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Mössbauer Studies of Iron(III) Complexes of Diacetyl Monoxime Thiosemicarbazone

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Recently several tridentate ligands, including pyrazine-carboxaldehyde thiosemicarbazone, have been found effective in reducing tissue iron levels in iron-loaded mice. The pyrazine-carboxaldehyde thiosemicarbazone acts as tridentate ligand with two nitrogen and one sulphur donor atoms and forms a complex with iron(III) in a molar ratio of iron(III) to ligand of 1:2 [1]. Like pyrazinecarboxaldehyde thiosemicarbazone, the diacetyl monoxime thiosemicarbazone is a tridentate ligand with two nitrogen and one sulphur donor atoms; it also forms a complex with iron(III) in a molar ratio of iron(III) to ligand of 1:2, which can be readily isolated. Several iron(III) complexes of the formula $Fe(DMT-H)_2X$, where DMT – H is an anion of diacetyl monoxime thiosemicarbazone and $X^- = Cl^-$, NO_3^-, N_3^-, NCS^- and CN^-, have been prepared. They are low-spin and their anions are associated with the iron(III) of $Fe(DMT-H)_2$ group in the solid state, as shown by their EPR spectroscopy and other physical studies [2]. In order to verify the association of anions in the $Fe(DMT-H)_2X$ complexes and to obtain more insight on this behavior, we have studied these complexes and Fe(DMT – H)(DMT – 2H), where DMT – 2H is the dianion of diacetyl monoxime thiosemicarbazone, by Mössbauer spectroscopy. Our Mössbauer studies show that the values of isomer shift (IS) of these complexes follow the order: $Fe(DMT-H)_2N_3 > Fe(DMT-H)_2NCS > Fe(DMT-H)(DMT-2H) > Fe(DMT-H)_2CN$. In addition, the quadrupole splitting (QS) values of these complexes also follow the same order.

Experimental

The $Fe(DMT-H)_2X$ complexes were prepared by literature methods [2].

Preparation of Fe(DMT – H)(DMT – 2H)

$FeCl_3$ (1 mmol) was dissolved in water containing a small quantity of dilute hydrochloric acid. The solution was mixed with the solution of the ligand (2 mmol) in the minimum quantity of methanol. The mixture was stirred for 10–15 minutes. Ammonium hydroxide solution (1:1) was added dropwise to the above solution to adjust the pH to between 6.5 and 7. The black precipitate obtained was filtered, washed with methanol, and dried in air. *Anal.* Found: C, 28.2; H, 4.0; N, 26.5%. Calcd. for $C_{10}H_{17}N_8S_2Fe$: C, 28.72; H, 4.1; N, 26.78%.

Physical Measurements

The Gouy method was used to measure the magnetic susceptibility of Fe(DMT – H)(DMT – 2H), and the $Hg[Co(NCS)_4]$ was used as a standard. The diamagnetic corrections were applied using Pascal's constants from the published work [3]. The electron paramagnetic resonance (EPR) spectrum of the polycrystalline Fe(DMT – H)(DMT – 2H) was recorded on a Varian E-112 spectrometer (X-band) using TCNE ($g = 2.00277$) as a marker. The electronic absorption spectrum was recorded on a Perkin-Elmer Model 402 spectrophotometer in dimethylformamide (DMF) solution. The molar conductance of Fe(DMT – H)(DMT – 2H) in DMF at room temperature was measured with a Systronics conductivity bridge (model 305) using a platinum cell having a cell constant of 0.0749 cm^{-1}.

Mössbauer spectra of the iron(III) complexes were recorded using an electromechanical transducer drive operating at a constant accelerator mode in conjunction with a 1024 channel analyser. Mössbauer absorbers were prepared using powdered samples. The spectrum of the standard iron foil had a linewidth of ~0.3 mm/sec.

