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Mössbauer Spectra of Some Tris(N,N-disubstituted dithiocarbamato)iron(III) Compounds

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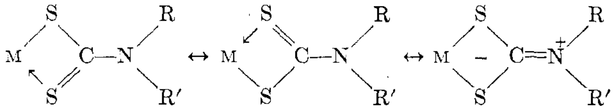
Mössbauer spectra have been measured at room temperature and at liquid nitrogen temperature for 24 tris(N,N-disubstituted dithiocarbamato)iron(III) complexes, 10 of which were unreported hitherto. There are no systematic variations in isomer shift but the quadrupole splittings are quite sensitive to the nature of the nitrogen substituents and to temperature. Ligands with straight-chain alkyl substituents on nitrogen and those ligands derived from cyclic secondary amines give small room-temperature splittings and have been interpreted as favoring covalent iron–sulfur bonding.

Introduction

The tris N,N-disubstituted dithiocarbamate complexes of iron(III), first prepared by Delepine in 1908,[1] have been the subject of numerous investigations since Cambi and his coworkers, in a long series of publications,[2–8] reported the preparation and discussed the chemical and physical properties, especially the very peculiar magnetic behavior, of a large number of these complexes. The iron(III), octahedrally coordinated by six sulfur atoms from the three bidentate ligands (the complexes are monomeric in solution),[9,10] exists in both low-spin ($^2T_2$) and high-spin ($^6A_1$) states in thermal equilibrium.[9,11] It appears that these complexes, among those of the Fe(III) S_6 type, are unique in that, for most of the complexes, the energy separation between the two spin states is very small at room temperature. The tris(N-monosubstituted dithiocarbamato)iron(III) compounds are typical high-spin complexes,[2,7] and similar bidentate sulfur ligands with -1 charge give either high-spin (*e.g.*, $(C_2H_5O)_2PS_2^-$)[12] or low-spin (RCS_2^-, $C_2H_5OCS_2^-$)[7,13]iron(III). Evidence has been presented that ferrihemoprotein hydroxides also exist in two spin states.[14] Similar equilibria between high-spin (*e.g.*, $^5T_2$) and low-spin (*e.g.*, $^1A_1$) states have been well established for several iron(II) compounds.[15–18]

In addition to the magnetic susceptibility measurements, Mössbauer,[19–24] nmr,[25,26] and electronic spectra[9,11,12] and X-ray absorption edges[27] have been measured for several tris(dithiocarbamato)iron(III) complexes.[28] The spectral properties show a very great dependence on the nitrogen substituent in the dithiocarbamate and on temperature.

The structure of a metal–dithiocarbamate linkage can be written as [29–32]



1 2 3

There is very strong evidence that canonical form **3** is an important contributor to the structure for a variety of transition metal ions (Ni(II), Cu(II), Fe(III), etc.) both from infrared spectroscopy,[29,30] which shows a C–N bond intermediate between a single and double bond, and from X-ray diffraction data,[33] which show C–S and C–N bonds of intermediate character, and the planarity of the MS_2CNC_2 grouping. [Unfortunately the X-ray structures of only two iron dithiocarbamate complexes, *viz.*, chlorobis(N,N-diethyl-

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TABLE I

ABBREVIATIONS USED FOR $RR'NCS_2^-$

R	R'	Abbrev	R	R'	Abbrev
CH_3	CH_3	ME	i-C_3H_7	$C_6H_5CH_2$	IPRBZ
C_2H_5	C_2H_5	ET	i-C_3H_7	C_6H_{11}	IPRCHX
n-C_4H_9	n-C_4H_9	NBU	C_6H_5	C_6H_5	PH
i-C_4H_9	i-C_4H_9	IBU	CH_3	C_6H_5	MEPH
s-C_4H_9	s-C_4H_9	SBU	C_2H_5	C_6H_5	ETPH
n-C_5H_{11}	n-C_5H_{11}	NPN	Picolyl	Picolyl	PC
n-C_6H_{13}	n-C_6H_{13}	NHX	$-CH_2CH_2CH_2CH_2-$		PYR
n-C_7H_{15}	n-C_7H_{15}	NHP	$-CH_2CH_2CH_2CH_2CH_2-$		PIP
CH_3	n-C_8H_{17}	MEOCT	$-CH_2CH_2CH_2CH_2CH_2CH_2-$		HMI
C_6H_{11}	C_6H_{11}	CHX			
CH_3	C_6H_{11}	MECHX			
$C_6H_5CH_2$	$C_6H_5CH_2$	BZ			AZA
CH_3	$C_6H_5CH_2$	MEBZ			

