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McMaster University, Hamilton, Ontario, Canada L8S 4M1**Iron-57 Mössbauer Spectroscopy of Dithiooxalato Complexes of Iron in the Solid State and in Frozen Aqueous Solution**

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Received May 21, 1975

AIC503531

Magnetic and Mössbauer data are reported for a series of tris(dithiooxalato)ferrate(III) complexes, in both the low- and high-spin configurations. No evidence for a ${}^2T_2 \rightarrow {}^6A_1$ spin equilibrium was obtained. Frozen solution studies showed that the preparation of these complexes from Fe(III) salts proceeds through a reduction of Fe(III) to Fe(II), followed by a subsequent reoxidation.

Sulfur-containing ligands such as dithiocarbamate, 1,2-dithiolate, thioxanthate, etc., form a variety of complexes with transition metals and extensive reviews on their chemistries exist.¹⁻³ Many of these systems undergo reversible one-electron transfer reactions, have magnetic moments intermediate between the high- and low-spin values, and exhibit a variety of structures. In cases where the transition metal is iron, Mössbauer spectroscopy has proved to be a useful spectroscopic tool.⁴ Recently, there has been an interest in the chemistry of dithiooxalato metal complexes and Coucouvanis and coworkers⁵⁻⁸ have reported extensively in this area pointing out the unique bifunctionality of the dithiooxalate ligand. While they find no evidence for reversible electron transfer reactions, which are common with 1,2-dithiolate complexes,² they were able to prepare tris(dithiooxalato)ferrate(III) complexes in both the high- and low-spin forms with the magnetic moments of the low-spin complexes varying considerably. Because ${}^{57}\text{Fe}$ Mössbauer has proved valuable in such spin equilibrium systems⁴ we decided to study these dithiooxalate (dto) complexes by this method.

We were unable to find evidence for any spin equilibration in our investigations but frozen solution studies show that the preparation of $[\text{Fe}^{\text{III}}(\text{dto})_3]^{3-}$ from Fe(III) salts proceeds via a reduction to Fe(II) with a subsequent reoxidation to Fe(III). Furthermore, $[\text{Fe}^{\text{III}}(\text{dto})_3]^{3-}$ complexes are obtained when either Fe(II) or Fe(III) salts are used in the preparations.

Experimental Section

All of the complexes were prepared according to the procedures of Coucouvanis and coworkers⁵⁻⁸ and the authenticity of the compounds was checked by elemental analyses. Magnetic measurements were made by the Gouy method and calibrated against $\text{HgCo}(\text{CNS})_4$. Mössbauer spectra were recorded with an Austin Science Associates drive system in conjunction with a PIP400A Victoreen multichannel analyzer. A cryogenic liquid transfer line and temperature controller Model LT-3-110C, fitted with Pt and Ge sensors from Air Products and Chemicals Inc., was used to obtain low-temperature Mössbauer spectra. Sample temperatures were controlled to $\pm 0.1^\circ$. Solution samples were syringed into the Mössbauer cell through a hole cut into a copper gasket sandwiched between two thin high purity aluminum foils. The samples were then frozen by plunging them into liquid nitrogen. The source was ${}^{57}\text{Co}$ in a Pd matrix obtained from New England Nuclear. Spectra were calibrated and referenced using the six lines of a standard iron foil, the center of which was taken as zero isomer shift. The source and the iron foil were at 298°K throughout and no corrections for second-order Doppler shifts have been made. Samples contained 10 mg/cm^2 of iron. Spectra were computer fitted to Lorentzian line shapes using an iterative least-squares procedure.⁹

Results and Discussion

Table I summarizes the data obtained for a series of dto complexes of iron(III). The ir and magnetic data agree well with those reported previously.⁶ Comparison of $\nu_{\text{C=O}}$ for these complexes with $\nu_{\text{C=O}}$ for the $[(\text{dto})_3\text{Co}^{\text{III}}]^{3-}$ complex, which is known to have Co chelated through sulfur,¹⁰ suggests that the iron complexes are also sulfur chelated. In the high-spin complexes $\nu_{\text{C=O}}$ was $\sim 1380 \text{ cm}^{-1}$ and this was taken to be an indication that the oxygen of the C=O was coordinated to

the cation in these complexes.⁶ More recently, Hollander and Coucouvanis¹¹ have shown that in the $[(\text{Ph}_3\text{P})_2\text{Ag}^{\text{I}}]_3[\text{Fe}^{\text{III}}(\text{dto})_3]$ complex the iron(III) is coordinated by the O,O bites of the three dto^{2-} ligands while the $[(\text{Ph}_3\text{P})_2\text{Ag}^{\text{I}}]^+$ cation interacts with the S,S bite of each ligand. These workers suggest that the ligand flips from S,S chelation to O,O chelation as a result of the $(\text{Ph}_3\text{P})_2\text{M}^+$ interaction and the high-spin state is to be expected by analogy to the iron(III) oxalate complexes which are high spin.

