Inorganica Chimica Acta, 21 (1977) 23–27
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Reaction of Iron(III) Dithiocarbamates with Iodine[1]

E. A. PASEK and D. K. STRAUB

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa. 15260, U.S.A.

Received May 6, 1976

The reaction of iodine with tris(N,N-disubstituted dithiocarbamato)iron(III) complexes, $[Fe(R_2dtc)_3]$, and with the iodobisdithiocarbamate complexes, $[Fe(R_2dtc)_2I]$, leads to several types of products, including those with stoichiometry $Fe(R_2dtc)_2I_2$ ($R = CH_3$, $i\text{-}C_3H_7$, $R,R = -(CH_2)_4-$), $Fe(R_2dtc)_2I_3$ ($R = C_2H_5$), and $Fe(R_2dtc)_3I_3$ ($R = i\text{-}C_3H_7$, C_6H_{11}, $C_6H_5CH_2$). Mössbauer spectroscopy shows that these complexes contain iron(III), except for the $Fe(R_2dtc)_3I_3$ complexes which contain iron(IV).

Introduction

The use of halogens to cause oxidation of metal N,N-dialkyldithiocarbamates [2] is well known. Gold(I) N,N-dialkyldithiocarbamates, $[Au(R_2dtc)]_2$, react with equimolar amounts of chlorine or bromine to produce the corresponding gold(III) complexes, $[Au(R_2dtc)X_2]$ [3] and with half the amount of chlorine, bromine and iodine to give the gold(III)–gold(I) complexes, $[Au(R_2dtc)_2]AuX_2$ [3, 4]. Similarly, the copper(I) complex, $[Cu(n\text{-}Bu_2dtc)]_x$, reacts with bromine to yield the copper(III) derivative, $[Cu(n\text{-}Bu_2dtc)Br_2]$ [5]. Copper(III) compounds can also be prepared either from $[Cu(Et_2dtc)]_4$ and bromine to give $[Cu(Et_2dtc)Br_2]$ or from $[Cu(Et_2dtc)_2]$ and bromine or iodine to give $[Cu(Et_2dtc)X_2]$ [6]. The reaction of chlorine or bromine with $[Ni(n\text{-}Bu_2dtc)_2]$ gives the nickel(IV) complex, $[Ni(n\text{-}Bu_2dtc)_3]X$ [7]. A nickel (IV) complex, $[Ni(Et_2dtc)_2Br_2]$, is prepared by the reaction of $[Ni(Et_2dtc)_2]$ and bromine [6]. The selenium analog of $[Ni(Et_2dtc)_2Br_2]$ is similarly prepared [8] Recently, it has been reported that iodine reacts with $[Ni(Et_2dtc)_2]$ and either $[Cu(Et_2dtc)]_4$ or $[Cu(Et_2dtc)_2]$ to produce the nickel(IV) and copper (III) complexes, $[Ni(Et_2dtc)_3]I_3$ and $[Cu(Et_2dtc)_2]I_3$ [9].

In addition to metal oxidation in the metal dithiocarbamates, ligand oxidation can also occur. For example, the dithiocarbamate ligand is readily oxidized to thiuram disulfide (tds) when $[M(n\text{-}Bu_2dtc)_2]$ complexes, where M is Zn(II), Cd(II) or Hg(II), react with bromine or iodine, thereby yielding the metal complex, $[MX_2(n\text{-}Bu_2tds)]$ [7]. The reaction of chlorine or bromine with iron(III) dithiocarbamates, $[Fe(R_2dtc)_2X]$ or $[Fe(R_2dtc)_3]$, causes oxidation of the dithiocarbamate ligand to a positive dication with an s-tetrathian ring and the iron(III) halogen anion, FeX_4^- [10]. Analogous results are obtained with cobalt(III), antimony and copper(I) dithiocarbamates.

In this paper we report on the reaction of iodobis (N,N-substituted dithiocarbamato)iron(III) and tris(N,N-disubstituted dithiocarbamato)iron(III) complexes with iodine.

Experimental

All reagents and solvents were reagent grade and used as received. Tris(N,N-disubstituted dithiocarbamato)iron(III) complexes were prepared and recrystallized as previously reported [11]. The iodobis (N,N-disubstituted dithiocarbamato)iron(III) compounds were obtained from the reaction between an iron(III) trisdithiocarbamate and hydriodic acid [12, 13]. The iodo complexes were collected, washed with ethanol, dried under vacuum and used without further purification.