TABLE II

ANALYTICAL RESULTS FOR TRIS(N,N-DISUBSTITUTED DITHIOCARBAMATO)IRON(III) COMPOUNDS

Compd	% C		% H	
	Calcd	Found	Calcd	Found
$Fe(PIP)_3$	40.28	40.83	5.63	5.71
$Fe(AZA)_3$	49.37	50.32	6.44	6.37
$Fe(HMI)_3$	43.58	43.62	6.27	5.94
$Fe(NHP)_3$	58.66	59.20	9.85	9.52
$Fe(IPRBZ)_3$	54.38	54.64	5.81	5.72
$Fe(MEOCT)_3$	50.67	51.54	8.51	8.28
$Fe(PC)_3$[a]	53.29	53.67	4.13	4.33

[a] Calcd: N, 14.34. Found: N, 14.39.

dithiocarbamato)iron(III)[34] and nitrosyliron bis(N,N-dimethyldithiocarbamate),[35] have been determined to date.]

Experimental Section

Starting materials were of reagent grade and were used without further purification.

Preparation of Complexes.—Most of the complexes were prepared following Cambi's method,[5,6,9] from a slurry of freshly precipitated ferric hydroxide in absolute ethanol by adding the secondary amine and then an equimolar amount of carbon disulfide, with stirring. The ferric hydroxide was in excess. Recrystallization by ethanol precipitation from benzene solution was repeated twice. Samples for elemental analyses were dried under vacuum over refluxing water for 2-4 hr. Because Cambi's work indicated some of these complexes (*e.g.*, the di-*n*-butyl case) existed in different forms with different magnetic susceptibilities,[8] depending on the previous temperature of the sample, the samples for Mössbauer work were dried under vacuum at a temperature not exceeding 56° (refluxing acetone) for 1–2 hr.

The above procedure was modified for those cases involving complexes soluble in absolute ethanol: the dipicolyl-, methyloctyl-, di-*sec*-butyl-, diisobutyl- and isopropylcyclohexyl-substituted complexes. The ethanol filtrate from the original reaction mixture was added to the chloroform extract of the filter cake, and the mixture was filtered and evaporated to dryness under vacuum at room temperature. The brownish black to black mass obtained was then recrystallized from hot petroleum ether or petroleum ether (bp 35–65°)–diethyl ether mixtures and dried as the other compounds. However, tris(N,N-dipicolyldithiocarbamato)iron(III) was best recrystallized by ether precipitation from benzene solution.

Diphenylamine does not react under the above conditions. Tris(N,N-diphenyldithiocarbamato)iron(III) was prepared by adding dropwise, with stirring at room temperature, a filtered solution of anhydrous iron(III) chloride in anhydrous ethanol to a filtered ethanolic solution of sodium N,N-diphenyldithiocarbamate (molar ratio of iron(III) to the dithiocarbamate was $1:>3$).[1,9,36] The brownish black precipitate was collected, sucked almost dry, and then extracted immediately with chloroform. (On the two occasions when the crude precipitate was allowed to dry in air overnight, extensive hydrolysis had taken place and only a little of the complex could be extracted into the chloroform.) The chloroform solution was treated in the standard manner.

Initial attempts to prepare tris(N,N-ethylenedithiocarbamato)-iron(III) and tris(N,N-dipropargyldithiocarbamato)iron(III) by the general method using ferric hydroxide were unsuccessful.