Carlin and Canziani¹² who studied the temperature variation of the magnetic moment for $\text{KBaFe}(\text{dto})_3 \cdot 6\text{H}_2\text{O}$ concluded that dto^{2-} is as efficient as CN^- in causing electron delocalization from metal to ligand. We confirm the large negative Weiss constant that these workers found for this complex. The related tris(ethylthioxanthate)iron(III) complex shows similar magnetic properties and while the low-spin state 2T_2 is the ground state, the high-spin state 6A_1 is slightly populated at room temperature. Coucouvanis et al.⁶ attempted to obtain evidence for such a ${}^6A_1 \rightarrow {}^2T_2$ crossover by means of ESR for the dithiooxalate complexes but were unsuccessful.

Mössbauer data which we have obtained for these complexes are summarized in Table I. The isomer shifts fall in the region expected for iron(III) complexes. Attempts to isolate $[\text{Fe}^{\text{II}}(\text{dto})_3]^{4-}$ complexes always gave the Fe(III) compounds with their characteristic spectra.

Shift values for iron(III) range from ~ 0.1 to $\sim 0.6 \text{ mm/sec}$ with the lower values usually associated with low-spin systems.⁴ Electron donation from ligand σ orbitals into metal d orbitals would result in a screening of the metal s electrons from the nucleus and cause an increase in isomer shift. This results when the ligand atoms are highly polarizable as in these sulfur chelated systems and hence relatively high isomer shift values are observed. If the dto^{2-} ligand was as efficient as CN^- in causing electron delocalization, as has been stated,¹² then one might have expected a much lower isomer shift since π back-donation from metal to ligand reduces the effective 3d population which in turn decreases the shift. The 1,2-dithiolene^{13,14} and dithiocarbamate¹⁵ complexes have similar shifts to the dithiooxalate complexes indicating that the extent of delocalization is about the same for all of these systems. The tetraphenylarsonium salt has a significantly higher isomer shift than the other low-spin complexes. This is the only salt which contains CH_3NO_2 rather than H_2O molecules incorporated into the crystal lattice from the solvent and perhaps the high value is an indication of a bonding interaction between the CH_3NO_2 and the central iron atom. Lower isomer shift values for the $[\text{Fe}(\text{dto})_2\text{NO}]^{2-}$ compounds reflect the powerful π bonding character of the NO^+ group. The two oxygen chelated complexes have shift values which compare favorably with other Fe(III) oxalates.¹⁶ Unfortunately these values are the same as those measured for the sulfur chelated dto complexes so that it is not possible to ascertain the mode of chelation from the isomer shift values.

High-spin Fe^{3+} has a 6A_1 electronic ground state and is spherically symmetric. Any electric field gradients will arise