Results and Discussion

The Fe(DMT – H)(DMT – 2H) is highly soluble in DMF, dimethylsulphoxide and dilute sodium hydroxide solution, slightly soluble in methanol, ethanol and water, and insoluble in petroleum ether, benzene, carbon tetrachloride, chloroform, diethyl ether and acetone. It shows electronic absorption maxima in DMF at 35,842 ($\epsilon_{max} = 46,874$), 31,847 (50,994) and 27,472 (12,362) cm^{-1}. It shows a molar conductance in DMF of 41.1 mhos cm^2 mol^{-1} at room temperature, which is lower than the 1:1 electrolyte value [4]. This complex shows a magnetic moment (μ_{eff}) value of 2.27 B.M. at 298 K and, therefore, it is a low-spin iron(III) complex. Other $Fe(DMT-H)_2X$ (where $X^- = Cl^-$, NO_3^-, N_3^-, NCS^- and CN^-) are also low-spin complexes with μ_{eff} values ranging from 2.09 to 2.34 B.M. This is supported by the EPR spectra, with two or three g values around 2 with tetragonal (chloro complex) or rhombic (all

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other complexes) distortion [2]. The EPR spectrum of Fe(DMT – H)(DMT – 2H) in a polycrystalline state at 77 K showing rhombic distortion is given in Fig. 1. The $Fe(DMT - H)_2NO_3$ shows a low intensity spectrum, indicating appreciable spin-pairing via exchange coupling [2].

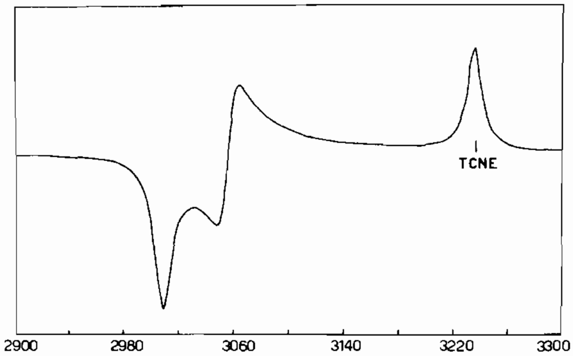

Fig. 1. EPR spectrum of polycrystalline Fe(DMT – H)-(DMT – 2H) at 77 K.

TABLE I. Mössbauer Parameters of $Fe(DMT - H)_2X$ (where $X^- = N_3^-$, NCS^- and CN^-) and Fe(DMT – H)(DMT – 2H) at 300 °K.

Compound	IS (mm/s)	QS (mm/s)
$Fe(DMT - H)_2CN$	0.00	0.67
Fe(DMT – H)(DMT – 2H)	0.07	2.2
$Fe(DMT - H)_2NCS$	0.08	2.4
$Fe(DMT - H)_2N_3$	0.12	2.7

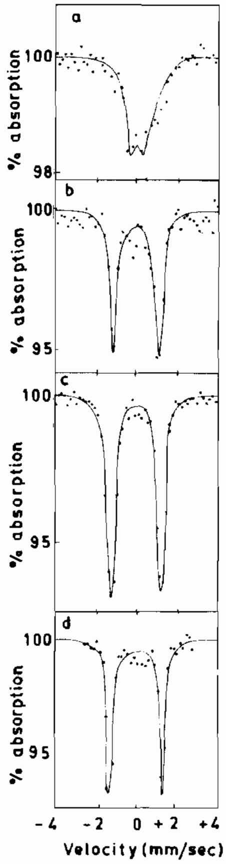

Fig. 2. Mössbauer spectra at 300 K of (a) $Fe(DMT - H)_2CN$, (b) Fe(DMT – H)(DMT – 2H), (c) $Fe(DMT - H)_2NCS$, and (d) $Fe(DMT - H)_2N_3$.