Because the systematic names of the tris(N,N-disubstituted dithiocarbamato)iron(III) complexes are cumbersome to use, abbreviations will be used in the remainder of this paper. A list of such abbreviations for the ligands under consideration is given in Table I. Most of the tris(N,N-disubstituted dithiocarbamato)-iron(III) complexes prepared for this investigation have already been well described in the literature and for this reason were not analyzed. Seven samples were analyzed, however, and the results are given in Table II.

Methyl Iodide Adduct of Tris(N,N-dipicolyldithiocarbamato)-iron(III).—A nearly saturated benzene solution of tris(N,N-dipicolyldithiocarbamato)iron(III) (100 ml) was treated with 5 ml of methyl iodide. A fine brown precipitate slowly formed. The mixture was allowed to stand at room temperature for 21 hr and filtered. The precipitate was washed well with benzene, methylene chloride (which caused the fine powder to become a hard gum), ether, absolute ethanol, and, finally, again ether. The dark brown powder was insoluble in benzene, ether, methylene chloride, and acetone, very slightly soluble in absolute ethanol, and soluble in methanol and water, giving deep brown solutions. *Anal.* Calcd for $[Fe(PC)_3] \cdot 4.5CH_3I \cdot 1.5CH_2Cl_2$: C, 32.86; H, 3.22; N, 7.66; I, 34.71. Found: C, 33.06; H, 4.05; N, 7.75; I, 34.68.

Mössbauer spectra were obtained using a constant acceleration drive in the time mode and a 400 channel analyzer.[37] Velocity scale calibration and isomer shift reference point were obtained by frequent measurements of sodium nitroprusside. Peak positions and approximate line widths were read from the oscilloscope or from a plot of the data. In the case of overlapping

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Table III

Mössbauer Results for Tris(N,N-disubstituted dithiocarbamato)iron(III) Complexes[a]

Complex	Room temp δ	Room temp Δ	Liquid nitrogen temp δ	Liquid nitrogen temp Δ
$Fe(ME)_3$	0.64	0.27	0.74	0.68
$Fe(ET)_3$	0.66	0.26	0.72	0.55
$Fe(NBU)_3$	0.63	0.19	0.75	0.66
$Fe(IBU)_3$	0.64	0.27	0.74	0.68
$Fe(SBU)_3$	0.62	0.48	0.73	0.94
$Fe(NPN)_3$	0.64	0.27	0.75	0.74
$Fe(NHX)_3$	0.62	0.27	...	...
$Fe(NHP)_3$	0.67	0.20	0.72	0.69
$Fe(MEOCT)_3$	0.65	0.13	...	~0.5
$Fe(CHX)_3$	0.64	0.58	0.72	0.73
$Fe(MECHX)_3$	0.63	0.26	0.75	0.76
$Fe(BZ)_3$	0.64	0.44	0.74	0.98
$Fe(MEBZ)_3$	0.66	0.41	0.75	0.98
$Fe(IPRBZ)_3$	0.63	0.47	...	...
$Fe(IPRCHX)_3$	0.63	0.31	0.74	0.54
$Fe(PH)_3$	0.64	0.43	...	...
$Fe(MEPH)_3$	0.64	0.55	0.72[b]	0.84[b]
$Fe(ETPH)_3$	0.67	0.31	0.71[b]	0.52[b]
$Fe(PC)_3$	0.63	0.56	...	...
$[Fe(PC)_3] \cdot 4CH_3I$	0.64	0.49	0.70	1.00
$Fe(PYR)_3$	0.65	0.22	...	~0.6
$Fe(PIP)_3$	0.64	0.23	0.74	0.74
$Fe(HMI)_3$	0.64	0.26	0.76	0.85
$Fe(AZA)_3$	0.65	0.21	0.75	0.61

[a] δ is the center shift (isomer shift) with respect to a sodium nitroprusside absorber. Δ is the quadrupole splitting. All values are in mm/sec. [b] Literature values.[19]

lines, the true peak positions were determined from tables of corrections computed for this purpose.