Table I. Magnetic and Spectroscopic Data for Iron Dithiooxalato Complexes^a

Complex	Temp, °K	Isomer shift, mm sec ⁻¹	Quadrupole splitting, mm sec ⁻¹	$\nu_{C=O}$, cm ⁻¹ ^a	μ_{eff} , μ_B
K ₃ Fe(dto) ₃ ·6H ₂ O	77	0.37	0.42		
	196	0.33	0.35		
	298	0.27	0.31	1553, 1520	2.36
K ₂ SrFe(dto) ₃ ·H ₂ O	4	0.37	1.06		
	77	0.36	1.09		
	298	0.26	0.68	1562, 1520	2.21
[Co(en) ₃]Fe(dto) ₃ ·H ₂ O	77	0.40	1.68		
	298	0.32	1.36	1575, 1518	2.34
	330	0.28	1.05		
(C ₆ H ₅ NH ₂) ₃ Fe(dto) ₃ ·H ₂ O	4	0.40	1.27		
	77	0.38	1.12		
	123	0.40	1.01		
	173	0.38	0.93		
	223	0.36	0.81		
	298	0.29	0.64	1580, 1510	2.61
(C ₆ H ₅ NH ₂) ₃ Fe(dto) ₃ ·H ₂ O ^b	77	0.38	1.14		
	298	0.29	0.64		
	298	0.29	0.64		
[(C ₆ H ₅) ₄ As] ₃ Fe(dto) ₃ ·3CH ₃ NO ₂	77	0.53	0.90		
	298	0.43	0.95	1630, 1560	2.93
	298	0.42	0.99		
[((C ₆ H ₅) ₃ P) ₂ Ag] ₃ Fe(dto) ₃	77	0.24	0.87	1380	5.81
	298	0.24	0.87		
	298	0.33	1.18		
[((C ₆ H ₅) ₃ P) ₂ Cu] ₃ Fe(dto) ₃	77	0.24	1.17	1385	5.93
	298	0.24	1.17		
	298	0.29	1.04	1558 ^c	2.24 ^c
[(C ₂ H ₅) ₄ N] ₂ Fe(dto) ₂ (NO) ^d	77	0.29	1.05		
	4	0.29	1.05		
	77	0.28	1.00		
	196	0.26	1.04		
[(C ₄ H ₉) ₄ N] ₂ Fe(dto) ₂ (NO)	77	0.36	0.67	1590	2.30
	298	0.36	0.67		
	77	0.28	1.03		
	298	0.28	1.03		
[(C ₄ H ₉) ₄ N] ₂ Fe(dto) ₂ (NO) ^b	77	0.28	1.03		
	298	0.35	0.68		

^a dto = dithiooxalato, en = ethylenediamine. ^b Prepared from ferrous salt. ^c 298°K. ^d $\nu_{NO} = 1688 \text{ cm}^{-1}$.

from charges external to the central ion by direct contribution or by indirect polarization. In such cases it is unlikely that there will be any low-lying excited levels and thermal alterations of the electron configuration should not occur; the quadrupole splitting will be small ($\sim 0.5 \text{ mm/sec}$) and independent of temperature. In a six-coordinate Fe(III) complex, quadrupole splitting would also arise from a reduction of the O_h symmetry at the iron; this splitting would depend upon the degree of distortion and be relatively temperature independent. The relatively large splitting, $\sim 1.0 \text{ mm/sec}$, observed for the high-spin complexes $\{[(C_6H_5)_3P]_2Ag(\text{or } Cu)^+\}_3[Fe(dto)_3]^{3-}$ suggests that there is a considerable distortion from O_h symmetry. In the case of the silver complex the iron environment is distorted from octahedral to trigonal prismatic and the dithiooxalato ligand is coordinated to the iron through the oxygen rather than the sulfur atoms.¹¹

These two complexes have the iron(III) at the center of a large molecule and it is well separated from other paramagnetic atoms. When the spin-spin interactions between iron atoms are reduced by incorporation into large molecules or by dilution in diamagnetic host lattices, hyperfine interactions are often observed.¹⁷ While hyperfine interactions were not observed in these two high-spin Fe(III) complexes we did find that the Mössbauer line widths were $\sim 0.5 \text{ mm/sec}$ rather than 0.25 mm/sec for the S-chelated low-spin complexes. Such line broadening does occur at the onset of hyperfine interaction.

Low-spin six-coordinate Fe(III) complexes with the 2T_2 configuration have an electron hole in a t_{2g} level. This invariably leads to a Jahn-Teller distortion, the degeneracy of these levels is removed, and a nonzero electric field gradient results. These levels are generally close enough to allow thermal excitation and since electrons in the d_{xy} orbital make a different contribution to the electric field than electrons in either d_{xz} or d_{yz} orbitals⁴ a temperature-dependent quadrupole splitting would be observed. Variation of the quadrupole splitting with temperature could also arise from the existence

of a spin crossover from the $^2T_2 \rightarrow ^6A_1$ state as the temperature is raised as has been observed for tris(dithiocarbamato)ferrate(III) salts.¹⁸

