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Tris(N,N-disubstituted dithiocarbamato)iron(IV) Tetrafluoroborates

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Several new iron(IV) complexes of N,N-disubstituted dithiocarbamates have been prepared by reaction of tris(dithiocarbamato)iron(III) complexes with boron trifluoride in the presence of air. These have been characterized as tris(N,N-disubstituted dithiocarbamato)iron(IV) tetrafluoroborates by a number of physical methods. The isomer shifts of these compounds (0.46 ± 0.02 mm/sec) are significantly lower than those of iron(III) dithiocarbamates (0.64 ± 0.03 mm/sec). The quadrupole splittings are 2 mm/sec or greater.

Introduction

Iron(IV) complexes are very rare; there appear to be only about six well-authenticated examples. These include various ferrates(IV), *trans*-dichlorobis(*o*-phenylenebis(dimethylarsine))iron(IV) tetrafluoroborate and the corresponding dibromo complex, $[Fe(diars)_2X_2](BF_4)_2$.[2] There are also certain bis-dithiolene chelates of iron which contain iron in a formal 4+ oxidation state,[3,4] but the possibility of ligand oxidation in the dithiolenes (such as the *cis*-dimercaptoethylene dianion) makes assignment of the true oxidation state of the iron ambiguous.[3]

In addition to these, there is good evidence that oxidized forms of horseradish peroxidase,[5] Japanese radish peroxidase, and catalase contain porphyriniron(IV) groups.[6] The exact coordination of the iron is unknown. The chemistry of iron(IV) is thus of biological interest since it appears to be involved in enzymatic oxidations.

We have been studying the synthesis and properties of iron dithiocarbamate complexes as model compounds for the magnetic and Mössbauer characteristics shown by naturally occurring iron–sulfur complexes, such as the ferredoxins.[7,8] During the course of these investigations we have prepared and characterized several new iron(IV) complexes. We present the results in this paper.

Experimental Section

All starting materials and solvents were reagent grade. The tris(N,N-disubstituted dithiocarbamato)iron(III) compounds were prepared from ferric hydroxide, the amine, and carbon disulfide as previously described[8] and were recrystallized from benzene–ethanol (or diethyl ether in the case of the diisopropyl complex) several times and dried under vacuum before use.

The following procedure was used for the preparation of the tris(*N*,*N*-dialkyldithiocarbamato)iron(IV) tetrafluoroborates. Gaseous boron trifluoride was bubbled for about 30 sec into a magnetically stirred benzene solution of a tris(*N*,*N*-dialkyldithiocarbamato)iron(III) complex contained in a plastic flask and open to the air. (These solutions were prepared by dissolving 3–6 g of the iron(III) complex in 150 ml of benzene, except for the dimethyl case, where 2 g was dissolved in 200 ml of benzene.) The black precipitate which started to form immediately was collected after stirring the solutions for an additional 0.5 hr, washed well with benzene, and recrystallized several times from methylene chloride (in the dimethyl and pyrrolidyl cases) or by benzene precipitation from very concentrated methylene chloride solutions. The yields of crude material were greater than 80%. Finally, the black crystals were dried for 2–3 days under vacuum over refluxing 2-propanol. The complexes appear to undergo slow decomposition when stored at room temperature.

Ligand abbreviations for $RR'NCS_2^-$ are R = R′ = CH_3, Me_2dtc; R = R′ = C_2H_5, Et_2dtc; R = R′ = *i*-C_3H_7, *i*-Pr_2dtc; R = R′ = cyclohexyl, *c*-Hx_2dtc, and R, R′ = $-(CH_2)_4-$, Pyr(dtc).

Preparation of "Fe(*i*-Pr$_2$dtc)$_2$BF$_3$."—A stirred solution of 7.0 g of [Fe(*i*-Pr_2dtc)$_3$] in 100 ml of benzene in a plastic flask was treated with gaseous boron trifluoride for 2 min. The mixture was stirred for 30 min and again treated with boron trifluoride for 2 min. After an additional 1 hr of stirring, the black product was collected, washed well with benzene, and dissolved in 100 ml of methylene chloride. The solution was filtered and treated with 400 ml of benzene to cause crystallization. The black crystals were recrystallized several times from methylene chloride–benzene mixtures and then dried under vacuum 20 hr over refluxing 2-propanol. *Anal.* Calcd for Fe(*i*-Pr_2dtc)$_2$BF$_3$: C, 35.30; H, 5.92; N, 5.88; S, 26.93; B, 2.27; F, 11.97. Found: C, 35.35; H, 5.29; N, 6.08; S, 26.84; B, 2.20; F, 12.12.