Results

Twenty-four different tris(N,N-disubstituted dithiocarbamato)iron(III) complexes were prepared, of which the following have not appeared in the literature: $Fe(MEOCT)_3$, $Fe(MECHX)_3$, $Fe(MEBZ)_3$, $Fe(IPRBZ)_3$, $Fe(IPRCHX)_3$, $Fe(PH)_3$, $Fe(HMI)_3$, $Fe(AZA)_3$, and $Fe(PC)_3$. In addition, a methyl iodide adduct of $Fe(PC)_3$ was prepared.

Mössbauer spectra were recorded for all of the complexes at room temperature and for most of the complexes also at liquid nitrogen temperature. The data obtained from these measurements are given in Table III. The spectra, at room temperature, consisted of simple doublets usually well resolved with narrow peaks, but in a few cases so badly overlapping as to appear as almost singlets (*e.g.*, $Fe(NBU)_3$ and $Fe(MEOCT)_3$). However, at liquid nitrogen temperature all spectra were well-resolved doublets, the quadrupole splittings having increased remarkably. Moreover, the peaks were 2–3 times as broad as they were at room temperature. Two complexes were measured at intermediate temperatures: $Fe(CHX)_3$ at 232°K had $\delta = 0.67$ and $\Delta = 0.67$ mm/sec and $Fe(PIP)_3$ at 235°K had $\delta = 0.72$ and $\Delta = 0.38$ mm/sec. Representative spectra are shown in Figures 1 and 2.

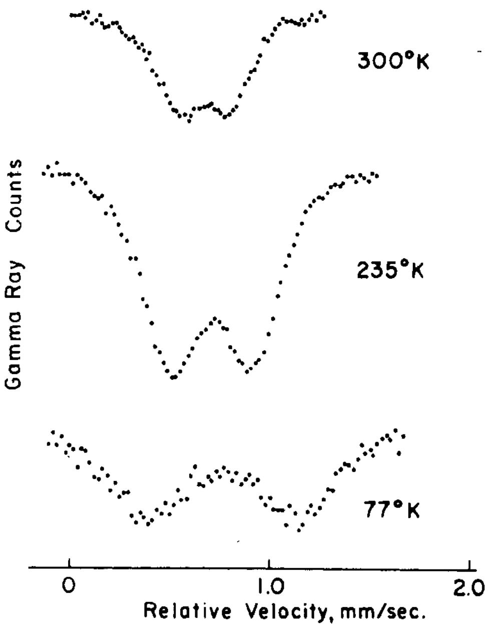

Figure 1.—Mössbauer spectra of $Fe(PIP)_3$ at three temperatures.

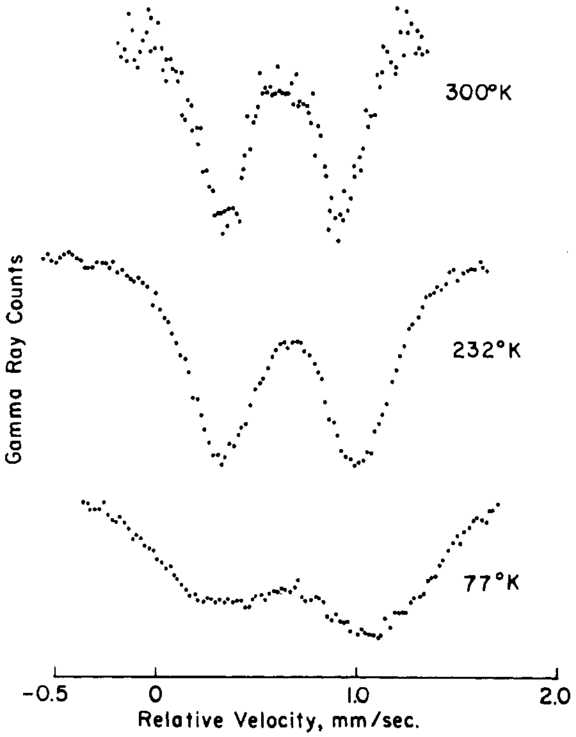

Figure 2.—Mössbauer spectra of $Fe(CHX)_3$ at three temperatures.