Low-spin iron(III) complexes with an octahedral arrangement of six equivalent ligands usually exhibit only small quadrupole splittings, e.g., $K_3Fe(CN)_6$ at $300^\circ K$, $\Delta = 0.28 \text{ mm sec}^{-1}$,¹⁹ and the magnitude of this splitting indicates that the t_{2g} levels are almost equally populated. Table I shows that the $[Fe(dto)_3]^{3-}$ complexes have splittings from 0.3 to 1.7 mm sec^{-1} indicating either varying degrees of distortion from O_h symmetry or that each complex contains differing proportions of the 2T_2 and 6A_1 configurations. If the latter, then one would have expected this to be reflected in the magnetic measurements, but this does not appear to be the case. The complex with the smallest quadrupole splitting, e.g., $KBaFe(dto)_3 \cdot 6H_2O$, should have the highest proportion of the high-spin configuration and hence the highest magnetic moment while $[Co(en)_3][Fe(dto)_3] \cdot 3H_2O$ should have the lowest moment since it has the highest quadrupole splitting. A further argument against a $^2T_2 \rightarrow ^6A_1$ equilibrium comes from an examination of the temperature dependence of the quadrupole splittings and the magnetic moments. It is apparent that while the Mössbauer parameter changes dramatically, in most cases, on lowering the temperature, no corresponding change in magnetic moment is observed (Table II). For the anilinium salt, which shows the greatest percentage change in the quadrupole splitting, a more complete temperature profile of the Mössbauer data was undertaken to ensure that the change observed was indeed smooth. This proved to be the case and we therefore believe that these complexes are not examples of spin equilibrium systems like the dithiocarbamate complexes.¹⁸

The quadrupole splitting variation from complex to complex probably arises from differing degrees of distortion from O_h symmetry caused by the cations and/or the molecules of solvation associated with each species. Both the cations and

Table II. Magnetic Data for Iron Dithiooxalates

Temp, °K	$\chi_M^{\text{corr}} \times 10^{-6}$ cgs	$1/(\chi_M^{\text{corr}})$, cgs	μ_{eff} , μ_B
(a) $(C_6H_5NH_3)_3Fe(dto)_3 \cdot H_2O$			
77	9001	111	2.36
105	6608	151	2.36
120	6230	160	2.36
154	4970	201	2.45
182	4214	237	2.48
202	3836	260	2.48
239	3396	294	2.50
261	3018	331	2.52
293	2892	345	2.61
(b) $[Co(en)_3]Fe(dto)_3 \cdot 3H_2O$			
85	7079	141	2.20
100	6173	162	2.23
125	5128	195	2.27
164	4000	250	2.30
205	3268	306	2.32
240	2816	355	2.33
297	2297	435	2.34
(c) $(Ph_4As)_3Fe(dto)_3 \cdot 3CH_3NO_2$			
90	10526	95	2.76
120	8333	120	2.84
166	6098	164	2.86
220	4545	220	2.84
245	4348	230	2.93
298	3585	279	2.93
(d) $[(C_6H_5)_4N]_2Fe(dto)_2(NO)$			
84	6850	146	2.15
105	5714	175	2.19
132	4545	220	2.20
170	3636	275	2.23
206	2994	334	2.23
242	2597	385	2.24
297	2103	475	2.24

solvent molecules will also make a lattice contribution to the quadrupole splitting but it is impossible to estimate the magnitude of this contribution without accurate crystallographic evidence. In any case, the lattice contribution would be temperature independent and these spectra depend markedly upon temperature (Table I and Figure 1). This temperature variation is then the result of thermal equilibration of the electron within the three lowest occupied levels. Following the procedure of Golding²⁰ and making use of the magnetic data, we estimate that the 2T_2 ground states are split $\sim 200 \text{ cm}^{-1}$ for $KBaFe(dto)_3 \cdot 6H_2O$ which has the smallest change in quadrupole splitting, up to $\sim 600 \text{ cm}^{-1}$ for $[C_6H_5NH_3]_3Fe(dto)_3 \cdot H_2O$ which has the greatest change in quadrupole splitting.