Reaction of $[Fe(R_2dtc)_2I]$ Complexes with Iodine

Approximately 0.3 to 0.6 g of the iodo complex was reacted with 1.0 g of iodine in 100 ml of methylene chloride. After the addition of 50 ml of cyclohexane the mixture was evaporated on a hot plate to one-fourth its initial volume, causing black crystals to separate. The mixture was cooled to room temperature, the crystals collected, washed with cyclohexane, recrystallized several times from methylene chloride–cyclohexane mixtures (or from methylene chloride for the $[Fe(Me_2dtc)_2I]$ case), and dried under vacuum at 56 °C for 12 hours.

Reaction of $[Fe(R_2dtc)_3]$ Complexes with Iodine

Five grams of iodine in 100 ml of benzene were added to a stirred benzene solution of the iron(III) trisdithiocarbamate (prepared by dissolving 10 mmol of the tris complex in 300–400 ml of benzene). Initially, a black gum formed which slowly crystallized in all but the dibenzyl case. The collected

TABLE I. Analytical Data.[a]

Reaction	Product	%C	%H	%N	%S	%I
$[Fe(Me_2dtc)_2I]+I_2$	$Fe(Me_2dtc)_2I_2$	13.13(13.10)	2.41(2.20)	5.21(5.09)	23.23(23.31)	45.83(46.14)
$[Fe(Et_2dtc)_2I]+I_2$	$Fe(Et_2dtc)_2I_3$	16.58(16.25)	2.52(2.75)	4.03(3.88)	17.74(17.49)	52.01(51.93)
$[Fe(i\text{-}Pr_2dtc)_2I]+I_2$	$Fe(i\text{-}Pr_2dtc)_2I_2+1/6C_6H_{12}$	26.70(26.67)	4.35(4.47)	4.31(4.11)	19.07(18.96)	37.56(37.53)
$[Fe(Me_2dtc)_3]+I_2$	$Fe(Me_2dtc)_2I_2$	13.29(13.10)	2.28(2.20)	5.31(5.09)	23.43(23.31)	46.08(46.14)
$[Fe(Pyrdtc)_3]+I_2$	$Fe(Pyrdtc)_2I_2$	20.04(19.93)	2.72(2.67)	4.66(4.64)	21.50(21.30)	42.04(42.16)
$[Fe(i\text{-}Pr_2dtc)_3]+I_2$	$[Fe(i\text{-}Pr_2dtc)_3]I_3+4/3CH_2Cl_2$	24.41(24.86)	3.82(4.17)	3.36(3.90)	18.08(17.83)	35.19(35.28)
$[Fe(Bz_2dtc)_3]+I_2$	$[Fe(Bz_2dtc)_3]I_3+4/3CH_2Cl_2$	41.08(40.71)	3.03(3.29)	3.00(3.08)	13.88(14.08)	27.08(27.85)
$[Fe(c\text{-}Hx_2dtc)_3]+I_2$	$[Fe(c\text{-}Hx_2dtc)_3]I_3$	37.88(38.84)	5.24(5.52)	3.66(3.48)	16.21(15.95)	32.52(31.48)

[a] Values in parentheses are calculated values.

TABLE II. Mössbauer Data at 298 °K.

Complex (Empirical formula)	Reactants	δ^a mm/sec	Δ^b mm/sec	Γ^c mm/sec
$Fe(Me_2dtc)_2I_2$	$[Fe(Me_2dtc)_2I] + I_2$	0.62	3.23	0.27
	$[Fe(Me_2dtc)_3] + I_2$	0.64	3.20	0.33
$Fe(i\text{-}Pr_2dtc)_2I_2$	$[Fe(i\text{-}Pr_2dtc)_2] + I_2$	0.62	2.96	0.26
$Fe(Pyrdtc)_2I_2$	$[Fe(Pyrdtc)_3] + I_2$	0.64	3.08	0.30
$Fe(Et_2dtc)_2I_3$	$[Fe(Et_2dtc)_2I] + I_2$	0.64	3.65	0.24
$Fe(i\text{-}Pr_2dtc)_3I_3$	$[Fe(i\text{-}Pr_2dtc)_3] + I_2$	0.45	2.23	0.30
$Fe(c\text{-}Hx_2dtc)_3I_3$	$[Fe(c\text{-}Hx_2dtc)_3] + I_2$	0.46	2.24	0.31
$Fe(Bz_2dtc)_3I_3$	$[Fe(Bz_2dtc)_3] + I_2$	0.46	2.07	0.37

