Calcd for $C_{24}H_{20}AsF_5Si$: C, 56.9; H, 4.0; As, 14.8; Si, 5.6; F, 18.8. Found: C, 56.6; H, 4.0; As, 14.7; Si, 5.6; F, 19.0. The infrared spectrum, in addition to absorptions characteristic of the cation, showed SiF_5^- peaks at 875 (vs, b), 776 (vs), 794 (vs) (doublet), 476 (s), and 448 (s) cm^{-1}.

Preparation of Tetrafluoroborates.—The tetrafluoroborates containing the tetramethylammonium, tetraethylammonium, tetra-*n*-propylammonium, and tetraphenylarsonium cations were obtained by treating a saturated methanol solution of the corresponding quaternary ammonium halide with an aqueous methanol solution of fluoroboric acid.

Reactions of the Pentafluorosilicate Ion with Donor Molecules.—Excess dry ammonia was condensed onto tetra-*n*-propylammonium pentafluorosilicate at −78° and allowed to stand for 1 hr. Removal of the ammonia at −78° left a white solid smelling strongly of ammonia, which could only be handled under dry nitrogen. The infrared spectrum of this solid did not show the characteristic 874-cm^{-1} band of SiF_5^- but rather bands characteristic of six-coordinate silicon[12] at 720 (vs, b) and 478 (s) cm^{-1}. When a sample of this product was kept under vacuum for 18 hr at 25°, only partial recovery of the ammonia was achieved, but the resulting solid showed the characteristic SiF_5^- infrared absorptions together with N-H absorptions at *ca.* 3300 cm^{-1}. Samples of the ammonia adduct, prepared by removal of excess ammonia from the pentafluorosilicate at −95°, were sealed under vacuum and then opened under concentrated sulfuric acid for determination of total nitrogen by the Kjeldahl method. The product from 0.1635 g of tetra-*n*-propylammonium pentafluorosilicate thus contained 0.0149 g of nitrogen (0.0148 g is required for the 1:1 adduct). The vapor pressure of the adduct in the temperature range −80–40° was determined, giving the data shown in Figure 1. The reversibility of this dissociation was also established by measurements of the vapor pressure during both cooling and warming cycles.

For other donor molecules, adducts could not be isolated, but infrared studies were conducted of acetonitrile solutions which were approximately 0.1 *M* in tetra-*n*-propylammonium pentafluorosilicate with varying concentrations of the base. Observations were made of the relative intensity of the 874-cm^{-1} band, characteristic of the SiF_5^- ion, at various concentrations of the base concerned. Only for diethylamine was the 874-cm^{-1} band destroyed completely at a 1:1 amine:silicon ratio. For pyridine, little interaction was apparent at the 1:1 ratio and five-coordinate silicon was still present at a 10:1 ratio of pyridine to silicon. The order of interaction with SiF_5^- was thus established as: $(C_2H_5)_2NH > (C_2H_5)_3N > (n\text{-}C_3H_7)_3N > C_5H_5N \sim (C_2H_5)_3P$.

Conductivity Measurements.—Conductances were measured at 25° using a dip-type cell of constant 0.1 cm^{-1} connected to a conductivity bridge, Model RC 18, Industrial Instruments Inc. Nitromethane (Fisher Scientific Co.) with a specific conductance of 25×10^{-7} ohm^{-1} cm^{-1} was used without further purification.

Infrared and Raman Spectroscopic Measurements.—Infrared spectra were measured on a Beckman IR 10 spectrometer and, through the courtesy of Dr. A. Lane, on an RIIC interferometer in the low-frequency region. Raman spectra of solutions were obtained on a Cary 81 Raman spectrometer, through the kindness of Dr. D. E. Irish of the University of Waterloo, and of solids on a laser Raman spectrometer, through the kindness of Dr. R. J. Gillespie of McMaster University. Infrared spectra were calibrated against water vapor and polystyrene, and carbon tetrachloride was used to calibrate Raman spectra. Frequencies were measured to an accuracy of ±3 cm^{-1}.