Solution Studies

In an attempt to ascertain the Mössbauer parameters for the $[Fe^{III}(dto)_3]^{3-}$ ion with the lattice contribution to the quadrupole splitting reduced as much as possible, we examined some frozen aqueous solutions containing this species. The spectra shown in Figure 2 were obtained from frozen aqueous solutions of ferric nitrate to which varying amounts of potassium dithiooxalate had been added. Clearly there is more than one iron species present in the system and the relative intensities of the absorptions depend upon the $Fe(III):dto^{2-}$ ratio. The intensities of the resonances do not seem to depend upon the rate at which the dithiooxalate solution is added to the ferric nitrate. For example, a 1:1 $Fe(III):dto^{2-}$ solution when adjusted to a 1:3 ratio, the spectrum re-recorded, and then adjusted to a 1:6 ratio gave the same spectra as if the 1:1 and 1:6 solution had been prepared directly. Table III summarizes the data obtained from these solution spectra which could only be interpreted in terms of two partially overlapping doublets, one due to a low-spin $Fe(III)$ and the other to a high-spin iron(II) species. In these frozen solution

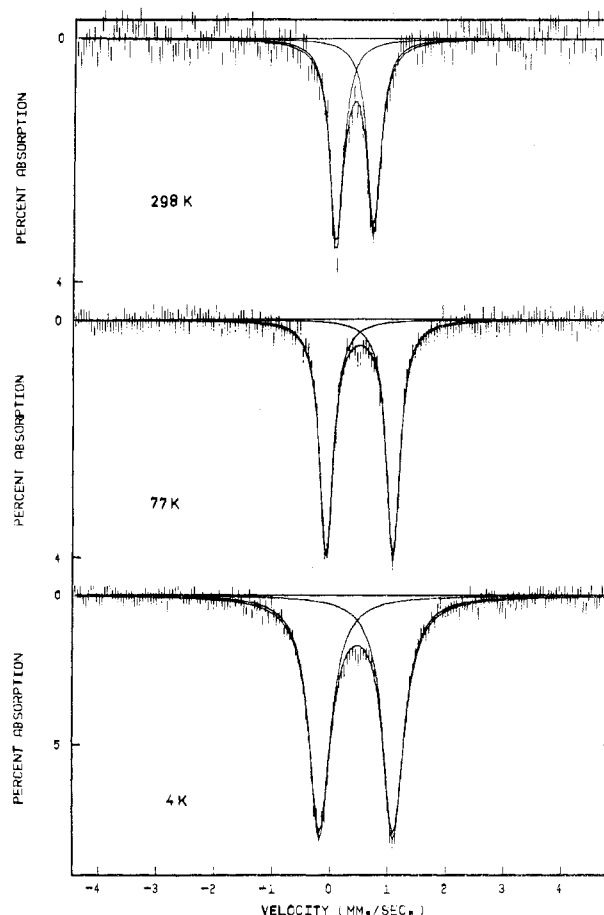


Figure 1. The ^{57}Fe Mössbauer spectra of $(C_6H_5NH_3)_3Fe(S_2C_2O_2)_3 \cdot H_2O$ at 298, 77, and 4 K.

Table III. Mössbauer Data for Frozen Aqueous Solutions of Mixtures of Ferric Salts and Potassium Dithiooxalate at 77°K

$Fe^{3+}:dto^{2-}$	Center shift, $mm \text{ sec}^{-1}$		Quadrupole splitting, $mm \text{ sec}^{-1}$	
	$Fe(III)$	$Fe(II)$	$Fe(III)$	$Fe(II)$
Ferric Nitrate				
1:0.00	~ 0.44		A broad resonance	
1:0.10		1.40		3.45
1:0.4		1.39		3.22
1:1.07 ^a		1.38		3.28
1:2.04		1.33		3.09
1:2.54	0.28	1.39	1.23	2.91
1:2.85	0.31	1.29	1.28	2.90
1:2.99 ^a	0.34	1.36	1.37	3.05
1:3.00	0.33	1.38	1.34	2.93
1:3.91	0.33	1.33	1.26	2.86
1:6.00	0.33	1.55	1.28	2.74
1:6.50 ^a	0.35	1.31	1.25	2.76
Ferric Sulfate				
1:0.00	0.52		0.44	
1:0.50	0.52		0.53	
1:3.00	0.36	1.38	1.34	3.31
1:6.00	0.38	1.42	1.23	3.05

^a From the same batch.