The experimental error based on replicate measurements was ±0.01 mm/sec for both δ and Δ. However Δ values at room temperature for NBU, NHP, and MEOCT are uncertain because the doublet was not resolved. It is only accurate to say they are no greater than 0.20 mm/sec.

Discussion

There is considerable evidence from measurements of several physical properties that the iron(III) ion in a tris(N,N-disubstituted dithiocarbamato)iron(III) complex is in thermal equilibrium between high-spin and low-spin states at ordinary temperatures.[9,11] The earliest discovered and perhaps the most unusual property of these complexes is an anomalous magnetic behavior. The magnetic moments at room temperature are intermediate between the limiting values of 2.3 BM for low-spin and 5.9 BM for high-spin octahedral iron(III). In view of these facts, two doublets might be expected in the Mössbauer spectrum—one doublet with small splitting corresponding to the high-spin state and a second doublet with large splitting for the low-spin state. Only one doublet has been discerned for all of the complexes so far reported, although there have been recent observations to the contrary.[38] The observation of a single doublet for a mixed-spin state complex implies that the time to change from one form to another is shorter than the lifetime of the Fe^{57} excited state (1.45×10^{-7} sec), so that the Mössbauer resonance "sees" only an average of the EFG's of the two states.[20] This is not a unique situation; the same condition prevails for certain iron(II) complexes.[15] On the other hand, Renovitch and Baker[17] have observed two doublets (at 77°K) in the Mössbauer spectrum of $Fe(amp)_3^{2+}$ (amp = 2-aminomethylpyridine), due to the two spin states of the iron(II), in equilibrium, but with long spin state lifetimes. Two forms are also found in the spectra of certain pyrazolylborate complexes.[18]

If it is assumed (to the first approximation) that the crystal field about the iron(III) in the tris(N,N-disubstituted dithiocarbamato)iron(III) complexes is essentially cubic, then the ground state for the weak-field case (small *Dq*) is $^6A_{1g}(t_{2g}^3e_g^2)$, arising from the ^6S ground state of the free ion. For the strong-field case (large *Dq*) the ground state is $^2T_{2g}(t_{2g}^5)$, arising from the ^2I excited state of the free ion. At a certain value of the splitting *Dq*, the two levels must cross. The field strength of the dithiocarbamate ligand places these iron(III) complexes in a region near the $^6A_{1g}$–$^2T_{2g}$ crossover point, so that the higher energy state is appreciably populated thermally at room temperature.[11, 28] This means that the $^6A_{1g} - {}^2T_{2g}$ energy difference must not be more than a few hundred wave numbers for most of the N,N-disubstituted dithiocarbamates so far studied. This energy difference is itself a small difference between two large energy values, the crystal field splitting and the electron pairing, and hence will be very sensitive to the Fe–S distance. Consequently, at higher temperatures as the Fe–S distance increases, the $^6A_{1g}$ state becomes firmly established as the ground state. At sufficiently low temperatures, the $^2T_{2g}$ state is the ground state.

The Mössbauer spectrum, interpreted in all cases as one doublet, is characterized by two parameters—δ, the isomer shift, and Δ, the quadrupole splitting. The δ values were insensitive to the nature of the nitrogen substituent averaging 0.64 ± 0.01 mm/sec at room temperature (see Table III). The liquid nitrogen average value, 0.74 ± 0.01 mm/sec, is shifted by the amount normally expected for the second-order Doppler effect. The value 0.64 mm/sec is not far from the limit of about 0.70 mm/sec found for highly ionic ferric salts, despite the fact that other properties (*e.g.*, optical and nmr spectra) reveal considerable covalent bonding. The difference is small because of the two contrary effects of covalency; *viz.*, donation of electrons by sulfur to iron will reduce the isomer shift insofar as the iron d^2sp^3 hybrid orbitals have some s character, at the same time increased d occupancy will increase the shielding and increase the isomer shift. These opposing effects also minimize any differences in δ due to varying R and R′. (However, it is necessary to invoke differences in covalency, *vide infra*, to help explain the effects of R and R′ upon the quadrupole splitting.)