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Mössbauer Spectra of Some Ferric Hydroxamates

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A variety of tris(hydroxamato)iron(III) complexes were prepared and their Mössbauer spectra were obtained. In many cases relaxation effects precluded a straightforward interpretation of peak positions even at room temperature. Otherwise most isomer shifts and quadrupole splittings were confined to a range of values typical of high-spin iron(III) with little covalent bonding. The trisodium salt of tris(benzohydroxamato)iron(III) was prepared pure in two hydrated forms, the higher hydrate apparently displaying a large relaxation effect. Unusually large splittings occurred in tris(salicylhydroxamato)iron(III) and tris(nicotinylhydroxamato)iron(III).

Introduction

Hydroxamic acids are rather weak acids ($pK_a \approx 9$) which have the general formula RCON(R′)OH, where R and R′ are hydrogen or some organic group.[1] In acid solution hydroxamic acids form deeply colored 1:1 complexes with iron(III), a reaction which has been known for a long time and which has been used for both qualitative and quantitative determinations of hydroxamic acids or active acyl compounds which can be converted to hydroxamic acids. In neutral solutions a tris(hydroxamato)iron(III) complex is formed, the hydroxamate anion acting as a bidentate ligand. These are very stable complexes in general, as indicated, for example, by the value of 28.3 for log β_3 for acetylhydroxamate (R = CH_3).[1] Iron(III) complexes of the primary hydroxamic acids (*i.e.*, R′ = H) can be further deprotonated by loss of the nitrogen proton in strongly basic solution. On the basis of visible spectroscopy, Aksnes has proposed the equilibria[2]

$$\underset{\text{medium acidic}}{Fe(RCONHO)^{2+}} \rightleftharpoons \underset{\text{weakly acidic}}{Fe(RCONHO)_2^{+}} \rightleftharpoons \underset{\text{neutral}}{Fe(RCONHO)_3} \rightleftharpoons \underset{\text{strongly alkaline}}{Fe(RCONO)_3^{3-}}$$

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[1] J. B. Neilands, *Struct. Bonding* (Berlin), **1**, 59 (1966).

[2] G. Aksnes, *Acta Chem. Scand.*, **11**, 710 (1957).

Hydroxamic acids are rather widely distributed in nature; they are usually secondary (*i.e.*, R′ is not H) and always form complexes with iron(III).[1] The X-ray structure of one of these naturally occurring (in fungi) complexes, ferrichrome A, has been determined.[3] The iron(III) is octahedrally coordinated to three hydroxamate residues from a cyclic hexapeptide containing N^5-hydroxy-L-ornithine. The exact biological function of the ferrichromes has not yet been determined.

Because of the occurrence of iron(III) hydroxamate complexes in nature and because of their generally very interesting chemical properties, we have begun an investigation of the nature of the bonding between iron(III) and the hydroxamate group $RCONR'O^-$ by Mössbauer spectroscopy. Up to the present, only the Mössbauer spectrum of ferrichrome A has been reported in the literature.[4]

Experimental Section

Starting Materials.—All solvents were reagent grade, as were the ferric nitrate and sodium and potassium hydroxides. Tris(acetylhydroxamato)iron(III) and tris(N-phenylbenzohydroxamato)iron(III) (from Eastman Organic Chemicals), benzohydroxamic acid and salicylhydroxamic acid (from Aldrich Chemical Co.), sodium naphthalhydroxamate, *o*-cresotylhydroxamic acid, and oleylhydroxamic acid (from K & K Laboratories), nicotinylhydroxamic acid (from Nutritional Biochemicals Corp.), and 2-pyridinethiol 1-oxide, sodium salt (from Columbia Organic Chemicals Co.), were used as received.

Preparation of Complexes. Tris(benzohydroxamato)iron(III).—A solution of 4.04 g (0.010 mol) of $Fe(NO_3)_3 \cdot 9H_2O$ in 10 ml of water was added with stirring to a solution of 4.11 g (0.030 mol) of benzohydroxamic acid and 1.2 g (0.030 mol) of sodium hydroxide in 30 ml of water. The thick semisolid brick red mass was filtered and the precipitate was dried at room temperature. The product was recrystallized from hot ethanol and air dried. Large crystals of the complex appear black, smaller crystals are red, and the powder is orange. *Anal.* Calcd for $Fe(C_7H_6O_2N)_3 \cdot 0.5H_2O$: C, 53.30; H, 4.05; N, 8.88. Found: C, 53.40; H, 4.80; N, 8.60.