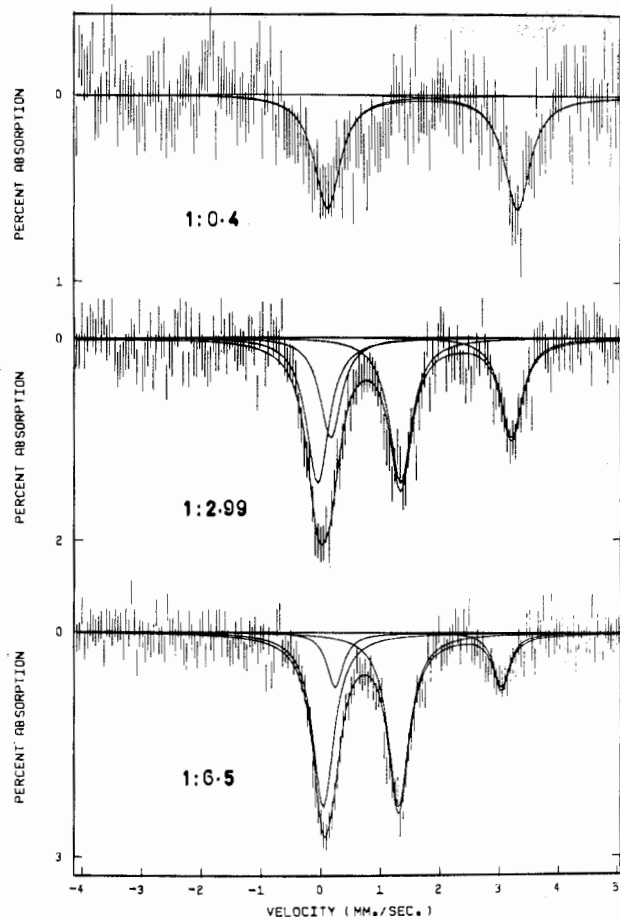


Figure 2. The ^{57}Fe Mössbauer spectra of frozen aqueous solutions of ferric nitrate and potassium dithiooxalate in the ratios $\text{Fe}^{3+}:\text{dto}^{2-}$ of 1:0.4; 1:2.99; 1:6.5.

studies we are aware of the danger, in the quick freezing process, that solute crystallites may segregate from the liquid. However, even if this does happen the presence of Fe(II), in what began as an Fe(III) system, cannot be in any doubt. At low ratios of $\text{Fe}:\text{dto}^{2-}$ the only detectable species is that attributable to high-spin iron(II) and only when the ratio approaches 1:3 is low-spin Fe(III) detectable. This latter species increases in intensity at the expense of the Fe(II) doublet as the ratio is increased and upon addition of a large cation the tris(dithiooxalato)ferrate(III) complex is isolated. The Mössbauer parameters for the Fe(III) species in solution are similar to those for the solid complexes and we therefore assign the resonance having $\delta = \sim 0.3$, $\Delta = \sim 1.3 \text{ mm sec}^{-1}$ to the $[\text{Fe}(\text{dto})_3]^{3-}$ ion. A considerable distortion from O_h symmetry of this ion in solution is reflected in the quadrupole splitting parameter. At low ratios of $\text{Fe(III)}:\text{dto}^{2-}$ only an iron(II) in a high-spin configuration is detectable, i.e., reduction of Fe(III) to Fe(II) has occurred. This does not, however, mean small amounts of dto^{2-} reduce all of the iron(III) present in solution. These facts can be rationalized when one considers that (i) frozen aqueous solutions of ferric nitrate give very broad resonances (ii) and in the presence of a species which gives a less complicated resonance, the ferric nitrate resonance is not readily detectable. Confirmation of this was achieved by examining solutions of ferric sulfate and dto^{2-} where, at low $\text{Fe}:\text{dto}^{2-}$ ratios, the Fe(III) resonance is clearly visible (Table III and Figure 3) and has different Mössbauer parameters from the Fe(III) species, i.e., $[\text{Fe}^{\text{III}}(\text{dto})_3]^{3-}$ observed at higher $\text{Fe}:\text{dto}^{2-}$ ratios.

Reduction of Fe(III) to Fe(II) by dithiooxalate is perhaps not unexpected since oxalates are good reducing agents particularly under acid conditions. The subsequent reoxidation

