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Low-Temperature Mössbauer Spectroscopy Study of Some Partially Solvated Tris(dialkyldithiocarbamato)iron(III) Complexes: The Possibility of Stabilization of a Spin-Quartet Ground State

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The low-temperature, zero-field Mössbauer spectra of tris(morpholinecarbodithioato)iron(III), partially solvated with CHCl_3 , CH_2Cl_2 , or C_6H_6 , and the pyrrolidyl analogue solvated with benzene are presented. Contrary to previous susceptibility studies in which limiting low-temperature magnetic moments of $\sim 4 \mu_B$ were used to suggest a sextet to ground quartet transition with decreasing temperature, the present Mössbauer spectra clearly indicate the presence of only spin-sextet and -doublet states; $S = 3/2$ is never the ground state. Slow paramagnetic relaxation spectra of the sextet fractions correspond to the expected limiting internal fields of ~ 450 kG while the spin-doublet fractions exhibit no hyperfine splitting, again as expected. Previous susceptibility results are reinterpreted in terms of a combination of zero-field splitting of a "permanent" fraction of $S = 3/2$ state, population of the $S = 1/2$ state, and weak antiferromagnetic interactions of the discrete FeS_6 cores involving metal-electron spin density delocalized to the thio ligands.

Introduction

Ferric dithiocarbamates generally exhibit a spin-state crossover between 2T_2 low-spin and 6A_1 high-spin states.²⁻¹¹ This behavior is very sensitive to changes in temperature, slight chemical modifications, external pressure, and solvent molecules included in the lattice.^{3,8-11} With solvents such as benzene and nitrobenzene, the spin equilibrium is shifted toward a *low-spin* ground state while with a group of solvents capable of hydrogen bonding such as water, chloroform, and dichloromethane, the system is shifted toward *high spin*. An interesting feature of the latter series is that as temperature decreases, the moment decreases below the value expected for high spin but does not reach values typical of low spin, $\sim 2-2.5 \mu_B$. The possibility of an intermediate state, $S = 3/2$, either as a ground state or as a low-lying excited state was speculated.⁹ The fact that in each of the complexes there is a distortion of the coordination sphere by solvent hydrogen bonding made this a possibility. In order to check on the existence of a low-lying $S = 3/2$ state, we undertook an investigation of the Mössbauer spectra, and the results are now reported. We have chosen to study solvates of tris(morpholinecarbodithioato)- and tris(pyrrolidinecarbodithioato)iron(III), for which in the unsolvated forms the latter is a *spin sextet* at all temperatures while the former is essentially completely converted to the spin doublet (nominally 2T) at low temperatures. The morpholine complex is abbreviated as FeM; the pyrrolidyl as FeP.

Experimental Section

The Mössbauer spectra were determined in a time mode by using a conventional constant-acceleration spectrometer as previously¹² described with a source consisting of 100-mCi ${}^{57}\text{Co}$ on rhodium vs. a 6 μm thick natural-iron foil calibrant. The various solvates were prepared as described previously.

Results

Pertinent Mössbauer spectra are shown in Figures 1-3 along with least-squares Lorentzian fits for the various fractions present. In the case of the FeM- CHCl_3 solvate (Figure 1), it is evident that only the spin-sextet ground state is present: a relatively stable solvate is formed, and $S = 5/2$ is favored by solvation with CHCl_3 in agreement with previous susceptibility results. The internal hyperfine field (H_n) has a value of 441 kG at 4.2 K, a value typical for the Fermi contact contribution (H_F) to H_n for *five unpaired electrons* (110 kG/unpaired electron) reduced somewhat by covalency effects.¹³ Such limiting spectra result for the present compounds from slow paramagnetic relaxation in the $S = 5/2$ spin manifold. This, in turn, is the result of negative zero-field splitting ($D \approx -1 \text{ cm}^{-1}$) such that the slowly relaxing $M_s = \pm 5/2$ Kramers doublet is lowest in energy.