The Mössbauer spectra of $Fe(DMT - H)_2X$, where $X^- = Cl^-$, NO_3^-, N_3^-, NCS^- and CN^-, and Fe(DMT – H)(DMT – 2H) are measured. The chloro and nitro complexes give hyperfine split spectra, indicating the presence of magnetic ordering. These spectra, are, however, difficult to resolve. The low intensity EPR spectrum of the nitro complex (see above) supports the presence of magnetic ordering. Other complexes give Mössbauer spectra with quadrupole split doublets. The IS and QS values of these complexes are given in Table I and their 300 K Mössbauer spectra are given in Fig. 2. The IS values of these complexes show that they are low-spin iron(III) complexes. The IS of these complexes follow the order $Fe(DMT - H)_2N_3 > Fe(DMT - H)_2NCS >$ Fe(DMT – H)(DMT – 2H) $> Fe(DMT - H)_2CN$. The order $Fe(DMT - H)_2N_3 > Fe(DMT - H)_2NCS > Fe(DMT - H)_2CN$ can be correlated in terms of decreasing values of partial isomer shift values [5] of the anion, X^-, in the $Fe(DMT - H)_2X$ (where $X^- = N_3^-$, NCS^- and CN^-). The lowest IS of cyano complex can be explained in terms of strong bonding of ligand-to-metal ($\sigma_{L\rightarrow M}$) and strong π-back donation ($\pi_{M\rightarrow L}$). In Fe(DMT – H)(DMT – 2H), the ligand DMT – 2H has a S^- as donor atom which also has relatively stronger $\sigma_{L\rightarrow M}$ and $\pi_{M\rightarrow L}$ interactions than S atom in DMT – H. The thiocyanato and azido complexes have relatively weaker $\sigma_{L\rightarrow M}$ interactions and possibly very weak $\pi_{M\rightarrow L}$ interaction. Thus the above IS order $Fe(DMT - H)_2N_3 > Fe(DMT - H)_2NCS >$ Fe(DMT – H)(DMT – 2H) $> Fe(DMT - H)_2CN$ is explained. The order $Fe(DMT - H)_2N_3 > Fe(DMT - H)_2NCS > Fe(DMT - H)_2CN$ correlates well with the average electronegativities of the anions if it is assumed that iron(III) and donor atoms of DMT – H have the same distances in these complexes [5, 6].

QS values of iron(III) complexes are also given in Table I. They follow the same order as the IS values. The complexes show large QS, values due to large non-zero electric field gradient (V_{zz}) around the iron atom [5]. This non-zero V_{zz} can arise from significant aspherical population of the d-orbitals due to crystal field splitting, $(V_{zz})_{CF}$, in these low-spin iron(III) complexes, because of their rhombic distortion as already found in their EPR measurements. In these low-spin iron(III) complexes the $(V_{zz})_{CF}$ is not pure but is always mixed with some anisotropic population of molecular orbitals, $(V_{zz})_{MO}$ [5]. It seems that an aspherical charge distribution in the ligand sphere denoted as $(V_{zz})_L$ is not the dominant mechanism causing large QS values, because the QS values in Fe(DMT – H)$_2$N$_3$, Fe(DMT – H)$_2$NCS and Fe(DMT – H)$_2$CN do not correlate with the order of the partial QS values of these anions [6]. On the other hand, the QS values correlate with the average electronegativity values of the anions (see above). Similar trends in IS and QS values obtained from their 77 °K spectra have been found.

The Mössbauer parameters of low-spin iron(III) complexes, such as Fe(DMT – H)$_2$N$_3$, Fe(DMT – H)$_2$NCS and Fe(DMT – H)$_2$CN, are dependent on the nature of anions. This shows that the anions are coordinated to iron(III) in these complexes. The ligand DMT – H has rigid tridentate structure and six donor atoms of two DMT – H are occupying all six corners of an octahedron, and the anion is occupying the position at one triangular face of the octahedron forming the capped octahedron [7]. However, the complex Fe(DMT – H)(DMT – 2H) seems to have octahedral geometry.

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