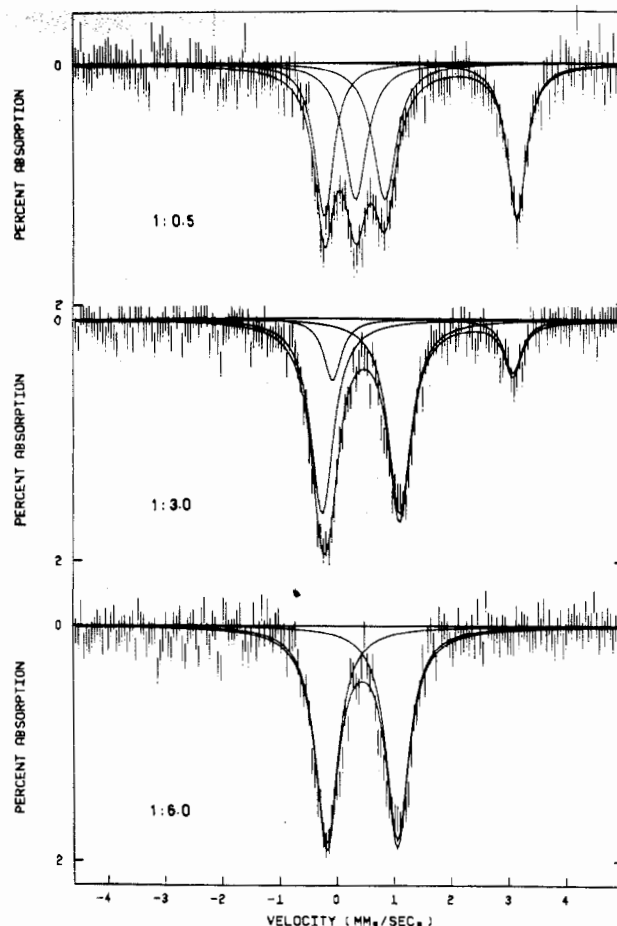


Figure 3. The ^{57}Fe Mössbauer spectra of frozen aqueous solutions of ferric sulfate and potassium dithiooxalate in the ratios $\text{Fe}^{3+}:\text{dto}^{2-}$ of 1:0.5; 1:3.0; 1:6.0.

was, however, surprising. That oxidation does occur is proven beyond doubt by these solution studies and by the fact that Fe(III) complexes are isolated even if iron(II) salts are used initially (Table I). We found that pH of these solutions varied from 3.1 to 4.8 for $\text{Fe}:\text{dto}^{2-}$ ratios 1:0.5 to 1:6.0. In order to see if the spectra were dependent upon pH some were recorded with these solutions buffered at both pH 3.1 and 4.8. At either pH, reduction and subsequent reoxidation occurred. When the solutions were made very acidic (i.e., 10% H_2SO_4) only an iron(II) species was detected but under these conditions no dithiooxalate complexes could be obtained.

The sensitivity of tris(oxalato)ferrates to light has been known for a long time and photochemical oxidation of Fe(II) to Fe(III) can occur,²¹ oxidation of Co(II) to Co(III) in the presence of the oxalate ion. Such a process could account for the reduction and oxidation in our solutions containing iron salts and the dithiooxalate ion. Mössbauer samples were prepared in normal light, in the dark, and also with strong irradiation in both uv and visible regions, but no detectable changes occurred in the spectra recorded. ESR spectra were also recorded under the Mössbauer conditions but no radical species could be detected. In 10% H_2SO_4 solution, radical species were detected and by analogy to the tris(oxalato)ferrate system²² are assigned to hydrogen atoms ($A = 500 \text{ G}$), $\text{HCS}\cdot$ ($A = 130 \text{ G}$) and a singlet which could be $\text{COS}\cdot$ or $\text{COSH}\cdot$. However, as stated earlier, we observed no oxidation of Fe(II) to Fe(III) under these conditions.

Further work on these systems is continuing in an attempt to ascertain the mechanism of the reactions which occur.

Acknowledgment. The National Research Council of Canada is thanked for financial support and the Canadian

International Development Agency for a scholarship to K.M.T.

Registry No. K₂Fe(dto)₃, 28628-06-0; K₂SrFe(dto)₃, 57091-10-8; [Co(en)₃Fe(dto)₃, 57091-11-9; (C₆H₅NH₃)₃Fe(dto)₃, 57091-13-1; [(C₆H₅)₄As]₃Fe(dto)₃, 29836-45-1; [(C₆H₅)₃P)₂Ag]₃Fe(dto)₃, 42531-93-1; [(C₆H₅)₃P)₂Cu]₃Fe(dto)₃, 29836-46-2; [(C₂H₅)₄N]₂Fe(dto)₂(NO), 57091-14-2; [(C₄H₉)₄N]₂Fe(dto)₂(NO), 57091-15-3.