The quadrupole splittings, on the other hand, show very great dependence on the nitrogen substituents R and R′ despite their remoteness from the iron nucleus. The quadrupole splitting is a complicated function of several variables (*E*, the energy difference between the two spin states, *Dq*, the cubic crystal field splitting, δ, the trigonal distortion, λ, the spin–orbit coupling, *k*, the orbital reduction factor) the separate effects of which cannot be quantitatively evaluated from the data given in Table III. Nevertheless, several qualitative conclusions on the bonding in these complexes can be reached from a consideration of the variation of Δ with R and R′, based on the following assumptions.

(1) For the high-spin configuration Δ is due to only the charges on the surrounding atoms, the so-called "lattice contribution." Typically, this contribution is less than 0.25 mm/sec, which on the basis of a point-charge calculation corresponds to a distortion of the SFeS angle of about 5° from a right angle. Because such small splittings cannot be extracted from the data with accuracy, observations in this range should not be used to judge the distortion.

(2) For the low-spin configuration Δ will include the lattice contribution which is small and essentially the same as for the high-spin case and is temperature independent. However, the dominant contribution to Δ at low temperature will be the valence contribution due to the noncubic symmetry of the iron's own electrons. Golding[21] has made a theoretical study of this valence contribution and its temperature dependence with particular application to the tris(N,N-disubstituted dithiocarbamato)iron(III) complexes. He has found that Δ(valence) reaches a maximum plateau at low temperature, the maximum value being greater the greater the distortion and the less the covalency.

(3) The fact that Δ is small at room temperature does not necessarily indicate a large fraction of the high-spin state. There may still be a large fraction of the low-spin state, but with an insignificant value of Δ (valence).

(4) Large Δ at room temperature will be considered evidence of the persistence of Δ(valence).

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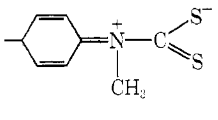
(38) P. Merrithew and P. Rasmussen, Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 1968, Paper No. 121.

It is now possible to ascertain the dependency of the two factors, covalency and distortion, on the nature of R and R′. As a key to this relationship we consider the relative importance of canonical form **3** (see Introduction) to the structure. We will assume that increasing importance of form **3** leads to greater covalency of the iron–sulfur bond because it shifts electronic charge toward iron. The importance of form **3** depends on R and R′ *via* their inductive and steric effects.

As for the distortion, there is no such straightforward correlation; to a first approximation the SCS angle is about 120 ° in all three resonance forms. If we use the bond lengths for C–S and Fe–S that were found for chlorobis(N,N-diethyldithiocarbamato)iron(III)[34] we find that a 120 ° SCS angle would make the SFeS angle only 81 °. Most likely both angles are compromised, SCS being between 120 and 144 ° while SFeS is between 81 and 90°. (As noted above, the latter range is consistent with the point-charge estimates.)[39]

Consider first the first group of nine compounds from Table III, which have only noncyclic alkyl substituents. Only the *sec*-butyl derivative $Fe(SBU)_3$ has an appreciable Δ at room temperature. However Δ for the isopropyl derivative has been reported as 0.36[21] and 0.65 mm/sec[20] at room temperature. We infer from the persistence of Δ(valence) that in these cases the distortion is great and covalency is small, and this is borne out by the very large Δ for $Fe(SBU)_3$ at low temperature. Thus isopropyl and *sec*-butyl seem to give ligands with relatively little covalency, which we must attribute to their similar branched structures. Among the others, in which form **3** is favored, the small differences in Δ at low temperature can be attributed to differences in distortion which we are unable to relate to structure at present.