In the case of the FeP- C_6H_6 solvate the limiting low-temperature spectrum, Figure 2d, clearly exhibits two fractions, a hyperfine-split 6A fraction ($H_n = 453$ kG) and a rapidly relaxing, nominally 2T fraction. These two fractions are not readily distinguished in the temperature range ($> \sim 6$ K) in which both rapidly relax: the Mössbauer spectroscopy parameters (δ , ΔE) are apparently no significantly different for the rapidly relaxing paramagnetic forms. This is, perhaps, expected for the highly covalent $\text{Fe}^{\text{III}}\text{S}_6$ chromophore involved. The ratio of the areas of the $S = 5/2$ to $S = 1/2$ form is 0.55, indicating a sizable reaction of sextet state at low temperature for this particular solvate sample. This ratio can only be taken as quite rough since the recoil-free fractions of these two forms are probably different. In any event, there is no evidence of an $S = 3/2$ ground-state quartet fraction. The expected value of H_n for a slowly relaxing spin quartet is ~ 330 kG, i.e., 110 kG/unpaired electron. This assumes no reduction by covalency-delocalization effects or dipolar (H_d) and/or orbital (H_l) contributions to H_n , which normally oppose H_F . While mechanisms exist for the *reduction* of H_n for a given spin value, we know of none for *enhancement* to the observed value of 453 kG. The latter is typical of $S = 5/2$ in a covalent environment. The central doublet is assigned to a $S = 1/2$ state rather than the $M_s = \pm 3/2$ component of the $S = 5/2$ state, because these are negligibly populated below 2 K.

Our results for FeM- CH_2Cl_2 are similar to those shown in Figure 2a-c, i.e., a hyperfine-split $S = 5/2$ fraction ($H_n = 440$ kG) and rapidly relaxing unsplit $S = 1/2$ fraction. It is not surprising that the spin-doublet fractions are rapidly relaxing. A typical sign doublet as found in $\text{K}_3\text{Fe}(\text{CN})_6$ does not exhibit

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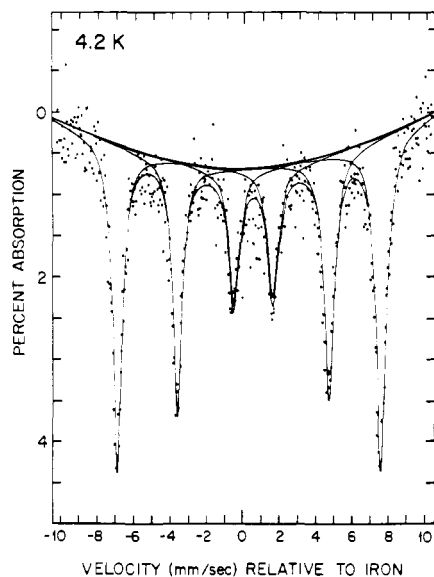


Figure 1. Mössbauer spectrum of tris(morpholinecarbodithiato)iron(III)-chloroform at 4.2 K.

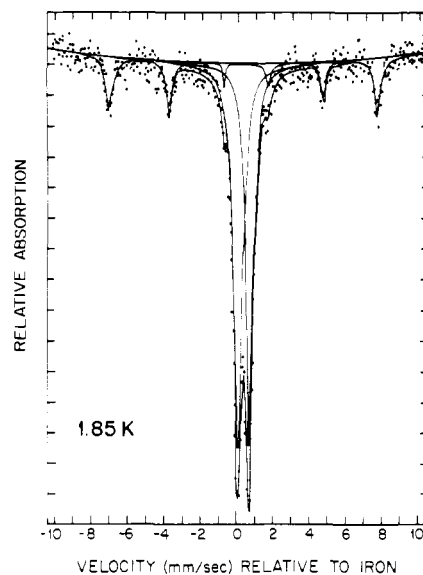


Figure 3. Mössbauer spectrum of tris(pyrrolidinecarbodithiato)iron(III)-benzene at 1.85 K.

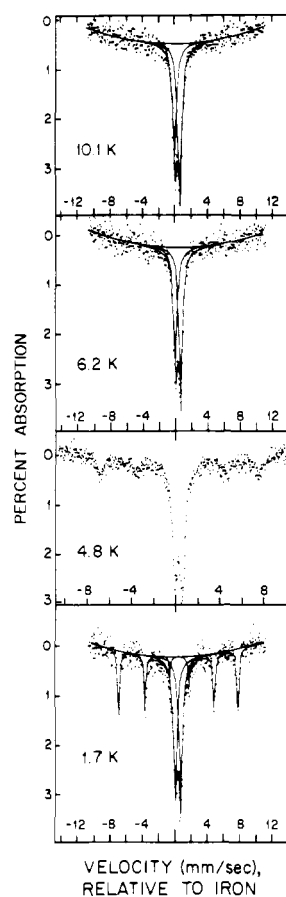


Figure 2. Mössbauer spectra of tris(morpholinecarbodithiato)iron(III)-benzene at (a) 10.1 K, (b) 6.2 K, (c) 4.8 K, and (d) 1.7 K.