Preparation of Tris(*N*,*N*-diethyldithiocarbamato)iron(IV) Hexafluorophosphate.—Approximately 0.5 ml of 18 *M* sulfuric acid was added to a partial solution of 4.00 g of [Fe(Et$_2$dtc)$_3$] and 1.84 g of KPF_6 in 100 ml of acetone, and dry air was bubbled through the mixture for 5 hr. The brown solution was filtered from a grayish white precipitate and the filtrate was evaporated to dryness under vacuum at room temperature. The black mass was extracted with 100 ml of methylene chloride, the solution was filtered, and 200 ml of benzene was added. A black oil which slowly crystallized was obtained upon evaporation of the benzene–methylene chloride mixture to 200 ml. The black crystals were washed with benzene and recrystallized six times from methylene chloride–benzene mixtures. The product was finally dried for 3 days under vacuum over refluxing 2-propanol.

Elemental analyses were performed by Alfred Bernhardt. An Industrial Instruments Model RC 16B2 conductivity bridge was used for the conductivity measurements. Infrared spectra were recorded on Beckman IR-8 and IR-12 spectrophotometers; visible and ultraviolet spectra, on a Cary 14 spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian A-60 instrument.

Mössbauer spectra were obtained with a scanned velocity spectrometer operating in the time mode. A 20-mCi source consisting of ^{57}Co diffused into chromium kept at room temperature was used. Calibration with sodium nitroprusside (quadrupole splitting 1.712 mm/sec) at room temperature was carried out before and after each run. Estimated error limits on δ and Δ were ±0.03 mm/sec. Frequent checks with ^{57}Fe foil were also made. A detachable tail cryostat obtained from Janis Corp., Boston, Mass., was used for the liquid helium measurements. A computer program, written originally by P. A. Flinn of Carnegie–Mellon University and modified by G. Von Nieda of this laboratory was used to fit the data with a least-squares approximation assuming lorentzian line shapes of equal width. A Calcomp plotter was used to plot data.

Results

Data from elemental analyses are given in Table I.

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TABLE I

ANALYTICAL DATA FOR THE TRIS(DITHIOCARBAMATO)IRON(IV) COMPLEXES

Complex	% C		% H		% N		% S		% B		% F	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Fe(Me_2dtc)_3]BF_4$	21.45	21.64	3.64	3.48	8.35	8.17	38.22	38.00	2.15	2.07	15.10	14.96
$[Fe(Me_2dtc)_3]BF_4$	21.45	21.41	3.64	3.45	8.35	8.26	38.22	38.01	2.15	2.28	15.10	15.38
$[Fe(Et_2dtc)_3]BF_4$	30.67	30.78	5.11	4.92	7.15	6.98	32.75	33.06	1.84	1.73	12.93	12.58
$[Fe(Et_2dtc)_3]PF_6$	27.91	28.24	4.67	4.77	6.51	6.64	29.79	29.88	...	...	17.66	17.92
$[Fe(i\text{-}Pr_2dtc)_3]BF_4$	37.56	37.88	6.30	6.03	6.26	6.43	28.64	28.51	1.61	1.50	11.29	11.16
$[Fe(Pyr(dtc))_3]BF_4$	30.99	31.25	4.16	4.02	7.23	7.32	33.00	33.06	1.86	1.94	13.05	13.21
$[Fe(Pyr(dtc))_3]BF_4$	30.99	31.19	4.16	4.28	7.23	7.25	33.00	33.26	1.86	1.86	13.05	13.21
$[Fe(c\text{-}Hx_2dtc)_3]BF_4$	51.36	51.88	7.29	5.63	4.61	4.54	21.09	20.86	1.18	1.16	8.33	8.13