Trisodium Salt of Tris(benzohydroxamato)iron(III).—A solution of 12.1 g (0.030 mol) of $Fe(NO_3)_3 \cdot 9H_2O$ in 50 ml of water was added with stirring to a solution of 12.3 g (0.090 mol) of benzohydroxamic acid and 3.6 g (0.090 mol) of sodium hydroxide in 120 ml of water. The mixture was filtered and the precipitate was washed with water. The moist filter cake was suspended in 40 ml of water; then 40 g of sodium hydroxide in 60 ml water was added and the mixture was stirred 1 hr at room temperature. The brick red suspension reacted with the sodium hydroxide to give a dark red-brown, crystalline suspension. The mixture was filtered and the precipitate was air dried overnight. The slightly moist product was recrystallized from hot absolute ethanol and the brown crystals were washed with acetone and ether. *Anal.* Calcd for $Na_3[Fe(C_7H_5O_2N)_3] \cdot 6H_2O$ (crystals dried *in vacuo* at room temperature): C, 39.51; H, 4.26; N, 6.58. Found: C, 39.67; H, 4.15; N, 6.19. Calcd for $Na_3[Fe(C_7H_5O_2N)_3] \cdot 3H_2O$ (crystals dried *in vacuo* 5 hr at 90°): C, 43.17; H, 3.62; N, 7.19. Found: C, 43.13; H, 3.76; N, 7.41.

Tris(salicylhydroxamato)iron(III).—A solution of 4.04 g (0.010 mol) of $Fe(NO_3)_3 \cdot 9H_2O$ in 60 ml of water was added with stirring to a solution of 4.59 g (0.030 mol) of salicylhydroxamic acid and 1.68 g (0.030 mol) of potassium hydroxide in 75 ml of water. The red-brown precipitate was collected by filtration, washed with water, and dried in air. The product was dissolved in methanol and precipitated by the addition of ether. The mixture was filtered and the powder was washed well with water and then ether and dried at 50–60° *in vacuo* 4 hr. (Drying at 90° causes some decomposition.) *Anal.* Calcd for $[Fe(C_7H_6O_3N)_3] \cdot 3H_2O$: C, 44.55; H, 4.27; N, 7.42. Found: C, 44.77; H, 4.02; N, 7.64.

Tris(naphthalhydroxamato)iron(III).—A solution of 1.00 g (0.0025 mol) of $Fe(NO_3)_3 \cdot 9H_2O$ in 20 ml of water was added with stirring to a solution of 1.58 g (0.0022 mol) of sodium naphthalhydroxamate in 80–90 ml of water. The orange precipitate was removed by centrifugation, washed well with water and methanol, and allowed to dry in air. The black vitreous mass was ground to an orange-red powder, treated with six 100-ml portions of hot methanol, and dried *in vacuo* 5 hr at 90°. *Anal.* Calcd for $[Fe(C_{12}H_6O_3N)_3] \cdot 2H_2O$: C, 59.36; H, 3.04; N, 5.77. Found: C, 59.36; H, 3.13; N, 5.66.

Tris(oleylhydroxamato)iron(III).—A solution of 2.02 g (0.0050 mol) of $Fe(NO_3)_3 \cdot 9H_2O$ in 20 ml of water was added with stirring to a mixture of 4.50 g (0.015 mol) of oleylhydroxamic acid and 0.84 g (0.015 mol) of potassium hydroxide in 20 ml of water. The solution was decanted from the brown, gummy precipitate which was washed well with water. The gum could not be induced to crystallize; consequently it was not analyzed.

Tris(nicotinylhydroxamato)iron(III).—A solution of 2.02 g (0.0050 mol) of $Fe(NO_3)_3 \cdot 9H_2O$ in 5 ml of water was added with stirring to a solution of 1.85 g (0.015 mol) of nicotinylhydroxamic acid and 0.84 g (0.015 mol) of potassium hydroxide in about 10 ml of water. The brown gum which initially precipitated upon continued stirring soon crystallized to a red-brown powder. The mixture was filtered and the precipitate was air dried. The powder was treated with 30 ml of absolute ethanol at room temperature, the mixture was filtered, and the filtrate was evaporated until clumps of red-brown needles formed. The crystals were dried *in vacuo* 5 hr at 90°. *Anal.* Calcd for $[Fe(C_6H_5O_2N_2)_3] \cdot H_2O$: C, 44.55; H, 3.53; N, 17.32. Found: C, 44.70; H, 3.66; N, 17.52.

