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Tris(*N,N*-disubstituted-dithiocarbamato)manganese(IV) and -cobalt(IV) Tetrafluoroborates

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The ability of the *N,N*-disubstituted dithiocarbamate ligand to stabilize high oxidation states of transition metal ions has been well established:[2] *e.g.*, complexes of Mn(III),[3] Fe(IV),[4] Ni(IV),[5,6] and Co(III)[5,6] are known. Until very recently, no dithiocarbamates were known for Mn(IV) or Co(IV), although the suggestion had been made that manganese(III) tris(diethyldithiocarbamate) oxidizes slowly and spontaneously to an Mn(IV) tetrakis complex.[7] A recent note has appeared on tris(dithiocarbamato)cobalt(IV) tetrafluoroborates.[8]

Only a few complexes of Mn(IV) are known.[9] These include salts of MnF_6^{2-}, $MnCl_6^{2-}$, and $Mn(CN)_6^{2-}$, anionic complexes with iodate, periodate, tellurate, and oxalate, a heteropolyvanadate and niobate, and [Mn(2,2′-bipy)Cl_4]. Tetravalent cobalt compounds are very rare,[10] comprising only Cs_2CoF_6, tetrakis(1-norbornyl)cobalt(IV),[11] a heteropolymolybdate (not well characterized), some oxides, *e.g.*, Ba_2CoO_4, and perhaps a bis(dicarbollyl) complex.[12]

The reaction between a tris(*N,N*-disubstituted-dithiocarbamato)metal(III) complex in solution and gaseous boron trifluoride in the presence of air, which led initially to the isolation of tris(dithiocarbamato)iron(IV) tetrafluoroborates,[4] has been extended to include manganese(IV) and cobalt(IV) complexes.

Experimental Section[13]

All starting materials and solvents were reagent grade. The tris(dithiocarbamato)cobalt(III) complexes [Co(Et_2dtc)$_3$] and [Co((*c*-Hx)$_2$dtc)$_3$] were prepared by mixing aqueous solutions of the potassium dithiocarbamate and a cobalt(II) salt.[14] Cobalt(II) is oxidized spontaneously to cobalt(III) under these conditions.[15] The precipitates were collected, air-dried, and recrystallized from methylene chloride or methylene chloride–diethyl ether mixture and dried under vacuum over refluxing 2-propanol for 1 day.

The tris(dithiocarbamato)manganese(III) complexes [Mn(Et_2dtc)$_3$] and [Mn((*i*-Pr)$_2$dtc)$_3$] were prepared by adding an aqueous solution of manganese(II) chloride to the potassium dithiocarbamate solution in a 1:3 molar ratio. Yellow precipitates of bis(dithiocarbamato)manganese(II) complexes formed immediately.[3,15] Upon bubbling air for several hours through, or adding hydrogen peroxide to, the stirred aqueous suspensions, the yellow color changed to the brown-purple of the tris(dithiocarbamato)manganese(III) complexes. The precipitates were collected, washed well with distilled water, air-dried, and recrystallized from methylene chloride–methanol mixtures. The crystals were finally dried under vacuum for 1 day.

Preparation of Tris(*N,N*-diethyldithiocarbamato)manganese(IV) Tetrafluoroborate. Boron trifluoride was bubbled for 5 minutes through a solution of 7 g of [Mn(Et_2dtc)$_3$] in 120 ml of methylene chloride contained in a plastic flask and open to the air. The mixture was stirred for about 8 min, followed by an additional 0.5-min bubbling of boron trifluoride gas. The solution was then evaporated to dryness under vacuum. The black oily residue solidified upon treatment with diethyl ether. The solid was washed well with 20-ml portions of benzene to remove unreacted material and dissolved in 80 ml of methylene chloride. Diethyl ether added to the filtered solution caused crystallization. This recrystallization process was repeated an additional four times. The product was finally dried under vacuum over refluxing acetone for 3 days. This sample analyzed for [Mn(Et_2dtc)$_3$]$BF_4 \cdot {}^1/_3 Et_2O$. A second sample, prepared similarly and dried at room temperature for 7 days under vacuum, analyzed for [Mn(Et_2dtc)$_3$]BF_4.