In the next group of compounds, all containing one or two cyclic substituents, Δ(valence) is generally more persistent, indicating a combination of high distortion and low covalency. The two extreme cases, CHX and MEPH, disfavor form **3** but for different reasons. In CHX we have a branched structure like SBU and isopropyl. However, MEPH disfavors form **3** because of competition from forms such as



The above form appears to be disfavored again in ETPH which, in view of its small Δ at low temperature, seems to favor form **3** and high covalency. In the case of ETPH steric factors can be blamed for disrupting phenyl conjugation; however, these factors may be important only in the crystalline state since it has been noted that the room-temperature magnetic moment is appreciably reduced (from 4.7 to 3.6 BM) upon solution in chloroform.[9] Mössbauer data[19] for the isoamylphenyl compound indicate its close similarity to ETPH. The result for PH suggests however that form **3** is not favored, probably because of competition from phenyl conjugation as shown above.

All of the benzyl derivatives appear surprisingly weak in form **3**, BZ and MEBZ showing the largest low-temperature Δ's. However, the inductive effect of the benzyl group is very much less than that of the alkyl groups and so does not favor form **3**. Very similar to the benzyl are the picolyl derivatives as expected from the similarity in structure.

The IPRCHX splittings seem surprisingly small considering that each substituent was expected to favor low covalency.

The four remaining entries in Table III are all derived from cyclic amines and all show small room-temperature Δ indicating a major form **3** contribution. It is likely that these have similar inductive and conformational effects. The complex that might have differed considerably, the ethylenimine derivative, has not yet been synthesized. The low-temperature Δ values indicate $Fe(HMI)_3$ to be the least covalent.

The piperidyl derivative, $Fe(PIP)_3$, has a room-temperature magnetic moment of 4.01 BM[9] suggesting about equal populations of low- and high-spin forms. Hence the small Δ implies that Δ(valence) has indeed become insignificant. A similar inference cannot honestly be made for $Fe(PYR)_3$ because its moment of 5.83 BM[9] shows it to be nearly all high spin. The low-spin state is evidently much higher in energy at room temperature, and this situation had been presumed[11] to prevail to absolute zero. Recent magnetic measurements in this laboratory[40] however showed a marked break in the Curie plot indicating the presence of a low-spin population below 100 °K which was confirmed by the initial Mössbauer observations. It thus belongs in this class of compounds.

Summary

The effects of structural variations in the nitrogen substituents in several tris(N,N-disubstituted dithiocarbamato)iron(III) complexes on Fe^{57} quadrupole splitting have been interpreted primarily in terms of their expected steric effect upon the covalency of the iron–sulfur bonding. Small values of the room-temperature quadrupole splitting have been taken as evidence of covalency, although, as discussed, many other factors are known to affect the spectra. Following this viewpoint, alkyl constituents favored covalency except if branched at the carbon joined to the nitrogen, while

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(39) Note Added in Proof. Recently the X-ray structure of $[Fe(NBU)_3]$ was reported [B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 1517 (1968)]. This complex has a structure intermediate between that of a trigonal prism and a trigonal antiprism; the SFeS angle is 73°. If a similar situation obtains for the other complexes, our arguments based on point-charge estimates would be vitiated.

(40) D. K. Straub, W. Swift, and C. Maricondi, to be submitted for publication.

cyclic, benzyl, and picolyl did not. Derivatives of five- or higher-membered cyclic amines can be classed with the *n*-alkyl derivatives.

