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Syntheses and Properties of Five-Coordinate Iron(III) Bisdithiocarbamates[1]

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Tris(N,N-disubstituted dithiocarbamato)iron(III) complexes, [Fe(R$_2$dtc)$_3$], react with silver salts, mercuric salts, alkyl halides and strong organic acids to form [Fe(R$_2$dtc)$_2$X] complexes. Mössbauer spectra of new complexes with X = NCO^-, NCS^-, $NCSe^-$, $CF_3CO_2^-$ and picrate show widely split doublets with quadrupole splittings in the range 2.2–3.0 mm/sec, increasing in the order $NCO^- < NCS^- < NCSe^- \sim CF_3CO_2^- <$ picrate.

Introduction

A spin quartet ground state, which is excluded by ligand field theory for iron(III) in a crystal field of cubic symmetry [2] is possible when the symmetry is lowered by tetragonal distortion [3]. Although a quartet ground state was suggested for chlorophthalocyaninatoiron(III) [4] (which has a questionable existence [5]) as early as 1959, it was not until 1966 that this ground state was first clearly established, in the halobis(N,N-dialkyldithiocarbamato)iron(III) complexes [6].

The rare occurrence of iron(III) in an S = 3/2 ground state and the unusual coordination of the iron atom have made the bis(dithiocarbamoto)iron(III) complexes an interesting series for study. Magnetic properties [7–9], electron spin resonance [9–11], infrared [7, 12], far infrared [13], electronic [7, 14, 15] and Mössbauer [9, 11, 13, 14, 16–19] spectra have been reported. The crystal structure of the diethyl complex, [Fe((C$_2$H$_5$)$_2$NCS$_2$)$_2$Cl], has been determined [6].

These complexes were first prepared by the reaction of a tetraalkylthiuram monosulfide or disulfide with either iron(II) or iron(III) halide [20]. Other methods of preparation have involved the reaction of a tris(N,N-disubstituted dithiocarbamato) iron(III) complex with iron(III) halide [16] or aqueous hydrohalic acid [6] and the reaction of an iron(III) halide with the calculated amount of an ionic dithiocarbamate [21]. Several [Fe(R$_2$NCS$_2$)$_2$X] complexes are known with various R substituents, but X has been only Cl, Br, I, NCS, and in one case, C$_6$F$_5$CO$_2$ [14]. In this paper we report new synthetic methods which may prove useful in the preparation of complexes having a variety of X ligands.

Experimental

Starting materials and solvents were reagent grade and used without further purification. The tris(N,N-disubstituted dithiocarbamato)iron(III) complexes were prepared as previously described [22]. Abbreviations used: Me$_2$dtc, $(CH_3)_2NCS_2^-$; Et$_2$dtc, $(C_2H_5)_2NCS_2^-$; i-Pr$_2$dtc, $(i\text{-}C_3H_7)_2NCS_2^-$; Pyrdtc, $(CH_2)_4NCS_2^-$; R$_2$dtc, $R_2NCS_2^-$. Phenylmercuric fluoride [23] and cyanide [24] were prepared by literature methods.

Reaction of [Fe(R$_2$dtc)$_3$] with R'HgCl

The reaction of either CH$_3$HgCl or C$_2$H$_5$HgCl (1.0 g) with [Fe(R$_2$dtc)$_3$], R = CH$_3$, C$_2$H$_5$, 1/2(CH$_2$)$_4$ (1.0 g) in either benzene or methylene chloride (100 ml) gave the corresponding [Fe(R$_2$dtc)$_2$Cl] in quantitative yields. The reaction was complete within ten minutes at room temperature. The resulting precipitates were collected, washed with the reaction solvent and dried in vacuum several days at 100 °C. *Anal.* Calc'd for [Fe(Me$_2$dtc)$_2$Cl]: Cl, 10.69. Found : Cl, 10.73. Calc'd for [Fe(Pyrdtc)$_2$Cl]: Cl, 9.24. Found: Cl, 9.17. The complexes were identical in all respects with authentic samples of the compounds.

