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Synthesis and Properties of Vanadium(III) Dithiocarbamates

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Attempts to synthesise vanadium(II) complexes from $VBr_2 \cdot 6H_2O$ and dialkylammonium NN-dialkyldithiocarbamates led to the isolation of the vanadium(III) complexes $[V(S_2CNR_2)_3]$, where R = Me, Et, Pr^n, and Bu^i. The magnetic behaviour and reflectance spectra are typical of six co-ordinate vanadium(III). The complex $[V(S_2CNEt_2)_3]$ and the corresponding chromium(III) and iron(III) complexes are isomorphous.

Introduction

Extensive studies have been carried out on the NN-disubstituted dithiocarbamato-complexes of most of the trivalent first row transition metals, but only a few tris(dithiocarbamato)vanadium(III) complexes, $[V(S_2CNEt_2)_3]$, $[V(S_2CNBz_2)_3]$ and $[V(S_2CNMePh)_3]$ are known [1, 2]. The first compound was prepared [1] by refluxing red-brown $[V(S_2CNEt_2)_4]$ in toluene for several hours, and the others by mixing ethanolic solutions of anhydrous vanadium(III) chloride with the sodium or lithium salt of the appropriate dithiocarbamate [2]. We wish to report a different synthesis of $[V(S_2CNEt_2)_3]$ and the new complexes $[V(S_2CNR_2)_3]$, where R = Me, Pr^n, and Bu^i (Table I), which does not involve the use of vanadium(IV) dithiocarbamates or anhydrous VCl_3, and was discovered during investigations of vanadium(II) complexes.

Results and Discussion

Orange-brown, microcrystalline complexes $[V(S_2CNR_2)_3]$ were obtained under anaerobic conditions by treating vanadium(II) bromide, $VBr_2 \cdot 6H_2O$ [3], in a de-gassed ethanol/triethylorthoformate medium, with the anhydrous diethylammonium dialkyldithiocarbamate dissolved in absolute ethanol. Rigorous exclusion of air was necessary since the vanadium(III) complexes darkened rapidly in air, and eventually became pale green. Previously [4], when vanadium(II) salts were treated under nitrogen with aqueous or aqueous ethanolic solutions of sodium dithiocarbamates, brown products were obtained which analysed approximately as bis(dithiocarbamato)vanadium(II) compounds, but some decomposition of the ligand and oxidation of the vanadium(II) had occurred because the magnetic moments were very low for vanadium(II) [3], and the compounds smelt of sulphide. This work was repeated with similar results. Triethylorthoformate was then used in the reaction media to react [5] with the water in $VBr_2 \cdot 6H_2O$ and any present in trace amounts in the ethanol in case it was involved in the decomposition. However, this produced the vanadium (III) dithiocarbamates. Since vanadium(II) is stable under nitrogen in ethanol/triethylorthoformate mixtures (see Experimental), the oxidation must occur on the addition of the dithiocarbamate salt, but this was not investigated further.

Magnetic Properties of $[V(S_2CNR_2)_3]$

The magnetic moments of the complexes at room temperature are somewhat below but close to the spin-only value for the d^2 configuration (2.83 B.M.) thus confirming the oxidation state of the metal ion. The susceptibilities followed the Curie–Weiss law with fairly large θ values (Table II). Since tris(dithiocarbamato)vanadium(III) complexes would be expected to be magnetically-dilute, the large θ values must be ascribed to a variation of magnetic moment arising from a combination of distortion and delocalization effects, and spin–orbit coupling. Tabulated theoretical data show [6] that temperature variation of the type reported here is expected for vanadium(III) complexes.

Electronic Spectra

Octahedral vanadium(III) compounds show [7] two spin-allowed *d–d* bands due to the transitions: $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)(\nu_2)$. A third, two-electron transition, $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ (ν_3), is frequently weak and masked by charge-transfer transitions. This appears to be the case for the vanadium(III) dithiocarbamates. The diffuse reflectance spectra (Table III) contain the expected bands ν_1 and ν_2 although the latter appears as a shoulder except in some low temperature spectra. The ligand field parameters Dq and B′ have been

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TABLE I. Analyses and Reflectance Spectra.