The preparation of each complex was repeated sometimes several times, and elemental analyses on two different preparations of the methyl and pyrrolidyl derivatives are given in the table. The formula of "$Fe(i\text{-}Pr_2dtc)_2BF_3$" is based entirely on the analytical results. All of these compounds crystallize as black crystals, soluble in acetone, methylene chloride, acetonitrile, and nitromethane, giving brownish solutions, and insoluble in benzene, cyclohexane, and carbon tetrachloride. The complexes melt (or decompose) at lower temperatures than the corresponding tris(dithiocarbamato)iron(III) complexes: $[Fe(Me_2dtc)_3]BF_4$, 263–266° dec; $[Fe(Et_2dtc)_3]BF_4$, 145–147°; $[Fe(i\text{-}Pr_2dtc)_3]BF_4$, 171–172°; $[Fe(c\text{-}Hx_2dtc)_3]BF_4$, 240–245° dec; $[Fe(Pyr(dtc))_3]BF_4$ 257–258°; and "$Fe(i\text{-}Pr_2dtc)_2BF_3$," 159–162°.

Equivalent Conductance.—The equivalent conductivities of 10^{-3} *M* nitromethane solutions at 25° lie in the range 84–95 mhos cm^2 for the five tetrafluoroborates and the hexafluorophosphate (see Table II). These values are exactly those expected for uni-univalent electrolytes in nitromethane solution.[9]

TABLE II

EQUIVALENT CONDUCTIVITY OF NITROMETHANE SOLUTIONS AT 25°

Complex	Molar concn	Equiv conductance, mhos cm²/equiv
$[Fe(Me_2dtc)_3]BF_4$	9.38×10^{-4}	95
$[Fe(Et_2dtc)_3]BF_4$	1.21×10^{-3}	87
$[Fe(Et_2dtc)_3]PF_6$	1.03×10^{-3}	89
$[Fe(i\text{-}Pr_2dtc)_3]BF_4$	1.17×10^{-3}	84
$[Fe(Pyr(dtc))_3]BF_4$	8.13×10^{-4}	95
$[Fe(c\text{-}Hx_2dtc)_3]BF_4$	1.12×10^{-3}	84
"$Fe(i\text{-}Pr_2dtc)_2BF_3$"	1.51×10^{-3}	52

The conductance of "$Fe(i\text{-}Pr_2dtc)_2BF_3$" is significantly lower than the other complexes and is further evidence that this material and $[Fe(i\text{-}Pr_2dtc)_3]BF_4$ are different compounds.

Metathetical Reaction.—A metathesis carried out between sodium tetraphenylborate and $[Fe(Et_2dtc)_3]BF_4$ in methylene chloride solution resulted in the precipitation of a white powder which had an infrared spectrum identical with that of $NaBF_4$.[10]

Electronic Spectra.—Electronic spectra were measured in the range 600–240 mμ on methylene chloride solutions of the iron(IV) complexes. There are six peaks in this range for each of the six complexes. The peaks occur at 479–487, 448–456, 351–359, 304–312, 260–269, and 241–244 mμ. The spectra are very different from the spectra of the corresponding iron(III) complexes, which have peaks at about 585, 510, 380, 350, 310, and 255–270 mμ. These differences are illustrated in Figure 1 for the diethyl derivative.

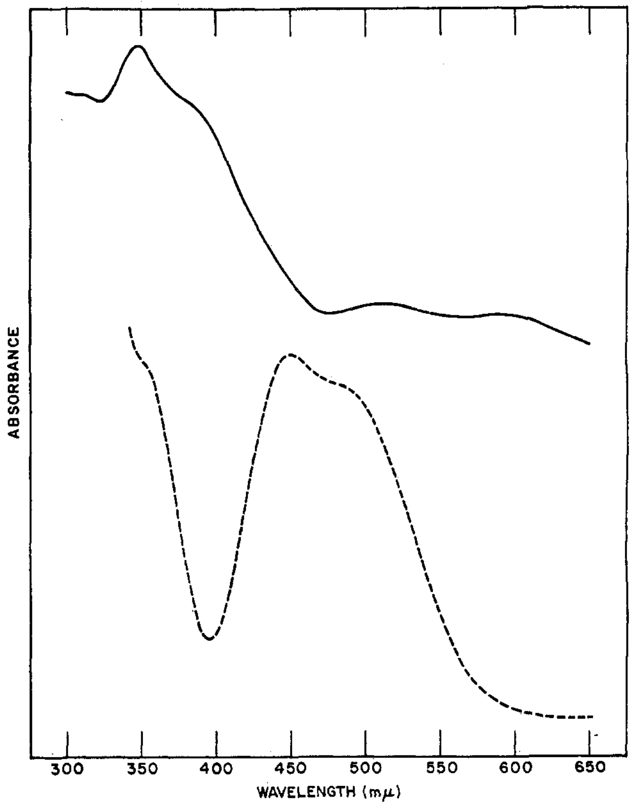

Figure 1.—Visible spectra of $[Fe(Et_2dtc)_3]$ (—) and $[Fe(Et_2dtc)_3]BF_4$ (- - - -) in methylene chloride solution.

