling.

Results and Discussion

The experimental magnetic susceptibility data for $(n\text{-}C_4H_9)_4NFe(MNT)_2$ are given in Table I, and magneitc susceptibility versus temperature plots are shown in Figures 2 and 3. The data were analyzed with the usual spin-spin coupling model based upon the $-2JS_1S_2$ Hamiltonian for $S_1 = S_2 = 1/2, 3/2$, and 5/2. The resulting equations used in the calculations have been sumarized by Earnshaw and Lewis.[9]

Table I. Temperature dependence of the magnetic susceptibilities of $(n\text{-}C_4H_9)_4NFe(MNT)_2$.

T(°K)	$10^6\chi_M^{corr}$	μ_{eff} (BM)*
371	1229	1.92
351	1213	1.85
320	1194	1.76
294	1145	1.65
270	1124	1.56
247	1085	1.47
221	1016	1.35
199	986	1.26
177	941	1.16
162	861	1.06
148	812	0.98
135	765	0.91
128	637	0.81
113	554	0.71
97	415	0.57
77	248	0.39

* Calc. from $\mu = 2.84(\chi_M^{corr}T)^{1/2}$.

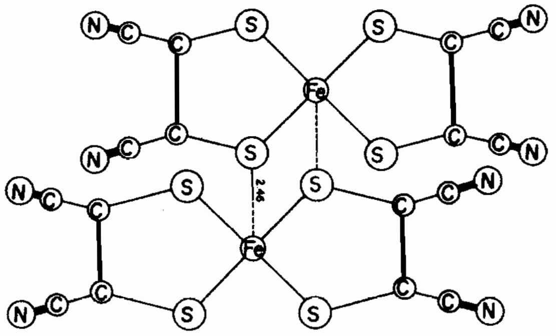

Figure 1. The structure of $[Fe(MNT)_2]_2^{2-}$.

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(2) G.N. Schauzer, *Accounts of Chem. Research*, 2, 72 (1969).
(3) G.N. Schrauzer, *Progr. Transition Metal Chem.*, 4, 299 (1968).
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(7) H.B. Gray and E. Billig, *J. Am. Chem. Soc.*, *85*, 2019 (1963).
(8) J.F. Weiher, L.R. Melby, and R.E. Benson, *J. Am. Chem. Soc.*, *86*, 4329 (1964).
(9) A. Earnshaw and J. Lewis, *Nature, 181,* 1262 (1962).

The antiferromagnetic behaviour may be attributed to the spin-spin exchange between two Fe^{3+} ions with $S_1 = S_2 = 3/2$ or $5/2$. The experimental results are best fit with $g = 2.00$, $-J = 119\ cm^{-1}$, $N\alpha = 5 \times 10^{-6}$ cgs units, and $S_1 = S_2 = 5/2$ or equally best fit with $g = 2.00$, $-J = 119\ cm^{-1}$, $N\alpha = 6 \times 10^{-6}$ cgs units, and $S_1 = S_2 = 3/2$. As noted by the poor fit shown in Figure 3, the experimental results are not consistent with a spin-spin interaction between iron-(III) ions with a spin of 1/2 each as reported by Hamiltonian and Bernal.[6]

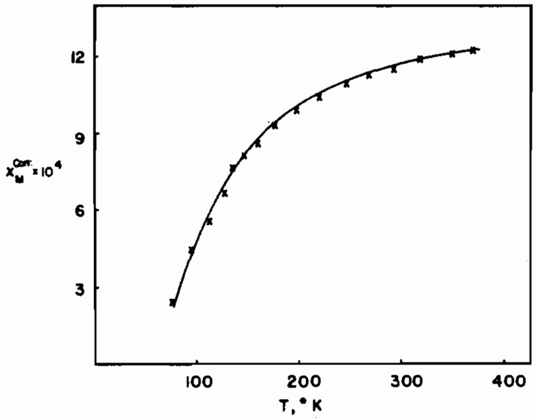

Figure 2. Plot of magnetic susceptibility vs. temperature (x, experimental points; ———, calculated) for $(n\text{-}C_4H_9)_4NFe(MNT)_2$. The same calculated curve is obtained for $g = 2.00$, $-J = 119\ cm^{-1}$, $N\alpha = 5 \times 10^{-6}$ cgs units, and $S_1 = S_2 = 5/2$ or for $g = 2.00$, $-J = 119\ cm^{-1}$, $N\alpha = 6 \times 10^{-6}$ cgs units, and $S_1 = S_2 = 3/2$.

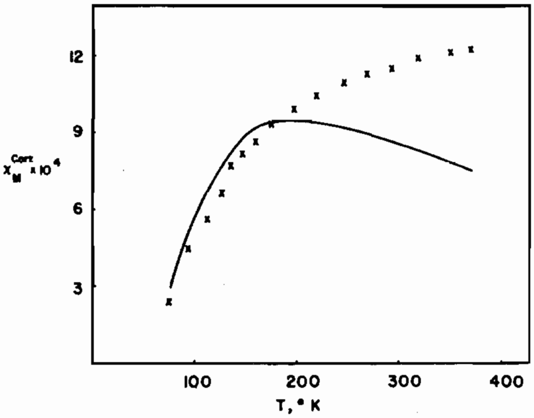

Figure 3. Plot of magnetic susceptibility vs. temperature (x, experimental points; ———, calculated with $g = 2.00$, $N\alpha = 0$, $-J = 111\ cm^{-1}$, and $S_1 = S_2 = 1/2$) for $(n\text{-}C_4H_9)_4NFe(MNT)_2$.