Attempted Preparation of Tris(*o*-cresotylhydroxamato)iron(III).—A solution of 2.02 g (0.0050 mol) of $Fe(NO_3)_3 \cdot 9H_2O$ in 10 ml of water was added with stirring to 2.50 g (0.015 mol) of *o*-cresotylhydroxamic acid and 0.84 g (0.015 mol) of potassium hydroxide in 20 ml of water. A small amount of a brown precipitate (ferric hydroxide) formed with simultaneous gas evolution and development of a wintergreen odor. The filtrate was colorless and clear and contained iron(II).

Tris(pyridine 1-oxide 2-thiolato)iron(III).—A solution of 2.02 g (0.0050 mol) of $Fe(NO_3)_3 \cdot 9H_2O$ in 25 ml of water was added with stirring to 2.25 g (0.015 mol) of the sodium salt of 2-pyridinethiol 1-oxide dissolved in 75 ml of water. The blue-black precipitate was collected by filtration, washed with water, and allowed to dry in air overnight. The powder was extracted with 500 ml of methylene chloride, the mixture was filtered, and the filtrate was evaporated until crystals formed. These black crystals were dried *in vacuo* at room temperature, redissolved in methylene chloride, reprecipitated by addition of ether, and dried *in vacuo*. *Anal.* Calcd for $[Fe(C_5H_4ONS)_3]$: C, 41.48; H, 2.79; N, 9.67. Found: C, 41.46; H, 2.80; N, 10.22.

Mössbauer spectra were obtained using a constant-acceleration drive operated in the time mode and a 400-channel analyzer. Velocity scale calibration and the isomer shift reference point were obtained by frequent measurements of sodium nitroprusside. A computer was used to find the positions and amplitudes of the peaks, assuming Lorentzian line shapes.

Infrared spectra were obtained on a Beckman Model IR-8 recording spectrophotometer on Nujol mulls.

Results

The following compounds were prepared analytically pure: tris(benzohydroxamato)iron(III), the trihydrate and hexahydrate of the trisodium salt of tris-

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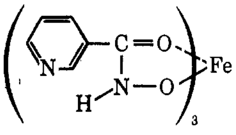
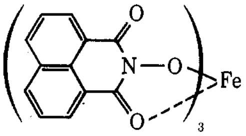
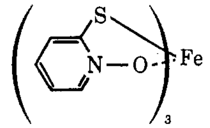
[3] A. Zalkin, J. D. Forrester, and D. H. Templeton, *Science*, **146**, 261 (1964).

[4] H. H. Wickman, M. P. Klein, and D. A. Shirley, *Phys. Rev.*, **152**, 345 (1966).

(benzohydroxamato)iron(III), tris(salicylhydroxamato)iron(III) trihydrate, tris(nicotinylhydroxamato)-iron(III) monohydrate, tris(naphthalhydroxamato)-iron(III) dihydrate, and tris(pyridine 1-oxide 2-thiolato)iron(III). These last three have the respective structures







The water is held very tightly in most of these complexes. It is retained even upon recrystallization from ethanol and drying *in vacuo* in some cases at 90°.

In addition to these, tris(acetylhydroxamato)iron-(III) and tris(N-phenylbenzohydroxamato)iron(III) were available commercially.

The Mössbauer spectra of these complexes were measured at room temperature and at liquid nitrogen temperature. These were all fitted with two lines, which were generally unequal in width and amplitude. From the positions of the two lines the values of the isomer shift, δ, and quadrupole splitting, Δ, listed in Table I were obtained. It is recognized that high-spin ferric ion spectral lines are usually broadened by relaxation effects even at room temperature. In the literature such broadening has generally been ignored in the reporting of Δ and δ values, usually with justification. The series of hydroxamate complexes reported here covered a wide range of relaxation effects. In the more severe cases such effects have rendered invalid the Δ and δ values naively derived as above, and before discussing any trends the validity of the Δ and δ values had to be judged. Some criteria used in making this judgment were (a) the ratio of line widths and amplitudes, (b) the reciprocity of these two ratios, and (c) the temperature dependence of apparent δ and Δ values. To give some indication of the extent of relaxation effects, Table I includes the ratios of line amplitudes, the higher energy line being the shorter in every case. Error limits of ±0.01 mm/sec can be assigned to δ values and ±0.03 mm/sec to the Δ values, based upon the reproducibility of replicate measurements, including the curve fitting.