The spectrum of "$Fe(i\text{-}Pr_2dtc)_2BF_3$" strongly resembles those of the iron(IV) complexes, in both position of the peaks (486, 453, 357, 309, 266, and 250 mμ) and their relative intensities.

Infrared Spectra.—Infrared spectra were measured in both KBr disks and Nujol mulls. The KBr data are given in Table III for the region 1600–900 cm^{-1}. This region includes the characteristic $C\overset{...}{=}N$, $C\overset{...}{=}S$, and NC_2 bands.[11] However, BF_4^- has strong bands in the 1000–1100-cm^{-1} region which overlap with the CS and NC_2 bands.

A comparison of the spectra of $[Fe(R_2dtc)_3]$ and $[Fe(R_2dtc)_3]BF_4$ reveals that the $C\overset{...}{=}N$ band (~1500 cm^{-1}) is noticeably affected by the oxidation state of the iron: the bands are at 1560, 1520, 1500, 1490, and 1525 cm^{-1} for the R = Me, Et, *i*-Pr, *c*-Hx, and Pyr complexes of iron(IV) and at 1520, 1480, 1470, and 1470 cm^{-1} for the corresponding iron(III) complexes. The average shift is 30–40 cm^{-1} toward higher

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TABLE III

INFRARED DATA IN THE REGION 1600–900 $\text{CM}^{-1\,a}$

[Fe(Me$_2$dtc)$_3$]BF$_4$

1560 vs, 1430 sh, 1392 vs, 1279 vw, 1234 s, 1158 vs, 1087 s, 1050 vs, 1030 vs

[Fe(Et$_2$dtc)$_3$]BF$_4$

1520 vs, 1490 sh, 1442 s, 1420 sh, 1380 m, 1352 s, 1292 sh, 1275 s, 1197 s, 1149 m, 1080 sh, 1052 vs, b, 995 sh, 905 w, b

[Fe(Et$_2$dtc)$_3$]PF$_6$

1520 vs, 1450 sh, 1430 m, 1380 w, 1350 m, 1275 s, 1194 m, 1150 m, 1070 m, b

[Fe(*i*-Pr$_2$dtc)$_3$]BF$_4$

1500 vs, 1440 m, 1363 s, 1332 vs, 1183 m, 1137 s, 1112 sh, 1080 sh, 1050 vs, 1026 sh

[Fe(*c*-Hx$_2$dtc)$_3$]BF$_4$

1490 s, 1465 w, 1445 m, 1379 m, 1350 m, 1312 s, 1270 w, 1245 m, 1164 w, 1150 w, 1094 w, 1062 sh, 1050 s, b, 995 w

[Fe(Pyr(dtc))$_3$]BF$_4$

1525 vs, 1430 vs, 1330 s, 1282 sh, 1250 m, 1220 m, 1182 sh, 1142 m, 1090 s, 1030 vs, b, 938 w, sh, 910 w

"Fe(*i*-Pr$_2$dtc)$_2$BF$_3$"

1500 vs, 1450 m, 1365 m, 1332 vs, 1185 m, 1140 m, 1112 m, 1080 s, 1040 s, b

[a] Spectra taken in KBr disks. Key: v, very; s, strong; m, medium; w, weak; sh, shoulder; b, broad. All values are in cm^{-1}.

