Magnetism and Mössbauer Spectra of Tris(diphenyldithiophosphinato)iron(III)

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(Received August 9, 1988)

Ferric complexes of dithiophosphinates, [Fe(R_2PS_2)$_3$], have been reported for R = CH_3 [1], C_2H_5 [2, 3], n-C_3H_7 [2] and C_6H_5 [1]. The magnetic moments at room temperature of the R = C_2H_5 (5.65 B.M. [2], 6.10 B.M. [3]), n-C_3H_7 (5.81 B.M. [2]) and C_6H_5 (5.91 B.M. [1]) complexes indicate purely high-spin iron(III), in contrast to the iron(III) complexes of the related dithiocarbamates [Fe(R_2NCS_2)$_3$], which are mixed low-spin high-spin cases, and the xanthates [Fe($ROCS_2$)$_3$], which are purely low-spin cases at room temperature.

The Mössbauer spectra at 203 K and 78 K of the R = C_2H_5 and n-C_3H_7 complexes show small quadrupole splittings of ~0.4 mm/s, with no temperature dependence [2].

In order to determine whether the [Fe(R_2PS_2)$_3$] complexes show unusual magnetic or Mössbauer properties at low temperatures (<78 K), the magnetic susceptibility of the R = C_6H_5 complex has been measured down to 2.8 K, and the Mössbauer spectrum measured at 4.2, 78 and 298 K. The results are reported in this paper.

Experimental

Tris(diphenyldithiophosphinato)iron(III) was prepared as follows. To a filtered solution of 10 g of diphenyldithiophosphinic acid (technical grade, Aldrich Chemical Co.) in 200 ml of absolute ethanol was added, slowly with stirring, a filtered solution of 1.6 g of anhydrous iron(III) chloride in 30 ml of absolute ethanol. The black precipitate was collected and washed well with anhydrous ethanol. The air-dried black powder was dissolved in methylene chloride, the solution filtered, and the complex precipitated by the addition of anhydrous ethanol, then dried in vacuum for several hours at 50 °C. The solid is analytically pure and stable indefinitely in air when prepared in this manner, in contrast to the diethyl complex [3]. The reduction of iron(III) to iron(II), as reported in ref. 4, was not observed.

The ^{57}Fe complex was prepared similarly, using 10 mg of 90% ^{57}Fe metal (Oak Ridge) dissolved in a small amount of concentrated aqueous hydrochloric acid, in place of the anhydrous iron(III) chloride.

Magnetic measurements in the temperature range 2.8–300 K were made on a Faraday-type balance, with an external magnetic field of 1.8 T. Diamagnetic corrections were calculated from Pascal's constants.

Mössbauer spectra were recorded using a 400 channel analyzer operating in the time mode, with a constant acceleration drive. A sodium nitroprusside absorber was used to calibrate the velocity scale and provide the zero reference for the isomer shift (nitroprusside splitting, 1.705 mm/s). Low temperature measurements were made using a Janis detachable tail Dewar. Data were fitted by a least-squares approximation assuming Lorentzian line shapes and plotted with a Calcomp plotter.

Results and Discussion

Magnetic Moments

A plot of the reciprocal corrected molar susceptibility *versus* temperature is linear over the temperature range 20–300 K, and yields a magnetic moment of 5.97 ± 0.03 B.M. (uncorrected for temperature-independent paramagnetism), with a Weiss constant $\theta = 0.0$ K. At 2.8 K, $\mu_{eff} = 4.64$ B.M.; at 5.0 K, 5.36 B.M.; and at 10 K, 5.76 B.M. Cavell *et al.* found $\mu_{eff} = 5.91$ B.M. in the range 90–300 K [1]. Of the types of bidentate sulfur ligands which form four-membered rings with metal ions (RCS_2^-, $R_2NCS_2^-$, $ROCS_2^-$, $RSCS_2^-$, $R_2PS_2^-$, $(RO)_2PS_2^-$) only the dithiophosphinates and dithiophosphates (such as $(i\text{-}C_3H_7O)_2PS_2^-$ [5]) appear to give purely high-spin octahedral iron(III) complexes regardless of the R substituent. The only high-spin dithiocarbamate complex which has been extensively studied, tris(pyrrolidyl-*N*-carbodithioato)iron(III), [Fe(Pyrdtc)$_3$], shows magnetic behavior very similar to that of [Fe((C_6H_5)$_2PS_2$)$_3$]. Figgis and Togood could not fit the low temperature magnetic susceptibility of [Fe(Pyrdtc)$_3$] with an equation derived by considering only zero-field splitting of the ^{6}A ground term [6]. Attempts at fitting this equation to the μ_{eff} values of [Fe((C_6H_5)$_2PS_2$)$_3$] in the temperature range 2.8–10 K with reasonable values of the zero-field splitting parameter *D* were similarly unsuccessful. (*D* would have to be positive and greater than ~10 cm^{-1}.) Marathe and Mitra have shown that the susceptibility data on [Fe(Pyrdtc)$_3$] can be fitted well with inclusion of magnetic field effects and fourth-order ligand field terms [7]; it appears that similarly extensive treatment will also be required for the dithiophosphinate.

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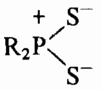
0020-1693/89/$3.50

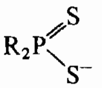
Mössbauer Spectra

Mössbauer spectra measured at 298, 78 and 4.2 K are shown in Figs. 1 and 2. At 298 K, the spectrum consists of a single symmetrical peak with an isomer shift of 0.76 ± 0.02 mm/s and a half-width at half-maximum of 0.34 mm/s. This isomer shift is significantly larger than the shifts for $[Fe(R_2NCS_2)_3]$ complexes, which average about 0.64 mm/s at 298 K [6]. Valov *et al.* found for $[Fe((C_2H_5)_2PS_2)_3]$ and $[Fe((n\text{-}C_3H_7)_2PS_2)_3]$ isomer shifts which were similarly 0.1 mm/s greater than those of the corresponding dithiocarbamates [2].