Computer-fitted curves for $Fe(npbz)_3$, $Fe(bz)_3 \cdot 0.5H_2O$, and $Na_3[Fe(bz\text{-}H)_3] \cdot 6H_2O$ at room temperature are shown in Figures 1–3. Data for $Fe(bz)_3 \cdot 0.5H_2O$ at liquid helium temperature are shown in Figure 4. No attempt was made to fit the liquid helium curves which generally indicated large relaxation effects. As indicated in Figures 1–3 very large relaxation effects also precluded obtaining valid δ and Δ values for $Fe(bz)_3 \cdot 0.5H_2O$, $Fe(npbz)_3$, or $Na_3[Fe(bz\text{-}H)_3] \cdot 6H_2O$.

There are two geometrical isomers possible for octa-

TABLE I

MÖSSBAUER PARAMETERS OF FERRIC HYDROXAMATES[a]

	300°K			77°K		
Compound[b]	δ	Δ	R	δ	Δ	R
$Fe(sal)_3 \cdot 3H_2O$	0.67	1.07	1.1	0.79	1.06	1.0
$Fe(ac)_3$[c]	0.68	0.69	1.2	0.79	0.68	1.2
$Fe(ol)_3$[c]	...[d]	...	...	0.74	0.81	1.0
$Fe(nic)_3 \cdot H_2O$	0.67	1.03	1.4	0.77	1.05	1.3
$Fe(nph)_3 \cdot 2H_2O$	0.62	0.80	1.1	0.76	0.92	1.1
$Na_3[Fe(bz\text{-}H)_3] \cdot 3H_2O$	0.65	0.80	1.4	0.75	0.83	1.4
$Fe(pto)_3$	0.65	0.65	1.3	0.78	0.67	1.3

[a] δ is the isomer shift with respect to a sodium nitroprusside absorber; Δ is the quadrupole splitting in mm/sec; R is the ratio of line intensities. [b] Abbreviations: bz, benzohydroxamate, $C_7H_6O_2N$; bz-H, $C_7H_5O_2N$; sal, salicylhydroxamate, $C_7H_6O_3N$; nic, nicotinylhydroxamate, $C_6H_5O_2N_2$; ac, acetylhydroxamate, $C_2H_4O_2N$; ol, oleylhydroxamate, $C_{18}H_{34}O_2N$; nph, naphthalhydroxamate, $C_{12}H_6O_3N$; npbz, N-phenylbenzohydroxamate, $C_{13}H_{12}O_2N$; pto, pyridine 1-oxide 2-thiolate, C_5H_4ONS. [c] Extent of hydration unknown. [d] Effect too small to measure.

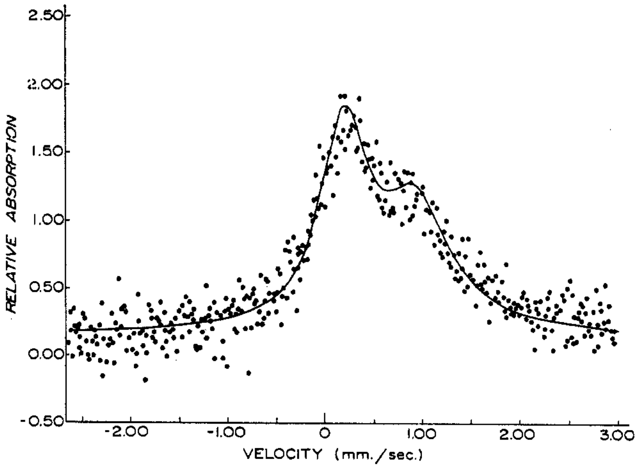


Figure 1.—Mössbauer spectrum of $Fe(npbz)_3$ at room temperature.

