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Transition Metal Monoalkyltrithiocarbonates

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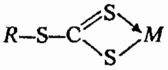
The following monoalkyltrithiocarbonates have been prepared: $Ni(S_2CSC_2H_5)_2$, $Ni(S_2CSC_3H_7)_2$, $Ni(S_2CSC_4H_9)_2$, $Cr(S_2CSC_2H_5)_3$, $Cr(S_2CSC_3H_7)_3$, $Cr(S_2CSC_4H_9)_3$, $Co(S_2CSC_2H_5)_3$, $Co(S_2CSC_3H_7)_3$, $Co(S_2CSC_4H_9)_3$, $Fe(S_2CSC_2H_5)_3$, $Fe(S_2CSC_3H_7)_3$, $Fe(S_2CSC_4H_9)_3$. The electronic spectra and magnetic properties are consistent with an octahedral coordination for the trivalent metal derivatives, and with a square-planar coordination for the Ni^{II} complexes. The diamagnetic behaviour found for tris(ethyltrithiocarbonate)Fe^{III} indicates a spin pairing in this compound. The infrared spectra of these compounds have been determined.

Introduction

While several studies of trithiocarbonic acid derivatives (dialkyl-, diaryl- and arylalkyltrithiocarbonates[1,2] and metal trithiocarbonates[3,4]) have been reported, only a few investigations have been carried out on metal monoalkyl derivatives,[5,6] the alkyltrithiocarbonates of alkali metals have been the most extensively investigated.[7,8] The present paper deals with the synthesis and characterization of some 3*d* transition metal complexes formed by ethyl-, *n*-propyl- and *n*-butyltrithiocarbonic acid, in which the ligand is behaving as a chelating agent:



$R = C_2H_5$, n–C_3H_7, n–C_4H_9

In order to investigate the properties of these complexes their infrared and electronic spectra and magnetic properties have also been studied.

Experimental Section

Physical Measurements. The infrared spectra were determined in KBr disks using a Perkin-Elmer Model 457 double-beam spectrophotometer. The electronic spectra of chloroform solutions were registered from 190 to 850 mμ, using 1 cm cells in a Perkin-Elmer Model 402 spectrophotometer. The magnetic susceptibilities were measured on solid powdered samples by a Gouy balance (Newport Instruments) at 25°C.

Preparation of the compounds. All the compounds were prepared by direct reaction of the alkali monoalkyltrithiocarbonate and the metal halide in aqueous or ethanol solutions. The resulting products are coloured powders; attempts to obtain single crystals by recrystallization were not always successful.

The analytical data is as follows:

Tris(ethyltrithiocarbonate)Co^{III}. Anal. Calcd. for $C_9H_{15}CoS_9$: C, 22.9; H, 3.2; Co, 12.5. Found: C, 22.7; H, 3.3; Co, 12.7.

*Tris(*n*-propyltrithiocarbonate)Co^{III}. Anal.* Calcd. for $C_{12}H_{21}CoS_9$: C, 28.1; H, 4.1; Co, 11.4. Found: C, 28.5; H, 4.2; Co, 11.3.

Tris(ethyltrithiocarbonate)Cr^{III}. Anal. Calcd. for $C_9H_{15}CrS_9$: C, 23.3; H, 3.3; Cr, 11.2. Found: C, 23.1; H, 3.2; Cr, 11.6.

Tris(ethyltrithiocarbonate)Fe^{III}. Anal. Calcd. for $C_9H_{15}FeS_9$: C, 23.1; H, 3.2; Fe, 11.9. Found: C, 23.3; H, 3.8; Fe, 11.4.

*Tris(*n*-propyltrithiocarbonate)Fe^{III}. Anal.* Calcd. for $C_{12}H_{21}FeS_9$: C, 28.3; H, 4.2; Fe, 10.9. Found: C, 29.0; H, 4.8; Fe, 10.5.

Bis(ethyltrithiocarbonate)Ni^{II}. Anal. Calcd. for $C_6H_{10}NiS_6$: C, 21.6; H, 3.0; Ni, 17.6. Found: C, 22.8; H, 3.8; Ni, 18.8.

*Bis(*n*-propyltrithiocarbonate)Ni^{II}. Anal.* Calcd. for $C_8H_{14}NiS_6$: C, 26.6; H, 3.9; Ni, 16.3. Found: C, 25.6; H, 4.3; Ni, 16.7.