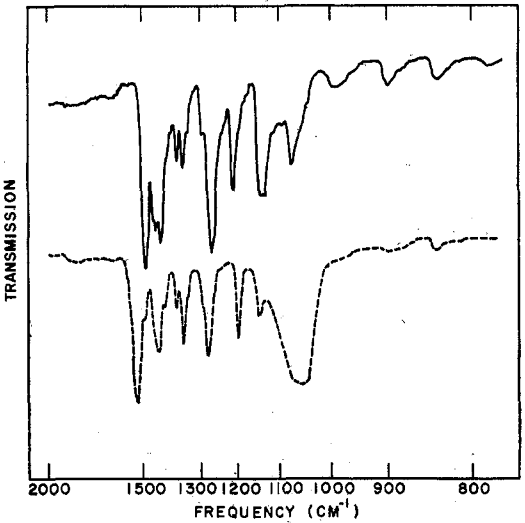

Figure 2.—Infrared spectra of [Fe(Et$_2$dtc)$_3$] (—) and [Fe(Et$_2$dtc)$_3$]BF$_4$ (- - - -).

values. Figure 2 shows a comparison of the infrared spectra of [Fe(Et$_2$dtc)$_3$] and [Fe(Et$_2$dtc)$_3$]BF$_4$.

The spectra of [Fe(*i*-Pr$_2$dtc)$_3$]BF$_4$ and "Fe(*i*-Pr$_2$dtc)$_2$BF$_3$" were measured in the Fe–S stretching region and compared with the spectrum of [Fe(*i*-Pr$_2$dtc)$_3$]. Data are given in Table IV. The Fe–S bands occur at 325–338 and 370–376 cm^{-1}.

TABLE IV

INFRARED DATA IN THE REGION 650–300 CM^{-1}

Na(*i*-Pr$_2$dtc)	[Fe(*i*-Pr$_2$dtc)$_3$]	[Fe-(*i*-Pr$_2$dtc)$_3$]BF$_4$	"Fe-(*i*-Pr$_2$dtc)$_2$BF$_3$"
	325 m	330 m	338 m
	370 m	376 s	374 s
	409 w	407 w	
475 b	478 m	475 m	471 m
529 w	534 m	525 s	528 m
581 m	589 s	584 s	584 s
638 w	642 w	617 m	616 m

[a] Spectra taken in Nujol mulls. Key: s, strong; m, medium; w, weak; b, broad. Values are in cm^{-1}.

Magnetic Moments.—Magnetic susceptibilities were measured in chloroform solutions by the nuclear magnetic resonance method of Evans[12] with the modification due to Rettig, cited in ref 13. Tetramethylsilane was used as internal and external standard. Diamagnetic corrections were calculated from Pascal's constants. The magnetic data in Table V represent averages of three different determinations which agreed to within ±0.05 BM of each other and assume simple Curie behavior. The dimethyl derivative was insufficiently soluble in either chloroform or methylene chloride to obtain good values of the moment.

TABLE V

MAGNETIC MOMENTS AT 31°

Complex	$10^6\chi_D$,[a] cgsu	$10^6\chi_M$,[b] cgsu	μ, BM
[Fe(Et$_2$dtc)$_3$]BF$_4$	−317	4425	3.28
[Fe(Et$_2$dtc)$_3$]PF$_6$	−350	4070	3.15
[Fe(*i*-Pr$_2$dtc)$_3$]BF$_4$	−389	4450	3.29
[Fe(Pyr(dtc))$_3$]BF$_4$	−300	4250	3.22
[Fe(*c*-Hx$_2$dtc)$_3$]BF$_4$	−567	4660	3.37

[a] Diamagnetic correction. [b] Corrected value.

A similar measurement of "Fe(*i*-Pr$_2$dtc)$_2$BF$_3$" gave the following results (using $\chi_D = -268 \times 10^{-6}$ cgsu): $\chi_M = 2810 \times 10^{-6}$ cgsu, $\mu = 2.61$ BM.

Mössbauer Spectra.—The Mössbauer spectra of the five tetrafluoroborates consisted of widely split doublets with peaks of equal intensity and width. A representative spectrum is shown in Figure 3. The isomer shifts (relative to sodium nitroprusside) varied from 0.45 to 0.48 mm/sec at room temperature (Table VI). A

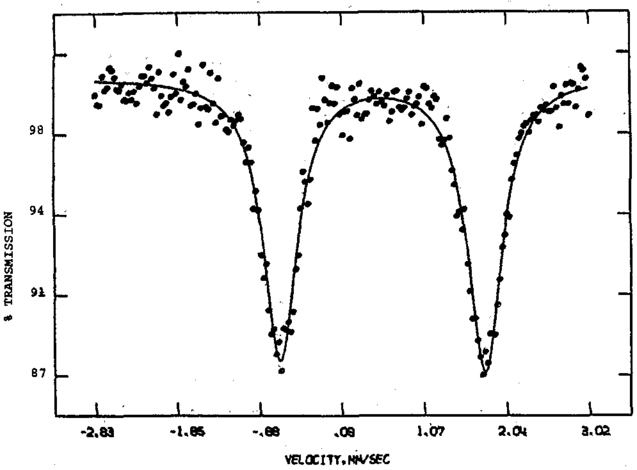

Figure 3.—Mössbauer spectrum of [Fe(Me$_2$dtc)$_3$]BF$_4$ at 4.2°K.