Reaction of [Fe(R$_2$dtc)$_3$] with Silver Salts

A benzene solution (75 ml) of a tris complex ([Fe(R$_2$dtc)$_3$], R= C$_2$H$_5$, i-C$_3$H$_7$, 1/2(CH$_2$)$_4$; 2.0 g) was refluxed for 30 min with an excess of a silver salt (cyanate, thiocyanate, selenocyanate). The silver salt is insoluble in benzene, but the reaction proceeds with precipitation of the bis complex. The mixture was cooled to room temperature, filtered and the solid washed with benzene to remove any unreacted tris complex. The residue was extracted with methylene chloride, the deep green solution filtered, and an equal volume of benzene added. After evaporating on a hot plate to one-half of its initial volume, the solution was cooled, the black crystals collected, washed with benzene, recrystallized several times from methylene chloride–benzene mixtures and finally dried under vacuum at 80 °C several days. The yield of crude material was greater than 80% of theoretical yield. *Anal.* Calc'd for [Fe(Et$_2$dtc)$_2$NCO]: C, 33.49; H, 5.11; N, 10.65; S, 32.52. Found: C, 33.46; H, 5.00; N, 10.58; S, 32.49. Calc'd for [Fe(Pyrdtc)$_2$NCO]: C, 33.84; H, 4.13; N, 10.74; S, 32.85. Found: C, 33.73; H, 4.11; N, 10.57; S, 32.65. Calc'd for [Fe(Pyrdtc)$_2$NCS]·1/6C$_6$H$_6$: C, 34.36; H, 4.09; N, 10.26; S, 38.22. Found: C, 34.61; H, 3.99; N, 10.12; S, 38.30. Calc'd for [Fe(i-Pr$_2$dtc)$_2$NCSe]: C, 35.09;, H, 5.49; N, 8.11; S, 24.98; Se, 15.38. Found: C, 35.61; H, 5.75; N, 7.94; S, 30.53; Se, 15.10.

Reaction of [Fe(R$_2$dtc)$_3$] with Alkyl Halides

A mixture of [Fe(R$_2$dtc)$_3$] (1.0 g; R = CH$_3$, C$_2$H$_5$, i-C$_3$H$_7$, 1/2(CH$_2$)$_4$) and iodomethane, 2-bromo-2-methylpropane, allyl bromide or α-chlorotoluene (10 ml) in benzene (100–200 ml) was allowed to stand at room temperature in a stoppered flask until the bis complex had crystallized from solution. This required from about one day for iodomethane, the most reactive, to about two months for the least reactive, tert-butyl bromide. The complexes were recrystallized from methylene chloride or methylene chloride–benzene or n-hexane mixtures and dried under vacuum at 80 °C for several days. The complexes so prepared, [Fe(Me$_2$dtc)$_2$X], X = Br, I; [Fe(Et$_2$dtc)$_2$Br], [Fe(i-Pr$_2$dtc)$_2$I], and [Fe(Pyrdtc)$_2$X], X = Cl, Br, I, were identical in all respects with authentic samples, thus were not analyzed.

Reaction of [Fe(i-Pr$_2$dtc)$_3$] with Strong Organic Acids

A solution of 2.0 g [Fe(i-Pr$_2$dtc)$_3$] in 50 ml methylene chloride was treated with an excess of trifluoroacetic or picric acid and allowed to stand at room temperature (18 hours for the picric acid reaction and 13 days for the trifluoroacetic acid reaction), then 50 ml cyclohexane was added and the solution evaporated under vacuum to 50 ml total volume. The crystals were collected, washed with cyclohexane, recrystallized several times from methylene chloride–cyclohexane mixtures, and dried several days in vacuum at 80 °C. *Anal.* Calc'd for [Fe(i-Pr$_2$dtc)$_2$OOCCF$_3$]: C, 36.83; H, 5.41; N, 5.37; F, 10.93. Found: C, 37.05; H, 5.31; N, 5.26; F, 11.06. Calc'd for [Fe(i-Pr$_2$dtc)$_2$OC$_6$H$_2$(NO$_2$)$_3$]: C, 38.09; H, 4.79; N, 11.11; S, 20.34. Found: C, 38.03; H, 4.64; N, 11.23; S, 18.93.

Elemental analyses were performed by Alfred Bernhardt. Electronic and infrared spectra were recorded on Cary 14 and Beckman IR-8 and IR-12 spectrophotometers. Mössbauer spectra were obtained with a scanned velocity spectrometer operating in the time mode. Calibration with sodium nitroprusside (quadrupole splitting, 1.712 mm/sec at room temperature) and iron foil was performed before and after each Mössbauer spectrum was recorded. The number of baseline counts averaged 2 X 10^6 for each spectrum. Estimated error limits on the Mössbauer data are ±0.03 mm/sec.