Preparation of Tris(*N,N*-diisopropyldithiocarbamato)manganese(IV) Tetrafluoroborate. This complex was prepared from [Mn((*i*-Pr)$_2$dtc)$_3$] and boron trifluoride in the same manner as the diethyl complex. It was recrystallized by ether precipitation from methylene chloride six times and finally dried under vacuum over refluxing acetone for 3 days.

Preparation of Tris(*N,N*-diethyldithiocarbamato)cobalt(IV) Tetrafluoroborate. Ten grams of [Co(Et_2dtc)$_3$] in 100 ml of methylene chloride in a plastic flask open to the air was saturated with boron trifluoride gas. The reaction mixture was evaporated to dryness in air overnight. The rather sticky crystals were extracted with benzene until the benzene was no longer colored green from the unreacted cobalt(III) complex. The dark brown oil which remained was treated with diethyl ether, which caused solidification. The blackish powder, which weighed 2.7 g, was dissolved in 50 ml of methylene chloride, the solution filtered, and 100 ml of diethyl ether added with stirring. Fine, black-green crystals formed and were collected after 1–2 hr. About 1.8 g was obtained. These were twice more recrystallized by ether precipitation from methylene chloride solution and finally dried under vacuum several days.

Preparation of Tris(*N,N*-dicyclohexyldithiocarbamato)cobalt(IV) Tetrafluoroborate. This was prepared from [Co((*c*-Hx)$_2$dtc)$_3$] and boron trifluoride using the same procedure as in the diethyl complex. The dark olive green crystals were recrystallized four times by ether precipitation from methylene chloride solution and dried for 3 days under vacuum over refluxing 2-propanol.

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

Results

Data from elemental analyses are given in Table I. The manganese(IV) complexes form dark purple crystals, soluble in methylene chloride, acetone, acetonitrile, and nitromethane, forming reddish purple solutions, and insoluble in benzene, cyclohexane, pentane, diethyl ether, and carbon disulfide. The cobalt(IV) complexes form dark greenish brown to black crystals, soluble in methylene chloride, acetone, aceto-

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(13) Abbreviations used: Et, ethyl, C_2H_5; *i*-Pr, isopropyl, C_3H_7; *c*-Hx, cyclohexyl, C_6H_{11}; R, alkyl; dtc, dithiocarbamate, $>NCS_2^-$.

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Table I. Analytical Data for Tris(dithiocarbamato)metal(IV) Tetrafluoroborates

	% C		% H		% N		% S		% B		% F	
Complex	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Mn(Et_2dtc)_3]BF_4 \cdot {}^1/_3Et_2O$	32.09	32.21	5.50	5.35	6.88	7.08	31.48	32.04	1.77	1.74	12.43	12.50
$[Mn(Et_2dtc)_3]BF_4$	30.72	30.59	5.16	5.24	7.16	7.30	32.80	32.90	1.84	1.65	12.97	13.32
$[Mn((i\text{-}Pr)_2dtc)_3]BF_4$	37.61	37.59	6.31	6.18	6.27	6.10	28.68	28.25	1.61	1.72	11.33	11.77
$[Co(Et_2dtc)_3]BF_4$	30.51	30.72	5.12	5.22	7.11	7.15	32.58	32.72	1.83	1.66	12.87	12.67
$[Co((c\text{-}Hx)_2dtc)_3]BF_4$	51.19	50.95	7.27	7.51	4.59	4.46	21.02	16.51	1.18	1.16	8.30	8.03

Table II. Equivalent Conductivities and Magnetic Moments[a]