An intermediate spin quantum number of 3/2 would be rare for the terivalent, five-coordinate iron. Normally, this oxidation state of iron would have a low spin of 1/2 or a high spin of 5/2. However, from our magnetic data and use of the appropriate equations,[9] it is not possible to differentiate between $S_1 = S_2 = 3/2$ and $S_1 = S_2 = 5/2$, because the $S_1 + S_2 = 4,5$ levels of the spin manifold for the latter are not significantly thermally populated at the temperatures investigated. The best-fit data for $S_1 = S_2 = 5/2$ yield an average deviation, $\sigma = [(\chi_{expl} - \chi_{calc})^2/n]^{1/2}$, of 22×10^{-6} cgs units while an average deviation of 24×10^{-6} cgs units is obtained for the 3/2 case. Obviously, the difference in average deviation is too small to allow ruling out the 3/2 case.

The best-fit data for $S_1 = S_2 = 1/2$ may be obtained for $g = 2.41$, $N\alpha = 271 \times 10^{-6}$ cgs units, and $-J = 169\ cm^{-1}$ with an average deviation of 50×10^{-6} cgs units. The fit is not nearly as good as for the 3/2 and 5/2 cases, and the g and $N\alpha$ values are much too high to be realistic for the five-coordinated iron(III). When reasonable values of g and $N\alpha$ ($g = 2.00$ and $N\alpha = 0$) are held constant, the best fit is obtained for $-J = 111\ cm^{-1}$ with an average deviation of 217×10^{-6} cgs units. For comparison this calculated curve and experimental data are shown in Figure 3.

The structure of the anion consists of a very tightly bound dimer. The tendency to dimerize is presumably caused by the vacancies in the highest metal orbitals which enhance axial interactions with donor molecules. The comparatively short out-of-plane Fe-S bond (2.46 A) is perhaps nearly as strong as the Fe-S in-plane bonds (2.23 A, average). This strong out-of-plane interaction in dimetallic dithiolene complexes has been demonstrated by Balch, Dance, and Holm[10] who showed by mass spectral studies that the dimeric structure of these complexes persisted even in the gas phase. For oxygen-bridged iron(III) dimers there appears to be a correlation between the extent of spin-spin coupling and the cordination of the bridging oxygen. $J = -100\ cm^{-1}$ for the complex witeh a linear two-coordinate oxygen,[11] $-17\ cm^{-1}$ for the complex with planar three-coordinate oxygens,[12] and $-7\ cm^{-1}$ for the complex with pyramidal three-coordinate oxygens.[13] It has been pointed out[12] that the degree of spin-spin coupling in these oxygen-bridged complexes appears to be dependent upon the availability of π orbitals on the bridging oxygen. A π-bonding mechanism for spin-spin coupling seems likely for the sulfur-bridged system of $[Fe(MNT)_2]_2^{2-}$, probably via the sulfur bridges. Due to the lack of magnetic data on a structural variety of sulfur-bridged iron(III) dimers, it is difficult to make comparisons with the oxygen-bridged systems. However, if the concept of spin-spin coupling being dependent upon the availability of π orbitals is valid for both oxygen- and sulfur-bridged systems, then the comparison of the spin-spin coupling constant for the pyramidal three-coordinate sulfur system of $[Fe(MNT)_2]_2^{2-}$ to that of the pyramidal three-coordinate oxygen system[13] clearly suggests that sulfur may be a better atom for promoting spin coupling in this type of structure.

Experimental Section

Preparations. Disodium 1,2-dicyanoethylene-1,2-dithiolate was prepared according to the published

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method.[14] This yellow hygroscopic salt was dried and stored over calcium chloride in a vacuum desiccator until prior to use.

Tetra-n-butylammonium bis(maleonitriledithiolato)-iron(III) was synthesized by a procedure similar to that described by Weiher and associates.[8] To a solution of 1.86 g of disodium 1,2-dicyanoethylene-1,2-dithiolate (0.01 mole) in 35 ml of boiling 95% ethanol was added a warm solution of 1.35 g of ferric chloride hexahydrate (0.005 mole) in 20 ml of 95% ethanol. The solution was heated to boiling and filtered, and to the filtrate a boiling solution of 1.61 g of tetra-n-butylammonium bromide (0.005 mole) in 15 ml of 95% ethanol was added. The solution was allowed to stand at room temperature for 48 hours, and the black crystals which separated were collected on a filter and washed with small portions of ice-cold absolute ethanol. Three preparations were made using this procedure, and elemental analyses were performed for each preparation by Galbraith Laboratories, Knoxville, Tenn. The analyses were found to be in good agreement with the required formulation. One preparation gave the following results.

Anal. Found: C, 49.61; H, 6.45; N, 12.14; S, 22.24. Calcd. C, 49.80; H, 6.28; N, 12.10; S, 22.16%.

Physical Measurements. Magnetic susceptibilities were determined as a function of temperature by the Faraday method and were found to be invariant for the three preparations examined. The equipment is very similar to that described in the literature by Hatfield.[15] Mercury tetrathiocyanatocobaltate(II) was used as the magnetic susceptibility standard[16] and diamagnetic corrections were estimated from Pascal's constants.[17]

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