Results

Electronic Spectra

These were recorded on methylene chloride solutions in the 650–240 nm range. Data for the new, non-halide complexes are given in Table I. Although it is not possible to assign the peaks at present, the data are useful in the characterization of a given complex. The peak positions depend upon X, with less dependence upon R, in [Fe(R$_2$dtc)$_2$X] complexes, and show the greatest variations in peaks 1 and 2. For peak 1 positions, the order (nm) is I$^-$< CF$_3$CO$_2^-$<Br$^-$, NCSe$^-$<picrate, Cl$^-$, NCS$^-$<NCO$^-$, *i.e.* the spectrochemical order, while for peak 2, the reverse order is found: NCO$^-$<Cl$^-$<Br$^-$<CF$_3$CO$_2^-$, picrate<I$^-$<NCS$^-$.

Infrared Spectra

Infrared spectra of these complexes were measured in KBr discs. Data are given in Table II for the 2300–900 cm^{-1} region which contains the C···N, C···S,

TABLE I. Electronic spectral Data in the 650–240 nm Region.

	Peak (nm)							
Complex	1	2	3	4	5	6	7	8
[Fe(Et$_2$dtc)$_2$NCO]	629	478	441		363	325	304	251
[Fe(Pyrdtc)$_2$NCO]	625	475	443		361	331	303	250
[Fe(Pyrdtc)$_2$NCS]	619	510	438	378	368	325	294	252
[Fe(i-Pr$_2$dtc)$_2$NCSe]	612		450	387	364	338	300	254
[Fe(i-Pr$_2$dtc)$_2$OOCCF$_3$]	609	500	441		366	325	303	251
[Fe(i-Pr$_2$dtc)$_2$picrate]	615	500	436	378	346		311	250

TABLE II. Infrared Data in the 2300–900 cm^{-1} Region.[a]

[Fe(Et$_2$dtc)$_2$ NCO]

2185 vs, 1510 vs, 1450 sh, 1440 m, 1378 w, 1352 m, 1295 sh, 1275 s, 1200 m, 1147 m, 1094 m, 1075m

[Fe(Pyrdtc)$_2$NCO]

2210 s, 1635 mb, 1520 vs, 1470 w, 1435 s, 1332 m, 1248 w, 1215 w, 1180 w, 1150 m, 940 w

[Fe(Pyrdtc)$_2$NCS]

2048 vs, 1635 wb, 1520 vs, 1465 w, 1440 s, 1330 m, 1310 sh, 1245 w, 1215 w, 1177 w, 1145 m, 937 w, 912 wb

[Fe(i-Pr$_2$dtc)$_2$NCSe]

2070 vs, 1620 wb, 1500 s, 1460 sh, 1440 m, 1378 sh, 1335 s, 1184 m, 1137 s, 1112 w, 1033 m

[Fe(i-Pr$_2$dtc)$_2$OOCCF$_3$]

1695 s, 1500 s, 1460 sh, 1445 m, 1397 sh, 1388 m, 1368 m, 1332 s, 1180 s, 1130 s, 1033 m, 903 w

[Fe(i-Pr$_2$dtc)$_2$OC$_6$H$_2$(NO$_2$)$_3$]

1605 s, 1575 m, 1530 sh, 1500 s, 1470 m, 1388 sh, 1370 sh, 1332 vs, 1275 m, 1183 m, 1138 s, 1077 m, 940 wb, 907 wb

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

CS$_2$, NC$_2$ and NCS$_2$ modes of the dithiocarbamate moiety.

The "thioureide" band (C···N stretch) [25] is sensitive to the nitrogen substituent, but not the fifth ligand X in these bis complexes. It occurs at *ca.* 1510, 1500 and 1520 cm^{-1} for the diethyl, diisopropyl and pentamethylene bisdithiocarbamates, respectively, while for the corresponding iron(III) trisdithiocarbamates, the band occurs at 1480, 1480 and 1470 cm^{-1}, respectively.

Other assignments are: 1035, 945, 905 cm^{-1}, CS [26] and CS$_2$ [27] modes; 1140 cm^{-1}, NC$_2$ [28] mode; 1130–1290 cm^{-1}, NCS$_2$ [29] group.

The bands at 2185 cm^{-1} in [Fe(Et$_2$dtc)$_2$NCO], 2210 cm^{-1} in [Fe(Pyrdtc)$_2$NCO], 2048 cm^{-1} in [Fe(Pyrdtc)$_2$NCS] and 2070 cm^{-1} in [Fe(i-Pr$_2$dtc)$_2$ NCSe] are due to the C–N stretch of cyanate, thiocyanate and selenocyanate.

The band at 1695 cm^{-1} in [Fe(i-Pr$_2$dtc)$_2$ OOCCF$_3$] is due to C = O stretching (the CF$_3$ bands overlap with dithiocarbamate in this complex) and the strong band at 1605 cm^{-1} in [Fe(i-Pr$_2$dtc)$_2$ OC$_6$H$_2$(NO$_2$)$_3$] is due to asymmetric NO$_2$ deformation.