TABLE VI

MÖSSBAUER PARAMETERS

Complex	Temp, °K	δ,[a] mm/sec	Δ, mm/sec	Γ,[b] mm/sec
[Fe(Me$_2$dtc)$_3$]BF$_4$	300	0.45	2.06	0.23
	4.2	0.55	2.37	0.45
[Fe(Et$_2$dtc)$_3$]BF$_4$	300	0.48	2.23	0.27
[Fe(Et$_2$dtc)$_3$]PF$_6$	300	0.47	2.32	0.38
[Fe(Pyr(dtc))$_3$]BF$_4$	300	0.48	2.30	0.25
	4.2	0.56	2.54	0.46
[Fe(*i*-Pr$_2$dtc)$_3$]BF$_4$	300	0.45	2.27	0.25
[Fe(*c*-Hx$_2$dtc)$_3$]BF$_4$	300	0.48	2.00	0.25
"Fe(*i*-Pr$_2$dtc)$_2$BF$_3$"	300	0.47	2.32	0.21
	4.2	0.57	2.49	0.37

[a] Relative to sodium nitroprusside. [b] Half-width at half-maximum.

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normal temperature dependence of the isomer shift was observed.

The quadrupole splittings varied from 2.0 to 2.3 mm/sec at room temperature and showed some temperature dependence. The peaks broadened considerably at liquid helium temperature but remained symmetrical. This behavior is very similar to that of the corresponding iron(III) complexes.[8]

The complex "Fe(*i*-Pr_2dtc)$_2BF_3$" gave Mössbauer spectra very similar to those of the iron(IV) tetrafluoroborates.

Boron-11 Nuclear Magnetic Resonance Spectra.—The ^{11}B nmr spectra were obtained on [Fe(*i*-Pr_2dtc)$_3$]BF_4 and "Fe(*i*-Pr_2dtc)$_2BF_3$" in methylene chloride solution through the courtesy of Professor James C. Carter and Br. Francis Swicker of this department, using a spectrometer operated at 80.2 MHz. Both complexes gave an asymmetric single peak with a shoulder on the higher frequency side. The peaks occurred at 15.7 and 15.8 ppm upfield from trimethyl borate for "Fe(*i*-Pr_2dtc)$_2BF_3$" and [Fe(*i*-Pr_2dtc)$_3$]BF_4, respectively. The peaks were sharp, especially for paramagnetic compounds: full width at half-maximum for the former complex was 18 Hz and for the latter, 8 Hz. It was unfortunate that the paramagnetic relaxation effects precluded the obtaining of structural information from ^{19}F splittings.

Discussion

It is known from previous work that the N,N-disubstituted dithiocarbamate ligand stabilizes higher oxidation states of the transition metals: aqueous solutions of cobalt(II), manganese(II), and iron(II) treated with a dithiocarbamate give complexes of the metal in the 3+ oxidation state.[14] Silver(II) dithiocarbamates are known, and very recently complexes of copper(III) and nickel(IV) were reported.[15] Thus it is not so surprising that iron(IV) dithiocarbamates can be prepared. However, the use of boron trifluoride to effect the oxidation of a tris(dithiocarbamato)iron(III) complex to the iron(IV) complex is novel and represents a completely unexpected reaction.

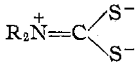
The formulation of the black crystalline compounds formed upon reaction of boron trifluoride with various tris(dithiocarbamato)iron(III) complexes as tris(dithiocarbamato)iron(IV) tetrafluoroborates is supported by several physical measurements. Elemental analyses for all elements except iron, the equivalent conductances, the infrared spectra (indicating the presence of tetrafluoroborate ion), and the metathetical preparation of sodium tetrafluoroborate from one complex are almost conclusive evidence for the composition Fe(R_2dtc)$_3BF_4$.

