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Iron Complexes with Rhodizonic Acid

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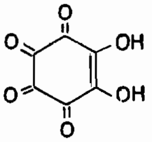
Thermogravimetric, Mössbauer, IR, magnetic and polarographic studies have shown that the reaction of ferrous ions with rhodizonic acid proceeded according to the redox mechanism and produced the trimeric, mixed-valence $Fe_2^{+3}Fe^{+2}L_2\cdot 10H_2O$ *complex. The ferrous ion being in the center of a trimeric species is bridged with two ferric ions via two reduced ligand molecules. The other coordination sites are occupied by water molecules.*

Introduction

Recent studies on iron complexes with ligands containing oxygen donor atoms such as oxalates, squarates or dihydroxybenzoquinones and derivatives [1–5] have shown that ferrous ions form usually polymeric species [2, 3], while ferric ion complexes exist as dimeric or trimeric complexes [1, 4, 5]. Wróblewski and Brown also studied the mixed-valence iron polymers in which ferrous ions were oxidized with I_2 in the solid state [3].

The rhodizonic acid, 5-cyclohexene-1,2,3,4-tetrone-5,6-dihydroxy acid, may be considered as



a higher analogue of squaric acid and the results obtained for its iron complexes are presented in this communication.

Experimental

Rhodizonic acid was prepared according to the method described earlier [6, 7] by reaction of $H_2C_6O_2Cl_8$ with 98% H_2SO_4. The crude product was extracted with ether. Analysis for $H_2C_6O_6\cdot 2H_2O$ gave C 34.92 (calc. 34.96), O 62.10 (calc. 62.12), H 2.91 (calc. 2.90).

The complex was obtained by adding 5 mmol $FeSO_4\cdot 7H_2O$ to an aqueous solution containing 5 mmol of sodium salt of rhodizonic acid. The solution was refluxed for 1 hour at 50 °C under nitrogen. The formed precipitate was filtered and washed with water and then with ethanol; finally it was air-dried at room-temperature over P_2O_5. The yield calculated for iron ion was 84%. *Anal.* Found: C, 21.2; H, 2.65; Fe, 24.9; calc. for $Fe_3L_2\cdot 9H_2O$: C, 21.6; H, 2.7; Fe, 25.1; for $Fe_3L_2\cdot 10H_2O$: C, 21.05; H, 2.92; Fe, 24.5. The same complex can be obtained with use of $FeCl_3\cdot 6H_2O$ salt but with much lower yield (17.5%). The small yield is caused by ligand decomposition (oxidation) during the reaction.

Physical Measurements

IR spectra were recorded on a Perkin Elmer 180 IR spectrophotometer. Samples were measured in KBr pellets. Mössbauer spectra were obtained as described previously [8]. Mössbauer lines were deconvoluted by assuming Lorentzian line contours superimposed on a parabolic baseline. The velocity was calibrated by means of SNP standard, and (isomer shift) IS was referred to SNP. The thermal decomposition was carried out on an 102 Derivatograph (MOM Budapest). Magnetic susceptibility was measured by Faraday's method in the 4.2–290 K temperature range.

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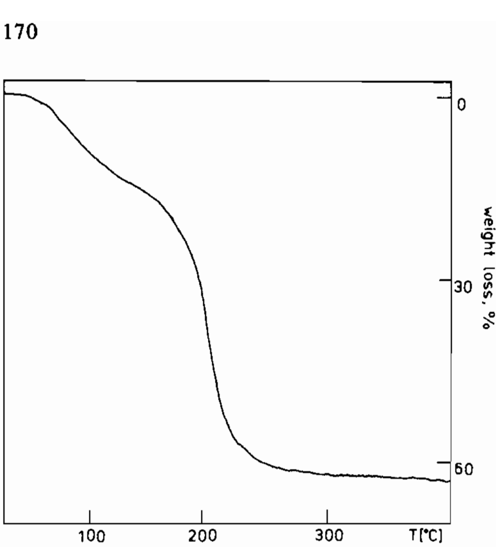


Fig. 1. The weight loss curve for $Fe_3L_2 \cdot 10H_2O$ complex.

Fig. 2. IR spectra of free (top) and complexed (bottom) ligand in the CO vibration region.

Results and Discussion

The elemental analysis suggests the complex formula to be $Fe_3L_2 \cdot 9H_2O$. The detailed number of water molecules (9 or 10) is however difficult to obtain precisely from the obtained analytical data (see Experimental).

The thermogravimetric study of the iron complex gives additional information about species composition. The complex undergoes thermal decomposition in two major steps (Fig. 1). In the first step (which ends at ~185 °C) water is removed, 26% of the total weight loss indicates 10 water molecules per trimeric unit of iron complex. The second step is a complicated process which proceeds at 220 °C and corresponds to the thermal decomposition of the bound ligand (38% loss of weight). The remaining ~36% corresponds to Fe_2O_3, which is the final product of the complex decomposition [1, 3]. The thermal analysis results correspond well to the formula $Fe_3L_2 \cdot 10H_2O$.

TABLE I. Mössbauer Data of the Iron Rhodizonic Acid Complex.

T	Fe^{+++}		Fe^{++}		Fe^{+++}/Fe^{++}
	IS[a]	QS[a]	IS[a]	QS[a]	
295 K	0.680	0.862	1.428	1.717	1.8
80 K	0.807	0.919	1.490	2.286	1.8

[a] IS and QS in mm s^{-1}.