[a] Isomer shift relative to sodium nitroprusside; all values are positive. [b] Quadrupole splitting (sign unknown). [c] Full width at half-maximum; uncorrected. Error limits on δ, Δ, Γ: ±0.03 mm/sec.

crystals were washed with benzene and recrystallized by dissolving them in the minimum amount of methylene chloride, filtering the solution, adding benzene, and reducing the volume of the mixture to the volume of benzene added. For the dibenzyl product crystals were precipitated from a methylene chloride solution of the gum by the addition of cyclohexane. After a minimum of five such recrystallizations, the products were then dried under vacuum at ~80 °C.

Elemental analysis for all these products are given in Table I.

Infrared spectra were recorded on KBr disks with a Beckman IR-8 spectrophotometer and electronic spectra on methylene chloride solutions with a Cary 14 spectrophotometer. Mössbauer spectra were measured using a scanned velocity spectrometer, as previously described [11]. Calibration was done with sodium nitroprusside (quadrupole splitting, 1.712 mm/sec). Linearity was periodically checked using iron foil and was linear over the entire range of measurements. Spectra were fitted with a least-squares approximation assuming two peaks with Lorentzian line shapes of equal width. The range of nonresonant (baseline) counts for the room temperature spectra was 1.7–2.7 × 10^6. Elemental analyses were performed by Alfred Bernhardt, West Germany.

Results and Discussion

Synthesis

Two types of products have been isolated from the reaction of iodine with $[Fe(R_2dtc)_2I]$ complexes: $Fe(R_2dtc)_2I_2$, with R = CH_3 and $i\text{-}C_3H_7$, and $Fe(Et_2dtc)_2I_3$. Other complexes also resulted but these have not been isolated in analytically pure form. Similarly, iodine reacted with $[Fe(R_2dtc)_3]$ complexes in benzene solutions to yield two types of complexes. When R = CH_3 or $1/2(CH_2)_4$, complexes having the empirical formula $Fe(R_2dtc)_2I_2$ were obtained. When R = $C_6H_5CH_2$, C_6H_{11} or $i\text{-}C_3H_7$, the resulting products were $Fe(R_2dtc)_3I_3$.

Although a detailed study of the effect of solvent, temperature, concentration of reacting species and the particular iron(III) dithiocarbamate used on the final product of the reaction of iodine with $[Fe(R_2dtc)_3]$ and $[Fe(R_2dtc)_2I]$ was not undertaken, it does appear that the nitrogen substituent R has an effect on the course of the reaction.

Identification of Products. Mössbauer Spectra

Mössbauer spectra were measured at room temperature; data are shown in Table II. The spectra generally consisted of two widely split peaks; in some cases there was a very small additional peak (or peaks) in the center of the spectrum, indicating slight contamination, probably with the tris complex $[Fe(R_2dtc)_3]$ (either from unreacted starting material, or formed from an iodobis compound during reaction). Spectra of $Fe(Me_2dtc)_2I_2$, $Fe(Et_2dtc)_2I_3$, and $Fe(i\text{-}Pr_2dtc)_3I_3$ are shown in Figures 1–3.

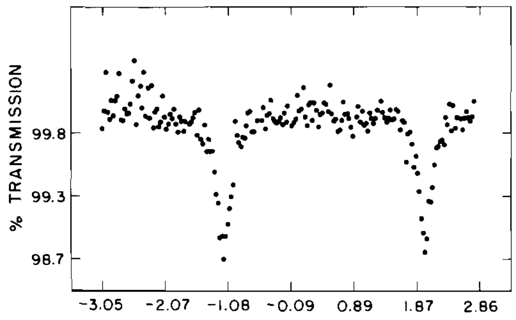

Figure 1. Mössbauer spectrum of $Fe(Me_2dtc)_2I_2$ at 298 °K.

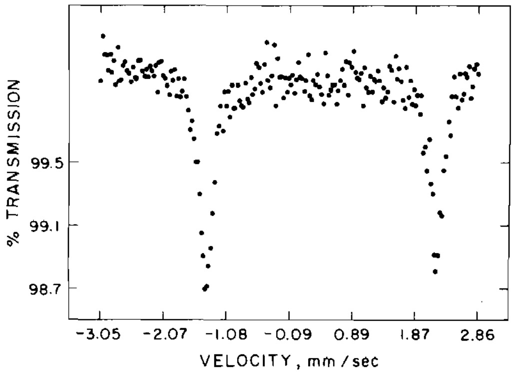

Figure 2. Mössbauer spectrum of $Fe(Et_2dtc)_2I_3$ at 298 °K.