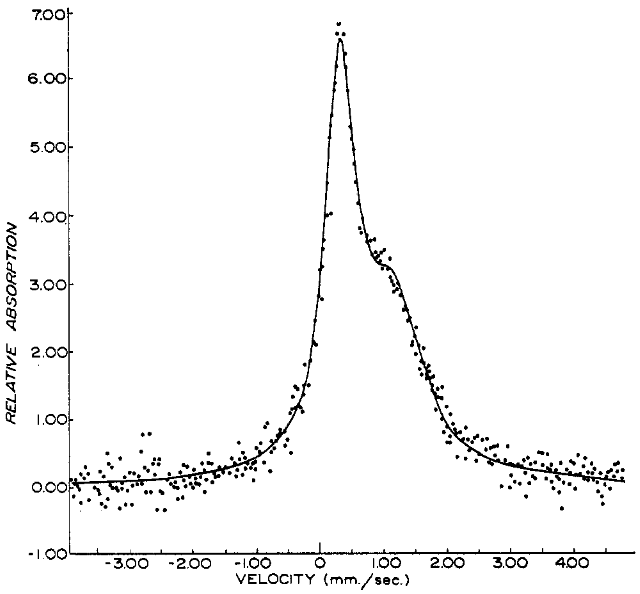


Figure 2.—Mössbauer spectrum of $Fe(bz)_3 \cdot 0.5H_2O$ at room temperature.

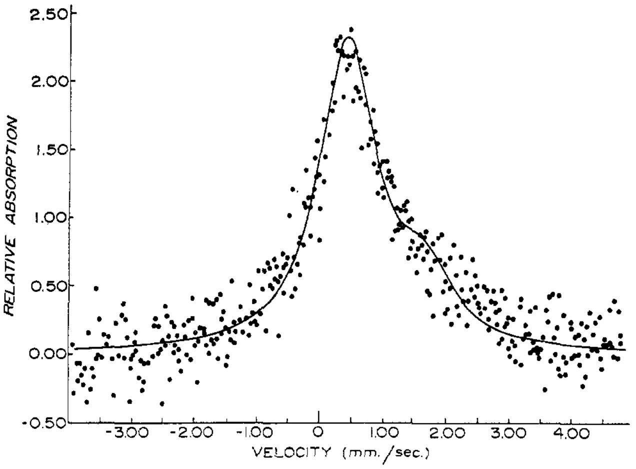


Figure 3.—Mössbauer spectrum of $Na_3[Fe(bz\text{-}H)_3]\cdot 6H_2O$ at room temperature.

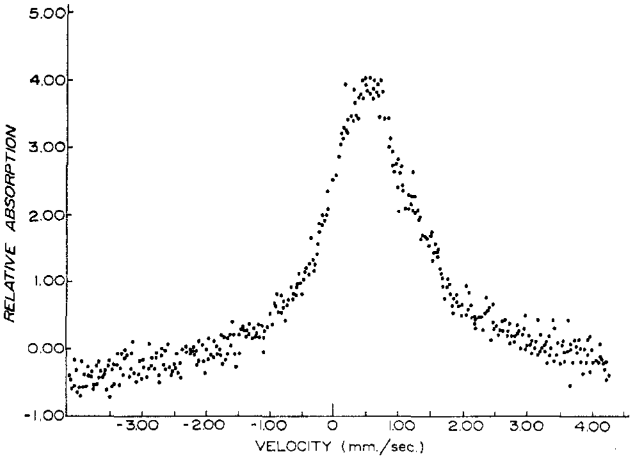
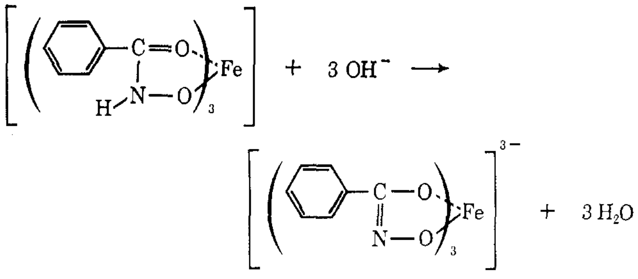


Figure 4.—Mössbauer spectrum of $Fe(bz)_3\cdot 0.5H_2O$ at liquid helium temperature.