relaxation broadening and magnetic hyperfine splitting until $T \lesssim 0.129$ K owing to rapid spin-lattice relaxation in the 2T ground state.¹⁴ It should also be noted that confirmed *spin-quartet* bis(dithiocarbamate) systems (FeL_2X , $X = Cl$,

Br, I) that have been characterized in detail typically exist in 4A ground states for which quadrupole splittings are large, typically >2.00 mm/s, and exhibit resolved magnetic hyperfine splitting ($H_n \lesssim 330$ kG) owing to slow paramagnetic relaxation in a ground $M_s = \pm 3/2$ Kramers doublet.¹⁵⁻¹⁷ We believe that these observations tend to further militate against the assumption of population of an $S = 3/2$ state for any of the present solvates. In view of our results for $FeM \cdot CH_2Cl_2$, the Rininger et al.¹⁸ interpretation of its Mössbauer spectrum at 77 K appears to be incorrect. They present the *composite* computer spectra of two and four Lorentzian peak computer fits, i.e., the alternatives of a *single* or *two* quadrupole doublets, where they favor the latter. They present neither the four separate Lorentzians corresponding to their presumed $S = 3/2$ and $S = 5/2$ quadrupole doublets nor their parameters. The signal to noise and computer fits (Figure 2a, b, ref 18) are not sufficient to unequivocally distinguish the possibility of (a) dynamic rapid interconversion (relative to the lifetime of the excited $I = 3/2$ spin state of ^{57}Fe) between $S = 5/2$ and a lower multiplicity, $S = 3/2$ or $S = 1/2$, or (b) static population of two spin multiplicities. Our results appear to indicate no population of $S = 3/2$ and that (a) is operative (for $S = 5/2$, $1/2$) even at very low temperatures until the $S = 5/2$ fraction undergoes slow paramagnetic relaxation.

Finally, we briefly mention our results for the $FeP \cdot 1/2 C_6H_6$ solvate system. Complete details along with the X-ray structure of this system at ~ 100 K will be presented elsewhere. Suffice it to say, now, that the $FeP \cdot 1/2 C_6H_6$ exhibits limiting Mössbauer spectral behavior generally similar to that shown in Figure 2, i.e., spectra in the paramagnetic temperature region that are *readily fit* for a *single* quadrupole doublet and exhibit slow relaxation to eight lines, $S = 5/2$ (6) and $S = 1/2$ (2). A previous¹⁷ Mössbauer spectroscopy investigation of the unsolvated form of the foregoing pyrrolidine system indicates slow relaxation—magnetic hyperfine splitting and the presence of $S = 5/2$ *only*. The zero-field splitting leading to the hyperfine splitting of the unsolvated form is clearly evident in the moment vs. temperature behavior of this system, which

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was also interpreted in terms of $S = 5/2$ only, with weak antiferromagnetic exchange.¹⁹ This apparently takes place mainly via ligand-delocalized electron spin density.¹⁹ A similar process could account for the anomalously low magnetic moments in the present, solvated, complexes. The results of this work (Figure 3) represent the first unambiguous spectroscopic evidence for the idea that solvation by nonpolar, non-hydrogen-bonding species favor the spin-doublet ground state in tris(dialkyldithiocarbamato)iron(III) systems. In the present case, this occurs for one that is clearly a spin sextet

at all T for its unsolvated form. However, it still appears to be the case that the sextet and doublet are not distinguished via Mössbauer spectroscopy in the rapidly relaxing paramagnetic-temperature region. Whether or not this is due to (1) an extraordinary accidental similarity of the parameters (δ , ΔE) for the 6A and 2T states or (2) more likely dynamic rapid interconversion between them is also not clear from the present study.

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Antiferromagnetically and Ferromagnetically Coupled Nickel(II) Dimers with and without Interdimer Coupling. Solvent Effects in the Preparation of Nickel(II) Dimers¹

