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Preparation and Characterization of Bis(dithiocarbamato)isothiocyanato Iron(III) Complexes

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The reaction of dithiocarbamate complexes with boron trifluoride has been shown to result in complexes containing metal ions in unusual oxidation states or environments [1–8]. The reaction has been employed with tris(dithiocarbamato)iron(III) [1], manganese(III) [2, 5], cobalt(III) [1, 6, 8], rhodium(III) [7, 8] and ruthenium(III) [3, 8] complexes. Reactions with iron(III) and manganese(III) compounds resulted in the isolation of tris(dithiocarbamato)metal(IV) tetrafluoroborate complexes, whilst the other complexes produced dimeric metal(III) species.

Although the necessity for boron and fluorine containing by-products from the reaction is obvious, only one minor by-product has been reported – 3,5-bis(N,N-diethyliminium)-1,2,4-trithiolane bis(tetrafluoroborate) [9]. This was isolated from the reaction of boron trifluoride with tris(diethyldithiocarbamato)ruthenium(III).

During the preparation of tris(dithiocarbamato)iron(IV) species which we used for the preparation of the bis(dithiocarbamato)isothiocyanatoiron(III) compounds reported here, a white material that has been characterized as orthoboric acid was isolated.

Experimental

Starting materials and solvents were reagent grade and were used without further purification. The tris(dithiocarbamato)iron(III) and iron(IV) tetrafluoroborate complexes were prepared as described elsewhere [1]. The iron(IV) products were obtained as black oils which were recrystallized from dichloromethane/benzene mixtures. After recrystallization a white material that was approximately five per cent of the amount of complex formed, was obtained. Small quantities of this compound are also formed after several months when the Fe(IV) compounds are stored in stoppered glass containers.

Abbreviations used: iPr$_2$dtc, (i-$C_3H_7)_2NCS_2^-$; c-Hex$_2$dtc, (c-$C_6H_{11})_2NCS_2^-$; Et$_2$dtc, $(C_2H_5)_2NCS_2^-$.

Reactions of Fe(RRdtc)$_3$BF$_4$ with NH$_4$SCN (R = i-Pr or c-Hex)

Fe(RRdtc)$_3$BF$_4$ (1.5 g) was dissolved in acetonitrile (100 cm^3) and the solution stirred and filtered. To the filtrate was added solid ammonium thiocyanate (3 g) and the solution was stirred for 0.5 hours, during which time a dense green precipitate formed. The solid was collected on a filter, washed with water and dried in air. Recrystallization from dichloromethane-acetonitrile (1:5 by volume) produced green needles (yield, 60% for both compounds). *Anal.* Calc. for Fe((i-$C_3H_7)_2NCS_2)_2$(NCS): C, 38.5; H, 6.0; N, 9.0; S, 34.4%. Found: C, 38.7; H, 6.1; N, 9.2; S, 34.6%. (M.W.; Calc., 466; Found, 468). Calc. for Fe((c-$C_6H_{11})_2NCS_2)_2$(NCS): C, 51.6; H, 7.1; N, 6.7; S, 25.5%. Found: C, 51.2; H, 7.0; N, 6.7; S, 25.0%. (M.W.; Calc., 627; Found, 637). Mass spectra were recorded on a JEOL JMS D100 Mass Spectrometer. Solid state magnetic moments were determined using the Gouy method [10], sample tubes were calibrated with Hg Co(CNS)$_4$ and diamagnetic corrections estimated using Pascal's constants [10]. Molecular weights were measured in chloroform solution on a Perkin Elmer 115 Molecular Weight Apparatus. Thermogravimetric curves were recorded on a Rigaku Denki Thermal Analysis System. Infrared spectra were recorded as KBr discs or Nujol mulls on a Perkin Elmer 457 Infrared Spectrometer. Ultraviolet–visible spectra were recorded on a Unicam SP800 Spectrophotometer.

Results and Discussion

The mass spectrum of the white solid isolated in the reaction between Fe(RRdtc)$_3$ and boron trifluoride in benzene indicated an apparent parent ion at m/e 64 with fragmentations indicative of loss of –OH$_2$, –OH and –O. A pair of peaks at m/e 10, 11 (in the intensity ratio 1:4) indicated the presence of boron. From the mass spectrum the compound was identified as orthoboric acid, B(OH)$_3$. The identification was confirmed by comparisons of melting point, infrared spectra and thermogravimetric analysis with those of an authentic sample.

One way in which B(OH)$_3$ may arise in these reactions is from reaction of boron trifluoride with water in the solvent

$$4BF_3 + 6H_2O \longrightarrow 3H_3O^+ + 3BF_4^- + B(OH)_3$$

with the tetrafluoroborate anion being produced in the process. Further reactions of oxygen and H$_3$O$^+$ may possibly be responsible for oxidation of the iron(III) [1].

When acetonitrile solutions of Fe(RRdtc)$_3$ (R = i-Pr or c-Hex) were treated with ammonium thio-

TABLE. Magnetic and Spectral Data.

Compound	μ_{eff} (B.M.)[a]	νNCS (cm^{-1})	Wavelength ($\log_{10}\epsilon$)[b] (nm)
$FeCl(Et_2dtc)_2$	4.00[c]		617 (3.3), 450 (3.6), 384 (3.6), 312 (4.1)[c]
$Fe(NCS)(i\text{-}Pr_2dtc)_2$[d]	3.77	2060	625 (3.6), 440 (3.9), 377 (3.9), 307 (4.2)
$Fe(NCS)(c\text{-}Hex_2dtc)_2$[d]	3.94	2050	628 (3.6), 442 (4.0), 384 (4.0), 309 (4.2)
$Fe(NCS)(i\text{-}Pr_2dtc)_2$[e]		2060	625 (3.6), 440 (3.9), 376 (3.9), 307 (4.1)

[a] Magnetic moments measured in the solid state at 297 K. [b] Measured in chloroform solution. [c] Ref. [13]. [d] Prepared from $Fe(RRdtc)_3BF_4$. [e] Prepared from $Fe(i\text{-}Pr_2dtc)_3$.

cyanate a dark green crystalline product was isolated. Microanalysis indicated the complexes to be of the form $Fe(RRdtc)_2(CNS)$ and molecular weight measurements showed that the complexes were monomeric in solution. They were non-electrolytes in nitromethane solution.

It has been suggested [11, 12] that in most cases thiocyanate complexes exhibit, in their infrared spectra, very sharp, well defined cyano stretching frequencies above 2100 cm^{-1}, whereas isothiocyanato complexes exhibit peaks around or below 2100 cm^{-1}. On the basis of the observed infrared stretching frequencies for the complexes prepared in this work (Table) it is proposed that the complexes are isothiocyanato iron complexes.

Five-coordinate iron(III) dithiocarbamate complexes $Fe(dtc)_2X$ (X = Cl, Br, I, NCS, NCSe *etc.*) have been isolated previously, either from reaction of $Fe(RRdtc)_3$ with the halo-acid [13], or silver salts in refluxing benzene [14, 15]. The magnetic moments and electronic spectra of the isothiocyanato complexes prepared in this work closely resemble those reported for the $Fe(dtc)_2X$ (X = Cl, Br, I) complexes which have been fully characterized as iron(III) species possessing square pyramidal geometry [13] (Table).

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