Complex	Concn, *M*	Conductance,[c] mhos	Equiv conductance, mhos cm²/equiv	$10^{-6}\chi_D$,[b] cgsu	$10^{-6}\chi_M$,[c] cgsu	μ,[d] BM
$[Mn(Et_2dtc)_3]BF_4$	1.05×10^{-3}	7240	97	−317	5652	3.74
$[Mn((i\text{-}Pr)_2dtc)_3]BF_4$	1.04×10^{-3}	8000	109	−389	5150	3.59
$[Co((c\text{-}Hx)_2dtc)_3]BF_4$	8.46×10^{-4}	6440	90	−567	4856	3.48

[a] Conductivities measured in nitromethane solutions at 25°; magnetic susceptibilities measured in methylene chloride solutions at 36°. [b] Diamagnetic correction. [c] Corrected value. [d] Estimated error limits: ±0.10 BM.

Table III. Electron Spectral Data in the 650–220-nm Range

	Peak, nm						
Complex	I	II	III	IV	V	VI	VII
$[Mn(Et_2dtc)_3]BF_4$	482 (13,200)[a]	422 (13,200)	406 (15,000)	320	288	252	235
$[Mn((i\text{-}Pr)_2dtc)_3]BF_4$	482 (13,700)	425 (14,500)	409 (15,200)	323	300	265	245
$[Co(Et_2dtc)_3]_4$[b]	620	415					
$[Co((c\text{-}Hx)_2dtc)_3]BF_4$	619	419	319			277	250

[a] Numbers in parentheses are absorption coefficients, ϵ, given in M^{-1} cm^{-1}. [b] Measured only in visible region.

Table IV. Infrared Data in the 1600–900-cm^{-1} Region[a]

$[Mn(Et_2dtc)_3]BF_4$: 1525 s, 1350 s, 1275 s, 1193 s, 1150 s, 1040 s, b, 990 sh, 903 w

$[Mn((i\text{-}Pr)_2dtc)_3]BF_4$: 1520 s, 1490 m, 1335 s, 1280 sh, 1187 s, 1140 b, 1090 b, 1055 b, 1030 b

$[Co((c\text{-}Hx)_2dtc)_3BF_4$: 1480 s, 1348 s, 1308 s, 1265 m, 1240 s, 1152 m, 1095 s, 1052 b, 1000 sh

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

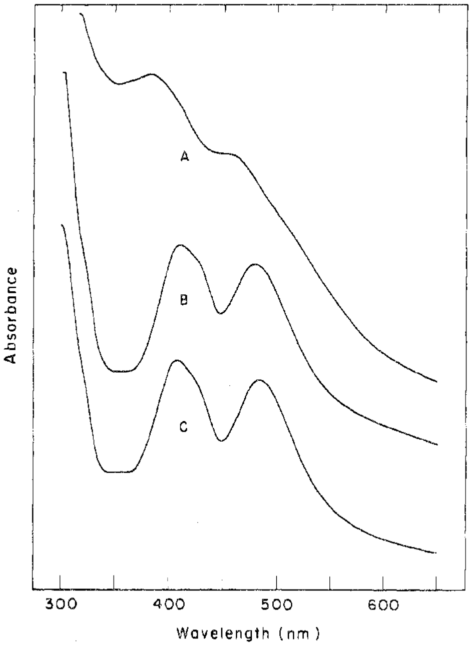

Figure 1. Visible spectra of (A) $[Mn((i\text{-}Pr)_2dtc)_3]$, (B) $[Mn((i\text{-}Pr)_2dtc)_3]BF_4$, (C) $[Mn(Et_2dtc)_3]BF_4$ in methylene chloride solution.

nitrile, and nitromethane, giving dark olive green solutions, and insoluble in benzene, cyclohexane, carbon disulfide, and diethyl ether. Both of the manganese(IV) and cobalt(IV) complexes appeared to decompose slowly over a period of weeks when exposed to air.

Equivalent Conductance. The equivalent conductivities, shown in Table II, indicate these complexes to be uni-univalent electrolytes in nitromethane.[16]

Magnetic Moments. Magnetic susceptibilities were measured by the nmr method,[17] with tetramethylsilane as standard. Dimagnetic corrections were calculated from Pascal's constants. Data are given in Table II and represent averages of four to six different determinations which agreed to within ±0.05 BM of each other.