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β-Diketone Complexes of Cobalt(III). III. Tris(β-diketonato)cobalt(III) and Bis(acetylacetonato)diaminecobalt(III) Trichelate Species[1a]

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The two geometrical isomers of tris(2,2-dimethyl-3,5-hexanedionato)cobalt(III) have been prepared, separated chromatographically, and identified by proton magnetic resonance (pmr) spectroscopy. The pmr of a series of bis(acetylacetonato)-diaminecobalt(III) complexes (diamine = ethylenediamine, N,N,N′,N′-tetramethylethylenediamine, 2,2′-bipyridine, or 1,10-phenanthroline) show the importance of both diamagnetic ring anisotropy and external environmental effects. Marked improvements have been made in the synthesis of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(III) and tris(1,1,1,5,5,5-hexafluoroacetylacetonato)cobalt(III). Electronic and vibrational energy levels are also discussed.

Introduction

A detailed study of bis(β-diketonato)cobalt(III) complexes is in progress in this laboratory to determine the σ and π ligand field effects on the reaction rates and the reaction stereochemistry of cobalt(III) complexes. Previous reports[1a,2,3] have demonstrated the usefulness of sodium dinitrobis(acetylacetonato)cobaltate(III) for the synthesis of bis(acetylacetonato)cobalt(III) complexes. A series of diamine complexes have been used to study effects on the β-diketone methyl group pmr (proton magnetic resonance) signals. The tris complexes of dhd and thd[4] have been prepared for the purpose of spectral correlations in the study of the bis complexes of these ligands now in progress. Co(thd)$_3$ has been prepared by an alternate method,[5] but no characterization has been reported. We have increased the yield of the tris complex and spectrally characterized it.

The volatility of hexafluoroacetylacetonate complexes makes them particularly useful in chemical research such as gas chromatography[6] and mass spectroscopy.[7] Unfortunately, previously reported methods of preparing the cobalt(III) complex[8,9] are less than satisfactory in terms of either yield (1%)[8] or safety (90% H_2O_2).[9] We have achieved the synthesis of Co(hfa)$_3$ in high yield with safe, commercially available reactants and are currently studying the reaction mechanism.

Results

Syntheses.—As previously reported[2,3] treatment of Co(β-dik)$_2$(NO$_2$)$_2^-$ with amines in the presence of activated carbon results in the formation of the diamine derivatives. This procedure has been used to form the N,N,N′,N′-tetramethylethylenediamine and 1,10-phenanthroline derivatives of bis(acetylacetonato)-diaminecobalt(III) perchlorate. The use of Norit A for the synthesis of the heterochelates is important. To illustrate, the reaction of *trans*-Co(acac)$_2$(NO$_2$)$_2^-$ and ammonia with neutral Norit or Norit FQP produces Co(acac)$_3$ rather than the *cis*- and *trans*-Co(acac)$_2$(NH$_3$)$_2^+$ species.[10]

The tris complexes of cobalt(III) with 2,2-dimethylhexane-3,5-dione and 2,2,6,6-tetramethylheptane-3,5-dione have been prepared in high yield by allowing

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(1) (a) Part II: B. P. Cotsoradis and R. D. Archer, *Inorg. Chem.*, **6**, 800 (1967); presented in part at 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968; (b) Department of Chemistry, University of Massachusetts, Amherst, Mass. 01002; (c) Department of Chemistry, Tulane University, New Orleans, La. 70118; (d) to whom correspondence should be sent.

(2) R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1584 (1965).

(3) L. J. Boucher, *ibid.*, **6**, 2162 (1967).

(4) Abbreviations used in this paper include: dhd, 2,2-dimethylhexane-3,-5-dionato; thd, 2,2,6,6-tetramethylheptane-3,5-dionato; en, ethylenediamine; bipy, 2,2′-bipyridine; *c*-phen, 1,10-phenanthroline; acac, 2,4-pentanedionato; hfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato; tmed, N,N,N′,N′-tetramethylethylenediamine.

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(8) M. Kilner, F. A. Hartman, and A. Wojcicki, *Inorg. Chem.*, **6**, 406 (1967).

(9) H. Veening, W. E. Bachman, and D. M. Wilkinson, *J. Gas Chromatog.*, **5**, 248 (1967).

(10) S. Golinger, unpublished results.