Spectra of Nujol mulls were measured in the 900–200 cm^{-1} region which contains the Fe–Cl, Fe–S, Fe–N stretching and NCO and NCS bends. The main peaks are listed in Table III for the new complexes and two chlorides for comparison purposes.

TABLE III. Infrared Data in the 900–200 cm^{-1} Region.[a]

Na(i-Pr$_2$dtc)	[Fe(i-Pr$_2$dtc)$_2$NCSe]	[Fe(Et$_2$dtc)$_2$Cl]	[Fe(Et$_2$dtc$_2$)NCO]	[Fe(Pyrdtc)$_2$CL]	[Fe(Pyrdtc)$_2$NCO]	[Fe(Pyrdtc)$_2$NCS]
289 w, b	290 w			258 m	261 m	262 m
						297 m
		314 m		317 s		
				331 m, sh	340 s, sh	340 m, sh
	380 s	362 s	366 s	357 s	362 s	363 s
	410 w			416 w	418 m	417 m
						482 w
581 m	584 m			583 w	586 w	586 w
	619 w	612 w	618 w		617 s	
	660 w			700 m	703 m	702 m, sh
726 w, b	723 m, b	723 m, b	725 m, b	724 m	725 m, b	724 s
789 m	795 m	780 w, b	780 w, b			770 w
847 s	848 m	847 m	852 w	833 m	833 m	830 w
				862 w	860 w	850 w, b

[a]Values in cm^{-1}; s, strong; m, medium; w, weak; b, broad; sh, shoulder.

TABLE IV. Mössbauer Parameters for $[Fe(R_2dtc)_2X]$ Complexes at 298 °C.

Complex	δ^a, mm/sec	Δ, mm/sec	Γ^b mm/sec
$[Fe(Et_2dtc)_2NCO]$	0.63	2.23	0.30
$[Fe(Pyrdtc)_2NCO]$	0.65	2.21	0.30
$[Fe(Pyrdtc)_2NCS]$	0.65	2.41	0.22
$[Fe(i\text{-}Pr_2dtc)_2NCSe]$	0.63	2.75	0.59
$[Fe(i\text{-}Pr_2dtc)_2OOCCF_3]$	0.64	2.76	0.49
$[Fe(i\text{-}Pr_2dtc)_2picrate]$	0.63	3.01	0.33

[a] Relative to sodium nitroprusside; all values are postive. [b] Full width at half-maximum. Error limits: ±0.03 mm/sec.

The bands at 314 and 317 cm^{-1} are due to Fe–Cl stretching in $[Fe(Et_2dtc)_2Cl]$ and $[Fe(Pyrdtc)_2Cl]$, respectively, and are in good agreement with values reported in the literature: 309 cm^{-1} for $[Fe(Et_2dtc)_2Cl]$ [6] and 311 cm^{-1} for $[Fe(Me_2dtc)_2Cl]$ [12]. The 357–380 cm^{-1} band is due to Fe–S in-plane stretching [12].

It has been suggested [30, 31] for N-bonded thiocyanate complexes the C–N stretch lies below 2100 cm^{-1}, the C–S stretch in the 780–860 cm^{-1} region and the NCS bend in the 460–490 cm^{-1} range. The bands at 2048, 850 and 482 cm^{-1} indicate N-bonded thiocyanate in $[Fe(Pyrdtc)_2NCS]$. Similarly, the band at 660 cm^{-1} for $[Fe(i\text{-}Pr_2dtc)_2NCSe]$ is probably the C–Se stretch for N-bonded selenocyanate [32]. Since no M–OCN complexes are known, it is assumed that the two cyanate complexes contain N-bonded cyanate.

Mössbauer Spectra

Mössbauer spectra were measured at room temperature; the data (δ, isomer shift; Δ, quadrupole splitting) for the new complexes are listed in Table IV and a representative spectrum is shown in Figure 1. The spectra consisted of widely split doublets with peaks of equal area. Many exhibited some relaxation broadening of the lower energy (*i.e.* left) peak [14, 16].

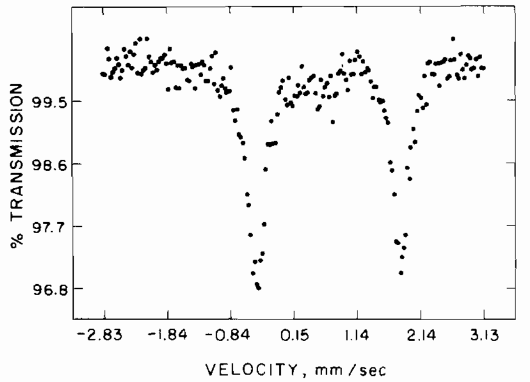

Figure 1. Mössbauer spectrum of $[Fe(Et_2dtc)_2NCO]$ at 298 K.