Electronic Spectra. These were measured on methylene chloride solutions in the 650–~220-nm range. Data are given in Table III. Visible spectra of two manganese complexes are shown in Figure 1 and the visible spectrum of $[Co((c\text{-}Hx)_2dtc)_3]BF_4$ is shown in Figure 2.

Infrared Spectra. Infrared spectra were measured on Nujol mulls. Data are given in Table IV for the 1600–900-cm^{-1} region which included the C$\overset{\cdot\cdot\cdot}{-}N, C\overset{\cdot\cdot\cdot}{-}$S, and NC_2 bands. (The Nujol peaks have been omitted.) Tetrafluoroborate has broad, strong bands in the 1000–1100-cm^{-1} region, which overlap with the CS and NC_2 bands. The CN band appeared at ~1520 cm^{-1} in the manganese(IV) complexes and at 1480 cm^{-1} in the cobalt(IV) complex.

Discussion

Manganese(IV) complexes, $[Mn(R_2NCS_2)_3]BF_4$, with R = C_2H_5 and $i\text{-}C_3H_7$, could be isolated readily from the $[Mn(R_2NCS_2)_3]$ + BF_3(g) reaction. The Co(IV) complexes $[Co(R_2NCS_2)_3]BF_4$, R = C_2H_5 and C_6H_{11}, were similarly synthesized but appeared to be less stable than either the Mn(IV) or Fe(IV)[4] complexes. Both series of complexes showed an increase of about 30 cm^{-1} in the position of the C$\overset{\cdot\cdot\cdot}{-}$N stretching frequency over that of the corresponding metal(III) complex, confirming the higher oxidation state.

Some orbital reduction in the spin-only value of 3.88 BM for octahedral Mn(IV) is expected,[18] and values of 3.7-3.8 BM at room temperature have been measured for some

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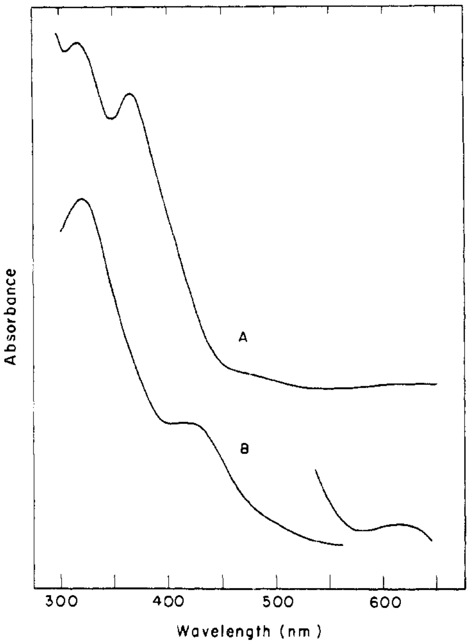

Figure 2. Visible spectra of (A) $[Co((c\text{-}Hx)_2dtc)_3]$ and (B) $[Co((c\text{-}Hx)_2dtc)_3]BF_4$ in methylene chloride solution.

Mn(IV) complexes.[9] Thus, $[Mn(R_2dtc)_3]BF_4$ complexes are high spin from the magnetic data given in Table II.

Magnetic moments expected for octahedral Co(IV), a d^5 ion, are ~2.1 BM for low-spin or 5.89 BM for high-spin complexes.[18] The measured intermediate magnetic moment of 3.5 BM for $[Co((c\text{-}Hx)_2dtc)_3]BF_4$ suggests a mixed low-spin-high-spin equilibrium state at room temperature, similar to the mixed spin states of the isoelectronic $[Fe(R_2dtc)_3]$ complexes.[19]

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Registry No. $[Mn(Et_2dtc)_3]BF_4\cdot{}^1/_3Et_2O$, 52699-13-5; $[Mn(Et_2dtc)_3]BF_4$, 52699-12-4; $[Mn((i\text{-}Pr)_2dtc)_3]BF_4$, 52699-15-7; $[Co(Et_2dtc)_3]BF_4$, 52637-78-2; $[Co((c\text{-}Hx)_2dtc)_3]BF_4$, 52637-82-8; $[Mn(Et_2dtc)_3]$, 15740-71-3; $[Mn((i\text{-}Pr)_2dtc)_3]$, 25753-58-6; $[Co(Et_2dtc)_3]$, 13963-60-5; $[Co((c\text{-}Hx)_2dtc)_3]$, 52637-81-7; BF_3, 7637-07-2.