Compound	Colour	Analyses[a]				T/*K*	Diffuse reflectance spectra		Calc. Dq[b]	Electron repulsion parameters		Calc. ν_3[b]
		V	C	H	N		ν_2[b]	ν_1[b]		B′	β[c]	
$[V(S_2CNMe_2)_3]$	chocolate-brown	12.2	27.0	4.6	9.5	295	19.0[d]	14.4	1.52	0.363	0.422	29.6
		(12.4)	(26.3)	(4.4)	(10.2)	90	19.5[d]	14.2				
$[V(S_2CNEt_2)_3]$	orange	10.2	36.5	6.2	8.3	295	19.4[d]	13.7	1.47	0.444	0.516	28.4
		(10.3)	(36.3)	(6.1)	(8.5)	90	19.4	13.7				
$[V(S_2CNPr^n_2)_3]$	orange-brown	8.7	43.5	7.5	7.0	295	19.5[d]	14.0	1.50	0.430	0.500	29.0
		(8.8)	(43.5)	(7.3)	(7.3)	90	19.4	14.0				
$[V(S_2(CNBu^i_2)_3]$	orange-brown	7.7	48.7	8.4	6.2	295	19.5[d]	14.4	1.50[e]	0.422[e]	0.491[e]	29.1[e]
		(7.7)	(48.8)	(8.2)	(6.3)	90	19.5[d]	14.1				

[a] Calculated percentages in parentheses. [b] In $cm^{-1} \times 10^{-3}$. [c] $\beta = B'/B$ where B is the free-ion value for V^{3+} (860 cm^{-1}). [d] These bands appear as shoulders on steeply rising charge-transfer absorptions. [e] This value was deduced from low temperature measurements in which ν_2 was resolved.

TABLE II. Magnetic Data.

$[V(S_2CNMe_2)_3]$, $\theta = 25°$, χ_L[a] = 213								
T (*K*)	295.7	262.9	231.0	198.5	166.6	135.3	103.4	89.5
$10^6 \chi_A$(c.g.s.)	2835	3091	3524	4016	4643	5525	6869	7838
μ_{eff}(B.M.)	2.60	2.55	2.55	2.53	2.49	2.44	2.38	2.37
$[V(S_2CNEt_2)_3]$[b], $\theta = 18°$, $\chi_L = 285$								
T (*K*)	295.0	262.5	230.3	198.3	166.3	135.1	103.0	89.0
$10^6 \chi_A$(c.g.s.)	3244	3581	4103	4721	5536	6719	8630	9828
μ_{eff}(B.M.)	2.78	2.74	2.75	2.74	2.71	2.69	2.67	2.65
$[V(S_2CNPr^n_2)_3]$, $\theta = 46°$, $\chi_L = 407$								
T(*K*)	295.2	262.6	230.8	198.5	166.6	135.0	103.0	89.0
$10^6 \chi_A$(c.g.s.)	3222	3533	3977	4483	5094	5969	7407	8349
μ_{eff}(B.M.)	2.76	2.72	2.70	2.67	2.61	2.54	2.47	2.45
$[V(S_2CNBu^i_2)_3]$, $\theta = 54°$, $\chi_L = 435$								
T (*K*)	295.4	262.5	230.3	198.6	166.5	134.9	104.0	90.3
$10^6 \chi_A$(c.g.s.)	3215	3459	3878	4325	4974	5713	6902	7748
μ_{eff}(B.M.)	2.76	2.69	2.67	2.62	2.57	2.48	2.40	2.36

[a] χ_L is $10^6 \times$ diamagnetic correction. [b] Values of μ_{eff} = 2.70 B.M. and $\theta = 12°$ for $[V(S_2CNEt_2)_3]$ are reported in ref. 1.

TABLE III. X-Ray Powder Patterns (d-spacings, Å).