The Mössbauer spectra indicate a higher oxidation state of the iron than 3+: the isomer shifts at room temperature were about 0.46 ± 0.02 mm/sec relative to sodium nitroprusside, a value significantly smaller than the approximately 0.64 ± 0.03 mm/sec expected for iron(III) dithiocarbamates (such as the halobis(dithiocarbamato)iron(III)[7] or the tris(dithiocarbamato)iron(III)[8] complexes). The value of 0.46 mm/sec is comparable to the isomer shifts at 298°K of *trans*-dichlorobis(phenylenebis(dimethylarsine))iron(IV) tetrafluoroborate, 0.47 ± 0.05 mm/sec, and the corresponding dibromo complex, 0.52 ± 0.05 mm/sec.[16]

The quadrupole splittings are large (2.0–2.3 mm/sec at room temperature) and show some temperature dependence, increasing with decreasing temperature. Magnetic hyperfine structure was not observed for the neat complexes at 4.2°K, although the peak widths increased somewhat.

The magnetic moments measured in solution at room temperature are 3.2–3.4 BM. For spin-paired iron(IV) in an octahedral environment, a magnetic moment of 3.6 BM is expected.[17] The measured magnetic moments at room temperature of the bis(diarsine)iron(IV) complexes are 2.8–3.2 BM,[2] indicative of strong (tetragonal) distortion from cubic symmetry. The distortion (probably trigonal) from cubic symmetry is expected to be less for the iron(IV) dithiocarbamates, surrounded as the iron presumably is by six sulfurs, and magnetic moments between the extremes of 3.6 and 3.0 BM are entirely reasonable.

The infrared spectra of metal dithiocarbamates have been extensively studied.[12,18,19] There is general agreement on the location of the CN band. This band is consistently higher in energy by 30–40 cm^{-1} in these novel iron(IV) complexes, compared to the corresponding iron(III) complexes, indicating that the resonance form



$$R_2\overset{+}{N}{=}C\begin{smallmatrix}\diagup S^- \\ \diagdown S^-\end{smallmatrix}$$

makes a greater contribution to the total structure in the iron(IV) cases. The importance of this form indicates greater S→Fe π bonding.[20]

All of the data (Mössbauer, magnetic susceptibility, and infrared) are consistent with iron in the 4+ oxidation state in these complexes. No evidence was found for ligand oxidation to the cyclic dication described by Willemse and Steggerda.[21]

The mechanism of the reaction of boron trifluoride with tris(N,N-disubstituted dithiocarbamato)iron(III) complexes must necessarily be complex. There must be boron-containing by-products since there is no other source of fluoride for BF_4^- than BF_3. (Some white powder can be isolated from the reaction mixture, but the composition of this material has not yet been determined.) The most probable oxidant is air, since the reactions are carried out in vessels open to the air. The iron(III) in the tris-dithiocarbamate complex does not disproportionate, since yields of greater than 50% based on the iron(III) complex are obtained, and it is known that iron(II) dithiocarbamates are quite unstable and easily oxidized.

Some experiments were carried out to determine if air was indeed the oxidant in these reactions. Black compounds which showed spectral properties similar to those of the iron(IV) tetrafluoroborate complex could be obtained by bubbling air through diethyl ether–benzene solutions of [Fe(*i*-Pr_2dtc)$_3$] or [Fe(*c*-Hx_2dtc)$_3$], acidified with sulfuric acid. These compounds (pre-

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sumably containing sulfate or bisulfate) were rather unstable and were never obtained pure. When, however, air was bubbled through an acetone solution of [$Fe(Et_2dtc)_3$] acidified with sulfuric acid and containing hexafluorophosphate ion, a stable hexafluorophosphate salt, [$Fe(Et_2dtc)_3$]PF_6, could be obtained analytically pure. It appears that the anion affects the stability of these iron(IV) complexes.