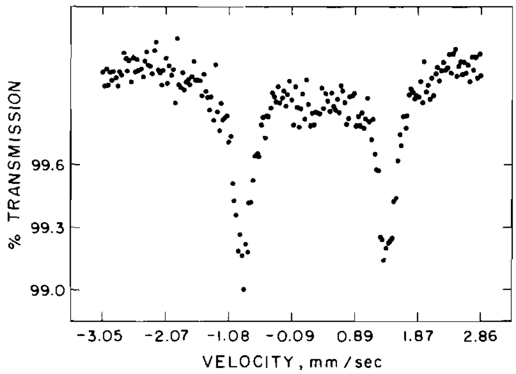

Figure 3. Mössbauer spectrum of $[Fe(i\text{-}Pr_2dtc)_3]I_3$ at 298 °K.

The isomer shifts at room temperature occur in two distinct ranges: 0.61–0.64 mm/sec and 0.45–0.46 mm/sec, relative to sodium nitroprusside. Values in the former range are comparable to the shifts expected for iron(III) dithiocarbamates, such as $[Fe(R_2dtc)_2X]$ [14] and $[Fe(R_2dtc)_3]$ [15]. The values in the latter range are consistent with the isomer shifts at room temperature for the iron(IV) dithiocarbamates, $[Fe(R_2dtc)_3]BF_4$, of 0.46 ± 0.03 mm/sec [11]. Thus, products having the empirical formulas $Fe(R_2dtc)_2I_2$ and $Fe(R_2dtc)_3I_2$ contain iron(III), and products with the empirical formula $Fe(R_2dtc)_3I_3$ contain iron (IV).

The complexes $Fe(R_2dtc)_3I_3$ had quadrupole splittings in the 2.1–2.2 mm/sec range observed for tris(dithiocarbamato)iron(IV) complexes [11], significantly lower than values expected for $[Fe(R_2dtc)_2I]$ (about 2.9 mm/sec [14]). Brinkhoff [9] has reported that the reactions of $[Ni(Et_2dtc)_2]$, $[Cu(Et_2dtc)_2]$ and $[Cu(Et_2dtc)]_4$ with iodine in either carbon disulfide or chloroform give the nickel(IV) and copper(III) complexes, $[Ni(Et_2dtc)_3]I_3$ and $[Cu(Et_2dtc)_2]I_3$. It is thus reasonable to formulate the compounds with the empirical formula $Fe(R_2dtc)_3I_3$, $R = C_6H_5CH_2$, C_6H_{11} and $i\text{-}C_3H_7$, as tris(N,N-disubstituted dithiocarbamato)iron(IV) triiodides, $[Fe(R_2dtc)_3]I_3$.

The best tentative structure for the $Fe(Et_2dtc)_2I_3$ complex is one containing coordinated triiodide, $[Fe(Et_2dtc)_2I_3]$. Since the triiodide ion is capable of charge delocalization, a weaker $Fe\text{–}I_3$ interaction in $[Fe(Et_2dtc)_2I_3]$ than an Fe–I interaction in $[Fe(Et_2dtc)_2I]$ is expected, and hence a larger quadrupole splitting for the triiodide (3.65 mm/sec) than the iodide (2.87 mm/sec [14]). The very large splitting of 3.65 mm/sec indicates very strong tetragonal distortion.

Unfortunately, for the remaining complexes $Fe(R_2dtc)_2I_2$, unambiguous structures are not so easily formulated from the Mössbauer data. These iron(III) complexes have large quadrupole splittings similar to those of the $[Fe(R_2dtc)_2I]$ complexes [14]. If these were 1:1 molar mixtures of $[Fe(R_2dtc)_2I]$ and $[Fe(R_2dtc)_2I_3]$, the Mössbauer spectra should show two doublets, since the splittings should differ by ~0.6 mm/sec, if the reasoning for $Fe(Et_2dtc)_2I_3$ given above is correct. These may be adducts of $[Fe(R_2dtc)_2I]$ with molecular iodine, *i.e.*, $2[Fe(R_2dtc)_2I]\cdot I_2$. The interaction between the molecular iodine and coordinated iodide in these cases persists in methylene chloride solutions since the characteristic visible peak of I_2 at 520–540 nm is missing.