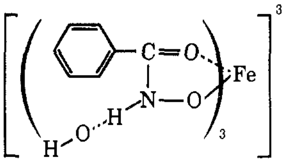
hedrally situated ions coordinated to three unsymmetrical bidentate ligands (*i.e.*, $M(AB)_3$ type): the facial or 1,2,3 isomer and the meridional or 1,2,6 isomer. Separation of these two geometrical isomers has not been reported in the literature for any tris(hydroxamato)iron(III) complex. Evidence that such separation might be possible by fractional crystallization from ethanol was obtained in the tris(nicotinylhydroxamato)-iron(III) case, as the crude product appeared to consist of two fractions: one quite soluble in ethanol and the other less soluble. Only the more soluble fraction was used in the present investigation. The separation of the pure geometrical isomers (assuming that both isomers are formed in the reaction) was not actively pursued for the present investigation because it was felt that the Mössbauer spectra of the two isomers should be quite similar: one certainly expects little difference in the isomer shift because the iron in both isomers is surrounded by oxygen atoms and the local symmetry, or microsymmetry, about each iron is thus identical with that about the other.

The deprotonation which the primary hydroxamate complexes undergo in strongly basic solution is a very interesting reaction. Such deprotonation was conjectured by Aksnes[2] to explain changes in the visible spectra of tris(acetylhydroxamato)iron(III) and tris-(benzohydroxamato)iron(III) with changes in the pH of the solution. The first analytically pure, crystalline trisodium salt was prepared by us for the present investigation from tris(benzohydroxamato)iron(III)



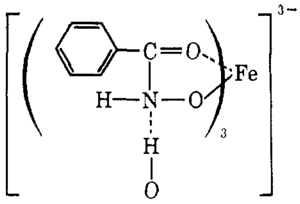
I

The salt is a water-soluble, brown, crystalline powder which was obtained initially as the hexahydrate. Upon heating *in vacuo* the trihydrate was formed. The last three water molecules are held very firmly by the complex, probably owing to strong hydrogen bonds. The infrared spectrum, taken on a Nujol mull, of $Fe(bz)_3\cdot 0.5H_2O$ shows a weak NH band at about 3170 cm^{-1}. In the spectrum of $Na_3[Fe(bz\text{-}H)_3]\cdot 6H_2O$, there is a broad peak at about 3350 cm^{-1}, due to OH, and a broad, poorly defined shoulder (on the CH peak) at about 3150 cm^{-1}, probably due to NH. There is also a strong peak at 958 cm^{-1} shown by the hexahydrate, but not by $Fe(bz)_3.0.5H_2O$. The spectrum of $Na_3[Fe(bz\text{-}H)_3]\cdot 3H_2O$ resembles that of the hexahydrate, but the OH and NH peaks are extremely weak. The hydrated sodium salts should perhaps be formulated with anions containing hydrogen-bonded hydroxide, *e.g.*



II

or



III

Mössbauer Spectra.—In order to observe the effect of salt formation on δ and Δ, the Mössbauer spectra of all the primary hydroxamate complexes in Table I dissolved in concentrated aqueous sodium hydroxide were measured. Although decreases in both δ and Δ did occur, we were unable to rule out the possibility that during the measurement decomposition to hydrated ferric oxide had taken place (these complexes are known to be unstable in strongly basic solution). Consequently, we report only the data obtained on the analytically pure trisodium salt of tris(benzohydroxamato)iron(III). The isomer shift for the trihydrate salt (see Table I) is slightly less (at both temperatures) than the values exhibited by the three best behaved compounds $Fe(sal)_3\cdot 3H_2O$, $Fe(ac)_3$, and $Fe(nic)_3 \cdot H_2O$, which we will term the "normal" values. (These δ values are among the largest observed for ferric ions and substantiate the primarily ionic character of the bonding.) Unfortunately, a comparative reproducible δ value for the parent compound, $Fe(bz)_3 \cdot 0.5H_2O$, cannot be cited until the question of a variable relaxation time is settled.