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Preparation and Structure of a New Derivative of Tetra-rhodium Dodecacarbonyl. Further Refinement of the Structure of Tetracobalt Dodecacarbonyl

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Received July 17, 1975

AIC50505S

The reaction of Ph₂PCH₂PPh₂ with Rh₄(CO)₁₂ gives as the major product a brown crystalline solid of composition (Ph₂PCH₂PPh₂)₂Rh₄(CO)₈. The solid compound has very low solubility and ¹³C NMR study of its structure and possible fluxionality was not feasible. The structure has been determined by a single-crystal x-ray study. It is derived from the C_{3v} structure of Rh₄(CO)₁₂ itself. The set of three bridging CO groups along one triangular set of edges is retained, but one terminal CO group on each rhodium atom is replaced by a phosphorus atom. The molecule is without any element of symmetry, rigorous or approximate. Some of the principal dimensions of the molecule are as follows: Rh-Rh, 2.671 (1)–2.740 (1) Å with a mean of 2.711 Å, Rh-P, 2.266 (4)–2.334 (4) Å with a mean of 2.30 Å; Rh-C(terminal), average 1.91 Å; Rh-C(bridge), average 2.09 Å. The crystallographic parameters are as follows: space group C2/c, a = 22.962 (6) Å, b = 17.230 (5) Å, c = 28.946 (8) Å, β = 97.42 (1)°, V = 11356 Å³, Z = 8, d_{calcd} = 1.64 g cm⁻³, d_{obsd} = 1.70 ± 0.02 g cm⁻³. The structure of Co₄(CO)₁₂ has been reinvestigated, in order to test more rigorously the disordered model previously reported by C. H. Wei. Using a much larger and more accurate data set, refinement of Wei's model has been carried to convergence anisotropically (R₁ = 0.078; R₂ = 0.089). The molecular structure (C_{3v}) and the disorder scheme proposed by Wei were confirmed and more precise dimensions have been obtained for the molecule.

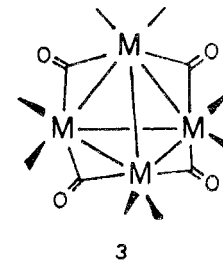
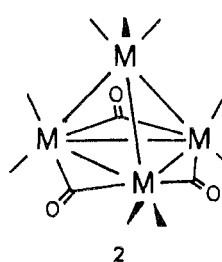
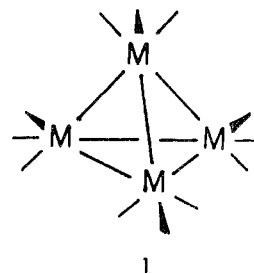
Introduction

The tetranuclear dodecacarbonyls of cobalt, rhodium, and iridium, M₄(CO)₁₂, and their derivatives, M₄(CO)_{12-n}L_n, have provided and continue to provide challenging and important problems concerning their structures, dynamical properties, bonding, and chemistry. Much effort has already been devoted to these problems especially over the last decade. Let us consider first the unsubstituted carbonyls, M₄(CO)₁₂, themselves.

Structurally, the iridium compound has been least troublesome. It has a tetrahedral core of iridium atoms, with three terminal carbonyl groups on each one, so oriented that the entire molecule has T_d symmetry, as shown in **1**. The crystal structure determination apparently presented no unusual features, though no report has yet appeared in the journal literature.¹ The structures of the rhodium and cobalt compounds have been described in detail; both presented difficult technical problems.² The two molecules are isostructural, but solution and refinement of the cobalt structure was rendered difficult by disorder while for the rhodium compound difficulties were caused by twinning. Because of these difficulties, neither structure is known with the accuracy ordinarily obtainable for molecules of this size and type. According to the x-ray work, both Co₄(CO)₁₂ and Rh₄(CO)₁₂ have the structure **2**, which has C_{3v} symmetry.

The question of whether the C_{3v} structure persists in solution has been controversial. The infrared spectra of Co₄(CO)₁₂ and Rh₄(CO)₁₂ are similar and it has been suggested³ that

these spectra, in the CO stretching region, support the structure **3**, although they provide no positive evidence against structure **2**. The probability that all of the structures, **1**, **2**, and **3**, are



of similar stability and that any given molecule might pass easily from one to another was recognized nearly a decade ago,⁴ even before the structural data for the crystalline