Conditions under which the [$Fe(R_2dtc)_3$]BF_4 complexes are prepared must be carefully controlled or other products may be obtained. Thus, when [$Fe(i\text{-}Pr_2dtc)_3$] was treated with excess boron trifluoride, a new compound which analyzed as "$Fe(i\text{-}Pr_2dtc)_2BF_3$" was formed. This complex is distinct from [$Fe(i\text{-}Pr_2dtc)_3$]BF_4 but resembles it and the other tetrafluoroborates in its physical properties. The magnetic moment is low, 2.61 BM, and may indicate weak antiferromagnetic coupling within the complex. It most likely contains iron(IV) also. The "BF_3" may be present as the ion F_3BO^{2-},[22] derived from F_3BOH_2 (there is considerable doubt about the existence of this ion[23]), although the analytical data are not in very good accord. *Anal.* Calcd for $Fe(i\text{-}Pr_2dtc)_2BF_3$: C, 35.30; H, 5.92; N, 5.88; S, 26.93; B, 2.27; F, 11.97. Calcd for $Fe(i\text{-}Pr_2dtc)_2OBF_3$: C, 34.16; H, 5.67; N, 5.63; S, 26.05; B, 2.19; F, 11.57. Found: C, 35.35; H, 5.29; N, 6.08; S, 26.84; B, 2.20; F, 12.12. Further speculation on the structure of this complex is premature until additional measurements are made.[24]

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[24] NOTE ADDED IN PROOF.—We have recently prepared analytically pure samples of [$Co(Et_2dtc)_3$]BF_4 and [$Mn(Et_2dtc)_3$]BF_4 by the reaction of BF_3 with [$Co(Et_2dtc)_3$] and [$Mn(Et_2dtc)_3$].

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Reactions of the 2,3,4-Tricarbahexaborane(7) System. Formation of Tricarbahexaboranylmanganese Carbonyl π Complexes[1]

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The reaction of 2-methyl-, 2,3-dimethyl-, or 2,4-dimethyl-2,3,4-tricarbahexaborane(7) with sodium hydride in diglyme removes the bridge proton and generates the corresponding monoanion. Treatment of the 2,4-$(CH_3)_2C_3B_3H_4^-$ ion with DCl yields the bridge-deuterated neutral carborane. The reaction of 2-$CH_3C_3B_3H_6$ and 2,3-$(CH_3)_2C_3B_3H_5$ with $Mn_2(CO)_{10}$ in the gas phase forms the respective volatile complexes (π-2-$CH_3C_3B_3H_5$)$Mn(CO)_3$ and (π-2,3-$(CH_3)_2C_3B_3H_4$)$Mn(CO)_3$. The reaction of $Na^+CH_3C_3B_3H_5^-$ with $BrMn(CO)_5$ in diglyme produces a red intermediate characterized as (σ-$CH_3C_3B_3H_5$)$Mn(CO)_5$, which at 100° loses 2 mol of CO to form (π-2-$CH_3C_3B_3H_5$)$Mn(CO)_3$. Evidence concerning the mechanism of formation of the π complexes is discussed.

Since the original discovery of methyl derivatives of 2,3,4-tricarba-*nido*-hexaborane(7),[2-4] at present the only known three-carbon carborane,[4a] several aspects of the chemistry of this cage system, including the preparation of the first transition metal–small carborane complex,[5] have been reported in short communications.[5,6] In this paper we present a more complete account of this work and in addition describe an alternate synthetic route to transition metal π complexes of the tricarbahexaboranes which appears capable of extension to other small carborane–metal complexes.

Results and Discussion

Deprotonation and Bridge Deuteration of Tricarbahexaboranes.—The structure in Figure 1 has been assigned to the 2,3,4-$C_3B_3H_7$ cage system on the basis of boron-11 and proton nmr, infrared, and mass spectroscopic evidence.[2,3] Analogy with other carboranes containing bridge hydrogen atoms (*e.g.*, 2,3-$C_2B_4H_8$ and 1,2-$C_2B_9H_{13}$), which react easily with sodium hydride to remove a bridge proton and produce the corresponding monoanion, suggested that the lone bridge hydrogen in the tricarbahexaborane cage should react similarly. This is in fact the case with the available 2-methyl, 2,3-dimethyl, and 2,4-dimethyl derivatives, all of which are easily deprotonated by excess NaH in dry diglyme or tetrahydrofuran (THF) at room temperature. The resulting methyl- and dimethyltricarbahexaborate(1−) salts are hydrolyzed on contact with water or moist air but are reasonably stable in dry solvents. Sodium 2,4-dimethyltricarbahexaborate(1−) in THF solution reacts readily with deuterium chloride to give the bridge-deuterated neu-

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