Electronic Spectra

Electronic spectral data are given in Table III. The spectra are generally complex and quite similar except for the iron(IV) complexes. In these three cases, the presence of I_3^- is clearly shown by the strong peaks at 360 and 290 nm. Ionic triiodides show just these two peaks in a variety of solvents [16, 17]. The peaks at ~480 and ~445 nm also occur in $[Fe(R_2dtc)_3]BF_4$ [11].

TABLE III. Electronic Spectral Data for Methylene Chloride Solutions in 650–240 nm Region.

Complex	Reactants	max, nm (relative intensity)											
$Fe(Me_2dtc)_2I_2$	$[Fe(Me_2dtc)_2I] + I_2$	588 (1.00)	~500 (1.49)		459 (2.00)		415 (2.20)	370 (2.76)		299 (5.14)		263 (6.48)	250 (6.79)
	$[Fe(Me_2dtc)_3] + I_2$	590 (1.00)	~500 (1.45)		456 (1.93)		413 (2.10)	373 (2.88)		298 (5.02)		262 (6.51)	248 (7.50)
$Fe(i\text{-}Pr_2dtc)_2I_2$	$[Fe(i\text{-}Pr_2dtc)_2I] + I_2$	583 (1.00)	~500 (1.76)		~450 (2.37)		~425 (2.43)	367 (4.82)		296 (8.55)		272 (7.82)	256 (7.35)
$Fe(Pyrdtc)_2I_2$	$[Fe(Pyrdtc)_3] + I_2$	588 (1.00)	~500 (1.56)		460 (2.04)		415 (2.27)	376 (3.10)		303 (5.21)		261 (6.66)	248 (7.50)
$Fe(Et_2dtc)_2I_3$	$[Fe(Et_2dtc)_2I] + I_2$	588 (1.00)	~500 (1.58)		460 (1.87)		417 (2.16)	374 (3.05)		299 (5.14)		263 (6.48)	250 (7.16)
$Fe(Bz_2dtc)_3I_3$	$[Fe(Bz_2dtc)_3] + I_2$			488 (1.00)		446 (1.20)			364 (3.41)	293 (6.20)	282 (5.96)		
$Fe(c\text{-}Hx_2dtc)_3I_3$	$[Fe(c\text{-}Hx_2dtc)_3] + I_2$			474 (1.00)		444 (1.13)			361 (3.40)	290 (6.03)			
$Fe(i\text{-}Pr_2dtc)_3I_3$	$[Fe(i\text{-}Pr_2dtc)_3] + I_2$			475 (1.00)		441 (1.13)			361 (3.28)	293 (6.20)			246 (3.25)

Iodobisdithiocarbamates have peaks at about 596, 500, 454, 420, 370, 398, 368 and 252 nm [14], closely resembling those for the iron(III) complexes in Table III. The peak at ~420 nm is characteristic for iodo complexes, *e.g.* $[Fe(R_2dtc)_2I]$, and does not occur for any other (non-iodo) bisdithiocarbamate derivatives.

Infrared Spectra

The C$\cdots$N band is shifted to somewhat higher wave numbers for these products compared to the corresponding $[Fe(R_2dtc)_3]$ complexes. The positions are: $Fe(Me_2dtc)_2I_2$, 1545 cm^{-1}; $Fe(Pyrdtc)_2I_2$, 1515 cm^{-1}; $Fe(i\text{-}Pr_2dtc)_2I_2$, 1490 cm^{-1}. For the $[Fe(R_2dtc)_3]$ cases, the positions are: R = CH_3, 1520 cm^{-1}; C_2H_5, $i\text{-}C_3H_7$, 1480 cm^{-1}; 1/2 $(CH_2)_4$, C_6H_{11}, $C_6H_5CH_2$; 1470 cm^{-1}.

Acknowledgment

Support for this work was granted by the Division of Biology and Medicine, Atomic Energy Commission, through contract AT(30-1)3859.

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1 Taken in part from the Ph. D. dissertation of E. A. Pasek, University of Pittsburgh, 1971.

2 Abbreviations used: R_2dtc, $R_2NCS_2^-$; Me, CH_3; Et, C_2H_5; i-Pr, $i\text{-}C_3H_7$; n-Bu, $n\text{-}C_4H_9$; c-Hx, C_6H_{11}; Bz, $C_6H_5CH_2$; Pyrdtc, $(CH_2)_4NCS_2^-$.

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