Discussion

The reaction of a tris(N,N-disubstituted dithiocarbamate)iron(III) complex with an alkyl (or aryl) mercuric chloride in either benzene or methylene chloride rapidly gave the corresponding chlorobis (N,N-disubstituted dithiocarbamato)iron(III) complex in quantitative yield. The bromide and iodide behaved similarly but these reactions were not investigated in detail. However, despite several attempts to obtain acetate, cyanide and fluoride complexes, none were obtained: phenylmercuric acetate did not react under the same conditions employed for the chloride (fusion of the acetate and tris complex resulted in decomposition), phenylmercuric fluoride caused complete decomposition of the tris complex, and phenylmercuric cyanide gave a green colored solution, indicating formation of the bis complex, but no pure cyanide complex could be isolated. Phenylmercuric nitrate reacted with $[Fe(Et_2dtc)_3]$ in methylene chloride solution to give an intractable black oil which decomposed upon standing at room temperature.

Silver salts reacted heterogeneously with tris complexes in benzene solution to give bis complexes. This method was used for the preparation of cyanate, thiocyanate and selenocyanate complexes. Silver nitrate and nitrite gave the same nitrosyl complex. Reaction was not observed, however, with silver carbonate or sulfate or disilver cynamide. Silver fluoride led to decomposition. Silver cyanide reacted with $[Fe(i\text{-}Pr_2dtc)_3]$ to give a green benzene solution, but an analytically pure cyano complex has not yet been prepared.

Various halobis(dithiocarbamato)iron(III) complexes were obtained from the relatively slow reaction of a tris complex with an alkyl halide in benzene solution. Methyl iodide was the most reactive of the halides tested (methyl iodide, allyl bromide, tert-butyl bromide and α-chlorotoluene). The rate of reaction also depended upon the R group in the tris complex, but the data at present are inadequate for definite conclusions as to the reactivity or selectivity of these halides towards various tris(dithiocarbamato)iron(III) complexes.

Strong organic acids in non-aqueous solution reacted with tris complexes to give bis complexes. This method was used for the preparation of a trifluoroacetate and a picrate complex. Several attempts to prepare pure complexes with weaker organic acids (acetic, monochloroacetic, dichloroacetic) were unsuccessful; the products isolated from the green solutions decomposed upon recrystallization.

The infrared spectra of these iron(III) bisdithiocarbamates reveal that the C•••N band of the dithiocarbamate is shifted to higher energy by some 20–40 cm^{-1} when compared to the corresponding iron(III) trisdithiocarbamates. This shift indicates that the dithiolate resonance form makes a greater contribution to the overall structure in the bis case, thus permitting greater S $\rightarrow$ Fe π-bonding [33]. A similar situation was reported for the iron(III) and iron(IV) trisdithiocarbamates [34].

The Mössbauer data of this study and that previously reported [14] indicate that the isomer shift values are relatively independent of both R and X in the $[Fe(R_2dtc)_2X]$ complexes. The average isomer shift for these complexes is 0.64 ± 0.02 mm/sec, relative to sodium nitroprusside. This constancy suggests that the total π-bonding in these compounds is invariant. The shifts are the same for the tris complexes, $[Fe(R_2dtc)_3]$, despite the difference in coordination number, symmetry and ligancy.

Although the quadrupole splittings are independent of R [14, 16], the values are dependent on X and vary from about 2.2 to 3.0 mm/sec. The splittings increase in the order $NCO^- < NCS^- < Cl^- < Br^- \sim NCSe^- \sim CF_3CO_2^- < I^- \sim$ picrate, an expected order which is inversely related to the spectrochemical series [14].

Summary

The syntheses presented here represent for the most part novel methods for the preparation of bis(N,N-disubstituted dithiocarbamato)iron(III) complexes and can be used for the preparation of complexes with a wide variety of X ligands. Not only the well-known chloride, bromide and iodide complexes, but new complexes containing cyanate, thiocyanate, selenocyanate, trifluoroacetate and picrate have been prepared. In many cases, the usual method for the preparation of the halide complexes, *e.g.* the treatment of a benzene solution of the tris complex ($[Fe(R_2dtc)_3]$) with aqueous acid, leads to little or no product.

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