[V(S_2CNEt_2)$_3$]	[Fe(S_2CNEt_2)$_3$]	[Cr(S_2CNEt_2)$_3$]
d_{hkl}[a]	d_{hkl}	d_{hkl}
8.65 s		
7.81 s	7.57 vs	7.86 vs
6.89 m	6.70 w	6.66 m
6.37 vs	6.30 vs	6.24 vs
5.06 m	5.10 m	5.13 m
4.87 w	4.91 w	4.90 w
4.30 m	4.31 m	4.34 s
4.06 s	4.05 s	
3.95 m	3.93 w	3.93 m
	3.74 vw	3.70 vw
3.66 vw	3.59 vw	3.68 vw
3.32 w	3.29 w	3.30 w

[a] Cu-K_α radiation; intensities estimated visually.

calculated from the equations given by Griffith [8], and are similar, as would be expected, to those [9] of [V(S_2PR_2)$_3$]. The calculated value of ν_3 occurs where there is intense charge transfer or intraligand absorption.

The shoulder at 19400 cm^{-1} was not detected by Bradley *et al.* [1] in the reflectance spectrum of [V(S_2CNEt_2)$_3$] although the band near 14000 cm^{-1} was. Their assumptions concerning the values of ν_2, ν_3, and B′ are fully borne out by our spectra.

The assumption of approximate octahedral symmetry in the spectral analysis is justified by the isomorphism (Table III) of the complexes [M^{III}(S_2CNEt_2)$_3$], in which M = V, Cr, or Fe. A full X-ray investigation has shown [10] that [Fe(S_2CNEt_2)$_3$] contains the iron(III) ion in a slightly distorted FeS_6 octahedron.

Experimental

Preparation of Complexes

The preparation of tris(NN-di-n-propyldithiocarbamato)vanadium(III) is described as an example.

A pale blue solution of $VBr_2 \cdot 6H_2O$ (2.8 g) in 1:1 ethanol/triethylorthoformate (20 cm^3) was treated with di-n-propylammonium di-n-propyldithiocarbamate (4.9 g) dissolved in the same solvent (20 cm^3). Fine orange-brown *crystals* separated quickly (yield ≃ 50%). They were filtered off, washed with ethanol, dried *in vacuo*, and ampouled. The complexes all changed colour on exposure to air, and one sample of [V(S_2CNMe_2)$_3$] ignited. This complex appeared less stable than the others and was more difficult to obtain pure; [V(S_2PMe_2)$_3$] behaved similarly [9].

The dialkylammonium dithiocarbamates were obtained from Ralph N. Emanuel Ltd. and were used without further purification, or were prepared by Uhlin and Akerström's method [11]. Ethanol and triethylorthoformate were purified by standard methods [12].

Ethanolic solutions of $VBr_2 \cdot 6H_2O$ were violet, with ν_1 and ν_2 at 17400 cm^{-1} (ϵ = 6.6 cm^2 mol^{-1}) and 11600 cm^{-1} (ϵ = 4.0 cm^2 mol^{-1}) respectively. The addition of small quantities of triethylorthoformate to the ethanolic solution gave a turquoise solution and slight bathochromic shifts; and in a 20:1 mixture ν_1 and ν_2 were at 16900 and 11050 cm^{-1}, with little change in extinction coefficients. Oxidation had not occurred because bands did not appear at 22000 and 15000 cm^{-1} where vanadium(III) alcoholates [13] absorb. Therefore the oxidation occurs on the addition of the dithiocarbamate salts.

Analyses and Physical Measurements

To destroy organic matter the complexes were fumed almost to dryness with a mixture of oxidising acids. The residue was then digested with concentrated perchloric acid (75%) containing a little concentrated sulphuric acid. The solution containing vanadium(V) was cooled, diluted carefully with water, and phosphoric acid added. An excess of standard iron(II) was then added and back titrated with potassium permanganate and ferroin as indicator.

X-Ray powder photographs were recorded on samples in sealed Lindemann capillaries with a Philips camera PW 1024/00 of radius 114.6 mm and copper K_α radiation and a nickel filter. Electronic spectra were recorded on a Unicam SP 700C spectrophotometer provided with a SP 735 diffuse-reflectance attachment and a lithium fluoride reference. The samples were sealed in cells under nitrogen. Magnetic measurements were carried out by the Gouy method on samples sealed *in vacuo* in Pyrex tubes. The apparatus, calibrated with Hg[Co(NCS)$_4$], was obtained from Newport Instruments Ltd.

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