*Bis(*n*-butyltrithiocarbonate)Ni^{II}. Anal.* Calcd. for $C_{10}H_{18}NiS_6$: C, 30.8; H, 4.7; Ni, 15.1. Found: C, 32.3; H, 5.3; Ni, 15.1.

Results and Discussion

The compounds share the common property of being very soluble in chloroform, ether and acetone,

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(1) H. C. Godt and R. E Wann, *J. Org. Chem.*, *26*, 4047 (1961).
(2) E. Wertheim, *J. Am. Chem. Soc.*, *48*, 826 (1926).
(3) J. Bankovskis and A. Ievins, *Latvijas PSR Zinatnu Akad. Vestis*, *3*, 123 (1957), from *Chem. Abstr.*, *52*, 5193 (1958).
(4) W. A. Deskin, *J. Am. Chem. Soc.*, *80*, 5680 (1958).
(5) F. Galsbøl and C. E. Schäffer, *Inorg. Synth.*, *X*, McGraw-Hill Book Company, New York, 42 (1967).
(6) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *J. Am. Chem. Soc.*, *91*, 761 (1969)
(7) E. Philippot, *Rev. Chim. Miner.*, *4*, 643 (1967), from *Chem. Abstr.*, *68*, 83864 (1968).
(8) W. T. Bishop, *U.S.* 2, 197, 964 Apr. 23, from *Chem. Abstr.*, *34*, 5463 (1940).

Table I. Infrared frequencies of alkyltrithiocarbonates (cm^{-1})

Ketc	Ni(etc)$_2$	Co(etc)$_3$	Cr(etc)$_3$	Fe(etc)$_3$	Naptc	Ni(ptc)$_2$	Co(ptc)$_3$	Fe(ptc)$_3$	Kbtc	Ni(btc)$_2$	tentative assignments
1050 s	1060 m	1045 m	1050 m	1060 m	1060 sh	1045 m	—	—	1020 vs	—	ν(C—S)
1000 vs	—	—	—	1000 sh	1000 vs	—	—	1010 m	1000 sh	—	
—	990 vs	980 vs	965 vs	980 vs	—	980 vs	980 vs	985 vs	—	990 vs	
950 w	935 vs	945 vs	930 vs	950 vs	—	945 vs	950 vs	955 vs	910 w	935 vs 910 sh	
850 s 840 sh	—	—	—	880 s	850 s 820 sh	—	—	875 s	855 s 840 sh	—	
740 m	770 m 760 sh	750 m	750 m	750 m	730 vw	730 w	720 w	720 w	715 w	740 w	ν(S—*R*)
490 w	520 m	510 m	510 m	525 w	490 m	510 w	510 w	530 w	480 w	525 w	$\nu\left(-\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{S}}{\mathrm{S}}\right)$?
—	460 w	460 w	470 m	460 w	440 m	—	460 w	455 w	405 w	—	ν(M—S)
350 w	375 m 350 sh	350 m	360 s	350 w	—	340 w	350 w	—	350 w	380 m	
—	—	320 w	310 w	310 vw	—	—	—	330 w	310 w	320 w	

etc, ethyltrithiocarbonate; ptc, *n*-propyltrithiocarbonate; btc, *n*-butyltrithiocarbonate; *R*, alkyl; s, strong; m, medium; w, weak; sh, shoulder.

Table II. Electronic transitions in alkyltrithiocarbonates spectra (wavenumbers in kK = 1000 cm^{-1})