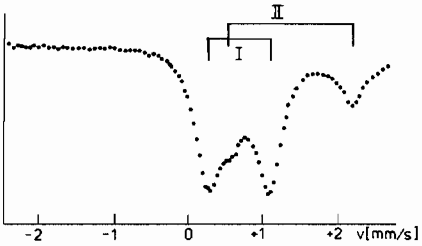


Fig. 3. Mössbauer spectrum of $Fe_3L_2 \cdot 10H_2O$ complex at 295 K.

The coordination of iron ion to the ligand molecule changes the IR spectra of the metal-free ligand (Fig. 2). In the latter case the broad band centered around 1470 cm^{-1} corresponds to CO group vibrations. In the complexed ligand this band splits into three bands, at 1630, 1400 and 1340 cm^{-1}. This suggests coordination of metal ion with oxygen donors of the ligand molecule. The considerable variations in the vibration energy observed for CO groups suggest the considerable variations of the C–O bond character, and (probably) the double-bond pattern of the ligand molecule in $Fe_3L_2 \cdot 10H_2O$ complex as compared to the metal-free ligand.

Mössbauer spectra of $Fe_3L_2 \cdot 10H_2O$ complex consist of two quadrupole doublets (Fig. 3, Table I). The magnitude of the isomeric shift (IS) and quadrupole splitting (QS) of the doublets clearly show the presence of ferric and ferrous ions in the studied complex (Fig. 3, Table I). The parameters of the doublet I correspond well to those obtained for the similar ferric complexes reported earlier [3]. The QS and IS values of the doublet II agree well with those observed for the ferrous complex e.g. $FeC_6H_2O_4 \cdot 2H_2O$ [3]. The intensity ratio of both doublets (Fe^{++}/Fe^{+++}/ is close (for the fresh samples) to 1:1.8

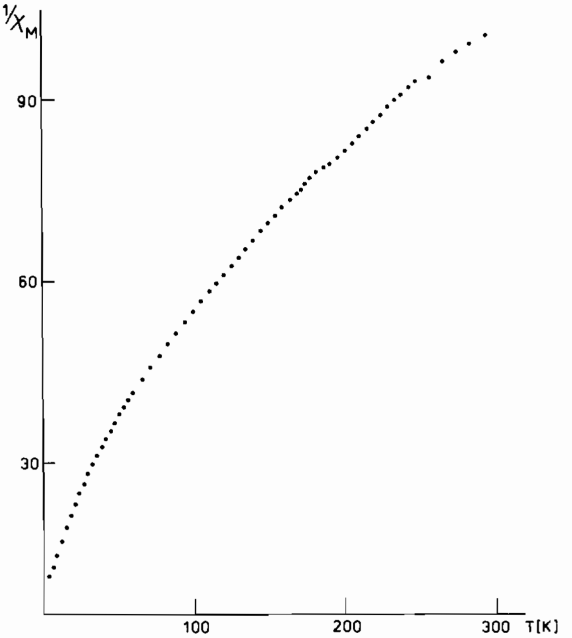
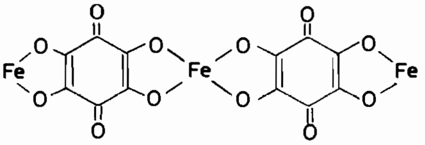


Fig. 4. The temperature dependence of magnetic susceptibility ($1/\chi$ *vs.* T).

for different samples used for the measurements. It could suggest that in the trimeric species two metal ions are ferric ions and one is the ferrous ion. The intensity ratio changes for the samples stored for more than 48 hours and it reaches a value close to 1:1 after several days.

The magnetic susceptibility measurements have shown that in the 80–290 K temperature range the Curie–Weiss law is obeyed with $\theta = -121.4$ K (Fig. 4). The magnetic moment of 5.62 BM per metal ion corresponds well to two ferric and one ferrous ion in the complex molecule. The presence of the ferric ions in the final product obtained from the ferrous salt, and the high yield of the reaction, strongly suggest that the rhodizonic acid is oxidizing $Fe^{+2} \rightarrow Fe^{+3}$ and the reduced form of ligand is likely to be present in the trimeric product.

The results presented above allow us to assume the following structure of the iron–ligand core:



The other 10 coordination sites of iron are occupied by water molecules.

Such a structure of the trimeric unit seems to explain the IR spectra of the complex (*i.e.* distinct changes of the CO vibration energy upon ligand coordination). It allows us also to fit the magnetic susceptibility (χ) dependence on temperature. Assuming no exchange between two ferric ions and the same interaction between ferric and ferrous ion, the values may well fit the theoretical curve with $-2J = 25$ cm^{-1} in the 70–290 °K temperature range. At lower temperatures than 70 K the χ *vs.* T plot is much more complicated, due most likely to long-range exchange interaction between different trimeric units. The assumption of an exchange interaction between two ferric ions within a trimeric unit does not satisfactorily explain the χ *vs.* T plot.

The primary polarographic results also seem to support the above structure. Sodium rhodizonate undergoes two step reduction with half-wave potentials $E_{1/2} = -0.55$ and -0.98 V in 0.1 *M* NaCl and the ligand concentration 10^{-3} *M*. Those values make clear the redox reaction in ferrous salt solution containing the rhodizonic acid (redox potential for Fe^{+++}/Fe^{++} couple $E = +0.77$ V). The addition of the ferrous ions into sodium rhodizonate solution causes the decay of the first reduction wave and the appearance of the ferric ions. These results support the conclusions mentioned above. The detailed polarographic studies of rhodizonic acid were reported recently by Fleury *et al.* [9].

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