The difficulty encountered in obtaining reproducible data for the three compounds $Fe(bz)_3 \cdot 0.5H_2O$, $Fe(npbz)_3$, and $Na_3[Fe(bz\text{-}H)_3] \cdot 6H_2O$ may be morphological in origin, with the longest relaxation times characteristic of the most perfect crystals. Similar behavior has been noted for certain alums by Campbell and DeBenedetti.[5] The argument that loss of water of hydration leads to concentration of the iron ions and hence to reduced spin–spin relaxation time could be applied in that case and also to our hexahydrate case. There was a striking difference in the character of the spectra between the trihydrate and the hexahydrate. In the other two ill-behaved cases some explanation other than just concentration would seem to be required.

The compounds $Fe(nph)_3 \cdot 2H_2O$ and $Fe(npbz)_3$ contain secondary hydroxamate ligands. The δ value for the $Fe(nph)_3 \cdot 2H_2O$ complex was slightly less than normal. Despite the well-resolved spectra, the Mössbauer parameters are unusual in that (a) the temperature shift for δ is somewhat higher than expected and (b) the temperature dependence of Δ is large for a high-spin ferric complex. These values were confirmed by repeated syntheses and measurements of the complex. The spectra of $Fe(npbz)_3$ were dominated by relaxation effects but the various estimates for δ were notably lower than normal.

The $Fe(pto)_3$ complex was investigated to determine the effect of substituting sulfur for oxygen. The effect on δ was slight, considering both 300 and 77°K values, and suggests little if any additional covalency due to sulfur. The splitting, Δ, was the smallest, matched only by that of $Fe(ac)_3$.

The splitting in high-spin ferric complexes is dominated by the lattice contribution and in these complexes will depend on (a) departure from octahedral symmetry and (b) inequality of charge on the two coordinating atoms. Except for the nph and pto ligands, and possibly the salts, the chelating ring is the same, and large differences in the geometry are not expected. All of the Δ values are large compared to ferric complexes with six equivalent ligands because of the intrinsic difference between the bonding oxygens. From consideration of resonance structures, one might have expected the aromatic hydroxamates to have greater equality of charge on the coordinating oxygens, yet both $Fe(sal)_3 \cdot 3H_2O$ and $Fe(nic)_3 \cdot H_2O$ exhibited the largest splittings, the Δ values being near the limit observed for high-spin ferric ions. The trend in $Fe(bz)_3 \cdot 0.5H_2O$ results is toward a Δ value of about 0.8 mm/sec, still notably large. The very large Δ's for $Fe(sal)_3 \cdot 3H_2O$ and $Fe(nic)_3 \cdot H_2O$ may be related to the fact that they contain Lewis base groups in the ring.

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Vibrational Spectra and Structure of Organolead Compounds. II. Tetraphenyllead, Hexaphenyldilead, Triphenyllead Halides, and Diphenyllead Dihalides[1]

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The infrared and Raman spectra of tetraphenyllead and of hexaphenyldilead have been recorded over the range 4000–70 cm^{-1} and assignments for the various fundamentals have been made. The spectra have been recorded both in the solid state and in solution. Those of hexaphenyldilead are consistent with the staggered ethane-type structure; the Pb–Pb stretching frequency in this molecule is at 114 cm^{-1} in the solid state and at 109 cm^{-1} in solution. The triphenyllead halides and the diphenyllead dihalides, where soluble, are shown to behave as monomers in benzene solution, and their infrared and Raman spectra over the range 450–70 cm^{-1} have been assigned satisfactorily on this basis. In the solid state, however, the spectra, as well as other evidence, suggest that the mono- and dihalides are polymeric by way of halogen bridging. Triphenyllead chloride in benzene or in cyclohexane solution shows an isotopic splitting of the Pb–Cl stretching mode of $\sim$6 cm^{-1}.

In part I of this series,[1] the infrared and Raman spectra of the trimethyllead halides and the dimethyllead dihalides were studied in the solid state as well as in solution. The compounds were shown to be monomeric in solution, but halogen-bridged polymeric in the solid state. The present investigation was aimed at making a similar study of the corresponding phenyl compounds, *viz.*, $(C_6H_5)_3PbX$ (X = F, Cl, Br,

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[1] Part I: R. J. H. Clark, A. G. Davies, and R. J. Puddephatt, *J. Am. Chem. Soc.*, **90**, 6923 (1968).