It seems clear from the isomer shift data that there is more ligand-to-iron(III) π-bonding with a dithiophosphinate than with a dithiocarbamate or xanthate. Jorgensen has proposed that the form



is much more important than the form



in metal complexes [8]. Several studies have confirmed this [9]. Unfortunately no crystal structure of a ferric dithiophosphinate has been reported, but in the several other metal dithiophosphinates whose structures have been determined, the P–S bond length averages 2.02 Å and shows little dependence on the metal*. A P=S bond is about 1.86 Å [11]; the P–S single bond length is about 2.10 Å. The dithiolate form is a strong π-base, and by destabilizing the t_{2g} level in an octahedral complex, gives high-spin iron(III). There is less contribution of the corresponding dithiolate form to the overall structure in dithiocarbamates and xanthates.

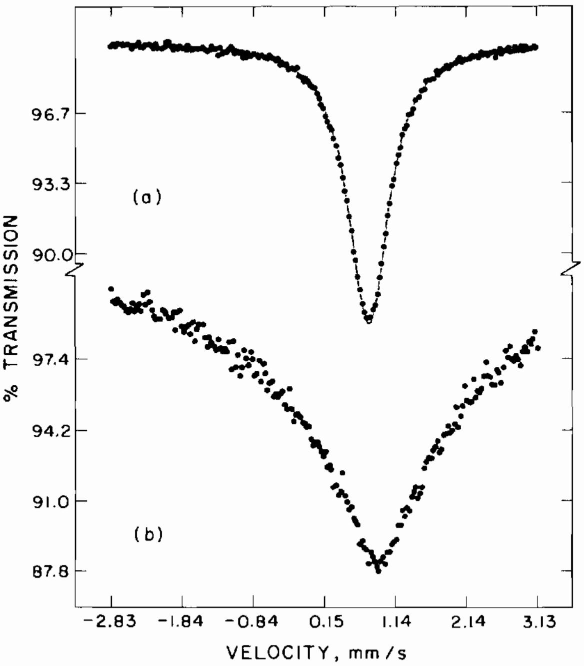


Fig. 1. Mössbauer spectrum of $[^{57}Fe((C_6H_5)_2PS_2)_3]$ at (a) 298 K, (b) 78 K.

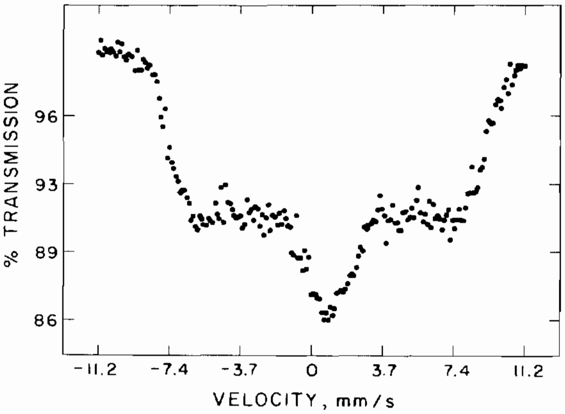


Fig. 2. Mössbauer spectrum of $[^{57}Fe((C_6H_5)_2PS_2)_3]$ at 4.2 K.

The spectrum of $[Fe((C_6H_5)_2PS_2)_3]$ at 78 K shows considerable magnetic broadening due to a decrease in the spin–lattice relaxation time. The magnetic hyperfine splitting is partially resolved at 4.2 K (Fig. 2). A five peak pattern with the central peak most intense indicates a relaxation time of ~5 × 10^{-9} s for the $Ms = \pm 5/2$ level in high-spin iron(III) [12]. $[Fe(Pyrdtc)_3]$ gives a well-resolved six line Mössbauer hyperfine pattern at temperatures of 6 K and below [13, 14]. The less resolved spectrum of $[Fe((C_6H_5)_2PS_2)_3]$ is due to one or more of the following factors: (i) a closer approach to cubic symmetry of the iron(III); (ii) a smaller energy separation between the $Ms = \pm 5/2$ ground state and the $Ms = \pm 3/2, \pm 1/2$ states of ^6A iron(III); (iii) a greater mixing of the $Ms = \pm 5/2$ ground state with excited states. These factors are dependent of one another: the more cubic the ligand field, the smaller the zero-field splitting parameter D. For $[Fe(Pyrdtc)_3]$, $D = -2.1$ cm^{-1} [13, 15] so it seems likely that for the dithiophosphinate, $D < |2.1|$ cm^{-1}.

Acknowledgements

We thank Prof. W. E. Wallace and Prof. R. S. Craig for use of their Faraday equipment, and the Division of Biology and Medicine, Atomic Energy Commission for financial support.

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*See ref. 10: (a) $[Ni((CH_3)_2PS_2)_2]$, (b) $[Ni((C_2H_5)_2PS_2)_2]$, (c) $[Ni((C_6H_5)_2PS_2)_2]$, (d) $[Co((C_2H_5)_2PS_2)_2]$ and $[Zn((C_2H_5)_2PS_2)_2]$, (e) $[Pr((C_6H_{11})_2PS_2)_3]$ and $[Sm((C_6H_{11})_2PS_2)_3]$, (f) $[Dy((C_6H_{11})_2)_3]$ and $[Lu((C_6H_{11})_2PS_2)_3]$.

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