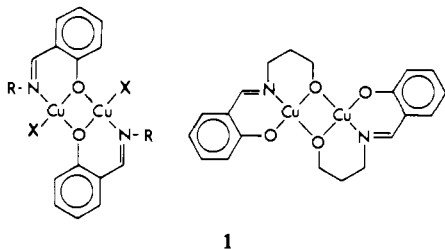
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The structural and magnetic properties are reported for a group of chemically similar nickel(II) dimers with salicylaldehyde ligands. Three general categories of compounds may be prepared for a variety of bidentate Schiff base (sb) nickel(II) complexes that have the same general formula $[\text{Ni}(\text{sb})(\text{NO}_3)_2\text{L}]_2$ and differ only in structural details and the type of Lewis acid solvent molecule (L) that is present during crystallization. Antiferromagnetic interactions are observed when the central Ni_2O_2 bridging group is approximately coplanar with the principal sb ligand plane. Ferromagnetic interactions are observed when these planes are approximately orthogonal. When $\text{L} = \text{C}_2\text{H}_5\text{OH}$, hydrogen bonding between L and the NO_3 groups of neighboring molecules forms an antiferromagnetic pathway along infinite chains of ferromagnetic dimers. The three categories are represented by the following complexes. $[\text{Ni}(\text{ps})(\text{NO}_3)_2(2\text{-pic})]_2 \cdot \text{CH}_2\text{Cl}_2$ (ps = phenylsalicylaldehyde): crystal data space group $P\bar{1}$, $Z = 1$, $a = 9.424$ (2) Å, $b = 11.327$ (3) Å, $c = 11.468$ (3) Å, $\alpha = 117.96$ (2)°, $\beta = 90.29$ (3)°, $\gamma = 91.62$ (2)°, $V = 1081$ Å³, $R = 4.5\%$ for 2342 reflections; magnetic data $g = 2.12$, $J = 8.7$ cm⁻¹, $D \approx 13$ cm⁻¹ ($zJ' = 0.07$). $[\text{Ni}_2(\text{ips})_2(\text{NO}_3)_2(\text{EtOH})_2]_n$ (ips = isopropylsalicylaldehyde): crystal data space group $P\bar{1}$, $Z = 1$, $a = 9.161$ (5) Å, $b = 9.183$ (2) Å, $c = 13.353$ (7) Å, $\alpha = 128.25$ (3)°, $\beta = 93.72$ (4)°, $\gamma = 110.44$ (3)°, $V = 764$ Å³, $R = 3.1\%$ for 1851 reflections; magnetic data $g = 2.15$, $J = 16.0$ cm⁻¹, $D \approx 15$ cm⁻¹ ($zJ' = 0.14$). $[\text{Ni}(\text{ips})(\text{NO}_3)_2\text{DMF}]_2$: crystal data space group $P\bar{1}$, $Z = 1$, $a = 9.506$ (2) Å, $b = 10.095$ (4) Å, $c = 10.588$ (3) Å, $\alpha = 94.80$ (2)°, $\beta = 126.59$ (2)°, $\gamma = 92.70$ (2)°, $V = 807$ Å³, $R = 5.5\%$ for 2039 reflections; magnetic data $g = 2.32$, $J = -9.2$ cm⁻¹, $D \approx 12$ cm⁻¹. The magnetic behavior is correlated with differences in exchange pathways as obtained from the crystal structures. Although it is demonstrated that D and zJ' cannot be estimated accurately from the magnetic data, the values of the intradimer interaction, J , are reliable.

Introduction

Copper complexes of bidentate Schiff bases are well-known to form binuclear antiferromagnetic copper(II) complexes of the types 1.³ The geometry of the copper complexes positions

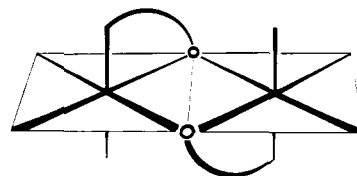


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the salicylaldehyde residue approximately parallel to the Cu_2O_2

bridge. Nickel(II) dimers containing salicylaldehyde ligands have been prepared; however, the only analogous nickel(II) complexes known to date have the salicylaldehyde residues at right angles to the Ni_2O_2 bridge and a ferromagnetic intradimer exchange interaction.

Nickel complexes of bidentate Schiff bases $\text{Ni}(\text{bsb})_2$ such as with salicylaldehydes (sal) or chlorobenzophenones (cbp) react with nickel nitrate in triethyl orthoformate (TEOF) or ethanol to form binuclear complexes $[\text{Ni}_2(\text{bsb})_2(\text{NO}_3)_2(\text{EtOH})_2]$ of the type 2.⁴⁻⁶ Hydrogen bonding between the



2, "cis"

ethanolic OH and the nitrate ligands of adjacent nickel binuclears leads to infinite chains of the neutral dinickel units.

- (1) Paper presented at the 176th National Meeting of the American Chemical Society, Miami, Fla., Sept 1978; see Abstracts, No. INOR 102.
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