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Continuous and Discontinuous Thermochromism of Copper(II) and Nickel(II) Complexes with *N,N*-Diethylethylenediamine[1]

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Some coordination compounds change color quite markedly with temperature. Such thermochromism is usually associated with temperature-dependent changes in the stereochemistry of the chromophore and depends on the nature of both the central metal ion and the ligand.

The bidentate ligand *N,N*-diethylethylenediamine (dieten, $H_2NCH_2CH_2N(C_2H_5)_2$) forms the three copper complexes $Cu(dieten)_2X_2$ ($X = BF_4, ClO_4, NO_3$) which change color reversibly from red to violet at higher temperatures.[2-4] This behavior has been attributed to a thermally sensitive tetragonal distortion in the copper atom environment.[4] However, both a blue and a red from can be isolated at normal temperatures.[4] Other copper complexes ($X = Br, I, AgI_2, PbI_3, {}^1/_2HgI_4, {}^1/_2CdBr_4$) are not thermochromic.

The analogous nickel complexes $Ni(dieten)_2X_2$ change from orange-yellow to bright red at higher temperatures. With $X = I, ClO_4$, and BF_4 the change is reported to be reversible.[5] We have found similar behavior with the anions of $X = NO_3$, $Br, AgI_2, PbI_3, {}^1/_2HgI_4$, and ${}^1/_2CdBr_4$. The compounds are diamagnetic, showing that the anions are not strongly coordinated.

Increasing temperature provokes a red shift in the visible absorption band of the copper complexes: the frequency of this band is shown in Figure 1. There is a small temperature range for each compound within which the red shift increases sharply. The largest shift is observed in the nitrate where it also occurs at the highest temperature. Above this transition temperature the absorption band ceases to be temperature sensitive and the compounds behave in the same way as the other copper complexes.

The d-d absorption bands of the thermochromic nickel complexes also shift to lower frequencies with increasing temperature, as shown in Figure 2. With $X = BF_4$ and ClO_4 the spectral change is quite sharp, but with the other compounds the red shift increases regularly.

The infrared spectra of the six compounds $M(dieten)_2X_2$ ($M = Cu, Ni$; $X = BF_4, ClO_4, NO_3$) are reversibly temperature sensitive. In the spectrum of $Cu(dieten)(NO_3)_2$, a band at 1750 cm^{-1}, assignable as the combination $\nu_1 + \nu_4$ ($a_1' + e' = e'$) of the unbound nitrate ion,[4] decreases in intensity and disappears above 130°, only to reappear with pristine intensity upon cooling back to room temperature. Lever, *et al.*,[4] have examined the ir spectrum of the blue unstable form of $Cu(dieten)(NO_3)_2$ and found two bands in the combination region, at *ca.* 1748 and 1760 cm^{-1}, whose intensity is considerably reduced relative to the combination band in the stable low-temperature form. Lever, *et al.*, assigned these two bands to coordinated nitrate ion, where the degeneracy of the e′ mode is lifted on account of reduced symmetry. These bands are not observed at higher temperatures because they broaden as the temperature rises. The infrared spectra of the fluoroborates and perchlorates exhibit bands characteristic of coordinated anion (BF_4^- 335 cm^{-1}, ClO_4^- 460 cm^{-1})[6,7] even at room temperature.[4] We also find a shoulder forming at 750 cm^{-1} with rising temperature in the spectrum of $Ni(dieten)_2(BF_4)_2$ similar to the band observed by Lever in the copper analog.[4]

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