$Co(S_2CSC_2H_5)_3$	$Co(S_2CSC_3H_7)_3$			$Cr(S_2CSC_2H_5)_3$	$Cr(S_2CSC_3H_7)_3$	
15.9	15.9		$^1\Gamma_1 \longrightarrow {}^1\Gamma_4$	15.7	15.6	$^4\Gamma_2 \longrightarrow {}^4\Gamma_5$
(20.0)	(20.0)		$\longrightarrow {}^1\Gamma_5$	19.8	20.0	$\longrightarrow {}^4\Gamma_4$
25.5	25.5		—	(22.5)	(22.5)	—
31.2	31.2		—	(25.5)	(25.7)	—
34.1	34.1		—	(30.3)	(30.3)	—
39.2	39.2		—	32.3	32.3	—
				(34.7)	(34.7)	—
				40.8	(40.8	—
$Ni(S_2CSC_2H_5)_2$	$Ni(S_2CSC_3H_7)_2$	$Ni(S_2CSC_4H_9)_2$		$Fe(S_2CSC_2H_5)_3$	$Fe(S_2CSC_3H_7)_3$	
(17.2)	(16.3)	(17.4)	$^1\Gamma_{11} \longrightarrow {}^1\Gamma_{t2}$	12.5	13.0	Electron transfer
20.4	19.6	20.2	$\longrightarrow {}^1\Gamma_{15}$	20.0	19.8	
21.9	22.2	24.7	—	(24.7)	(24.7)	
29.8	29.8	29.8	—	31.8	32.7	
34.1	33.9	35.3	—	39.2	39.2	
39.2	39.2	39.2	—			

slightly soluble in ethanol and methanol, and insoluble in water. The analytical data of the compounds sometimes is not precise, as the products are often unstable (particularly the Ni derivatives which decompose at the air) and difficult to purify; Co^{III}, Fe^{III} and Cr^{III} butyltrithiocarbonates and Cr^{III} propyltrithiocarbonate, were isolated as tars and therefore were not analyzed. Aqueous solutions of Co^{II} and S_2CSR^- are immediately oxidized to dark-green $Co(S_2CSR)_3$. Conductivity measurements, in chloroform solutions at room temperature, indicate the compounds are non-electrolytes.

The infrared spectra, recorded from 4000 to 250 cm^{-1}, are closely similar for all the complexes (Table I). The most remarkable feature concerns the carbon-sulphur stretching vibrations, which give very strong bands shifted to 990-980 and 950-940 cm^{-1} with respect to the values of about 1050 and 850 cm^{-1} as found for the alkali trithiocarbonates; in the spectra of Fe^{III} derivatives a further strong band near to 880 cm^{-1} is observed. The three bands at about 460, 360 and 320 cm^{-1} can be assigned to the metal-sulphur stretching vibrations, according to the assignments given for other metal complexes with sulphur-containing ligands.[9,10]

Concerning the magnetic properties, the following conclusions can be made: tris(ethyltrithiocarbonate)-Cr^{III} exhibits a magnetic moment of 3.94 B.M., which is very close to the spin-only value (3.88 B.M.), the octahedral Cr^{III} complexes having three unpaired electrons, irrespective of the ligand field strength. Tris(*n*-propyltrithiocarbonate)Fe^{III} is paramagnetic with $\mu = 2.35$ B.M., indicating a low-spin octahedral complex with a considerable orbital contribution as frequently observed. On the contrary, tris(ethyltrithiocarbonate)Fe^{III} is diamagnetic, indicating some spin pairing perhaps through a Fe—Fe interaction, as observed in ethylthiobis(ethyltrithiocarbonate)Fe^{III},[6] or through a Fe—S—S—Fe interaction between molecules or a change in symmetry due to packing. The Co^{III} and Ni^{II} alkyltrithiocarbonates are all diamagnetic, indicating a low-spin octahedral and a square-planar coordination for Co^{III} and Ni^{II} respectively.

The electronic spectra of Cr^{III}, Fe^{III} and Co^{III} alkyltrithiocarbonates are closely similar (Table II) to those already observed for Cr^{III}, Fe^{III} and Co^{III}

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(9) D. A. Adams, « Metal-Ligand and Related Vibrations », Edward Arnold Ltd, London, 317 (1967)

(10) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, *87*, 1483 (1965).

octahedral complexes with sulphur-containing ligands,[11,12] while the spectra of the Ni^{II} complexes indicate square-planar coordinations[13,14] in agreement with the magnetic properties.

The X-ray structural analyses of $Ni(S_2CSC_2H_5)_2$, $Co(S_2CSC_2H_5)_3$, $Co(S_2CSC_3H_7)_3$ and $Fe(S_2CSC_3H_7)_3$ are being carried out at present in our laboratory.

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(11) C. K. Jørgensen, *Inorg. Chim. Acta Reviews*, 65 (1968).
(12) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, *24*, 1571 (1962).
(13) A. Ouchi, M. Nakatani, and Y. Takahashi, *Bull. Chem. Soc. Japan*, *41*, 2044 (1968).
(14) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, *86*, 4594 (1964).