COMPLEXES WITH SULFUR AND SELENIUM DONORS-X

CHROMIUM(III) PIPERIDYLDITHIOCARBAMATES*

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Abstract—I.r. $(4000-200 \text{ cm}^{-1})$, electronic and ESR spectroscopy have been used to characterize tris-(piperidyldithiocarbamoto)chromium(III) chelates. The properties of the complexes were compared to those of the corresponding diethyl derivative. The compounds have g-values of about 1-98 and the zerofield splitting parameters are small. The effective spin-orbit coupling constants for Cr(III), oscillator strengths of electronic transitions, and nephelauxetic parameters for the complexes are all indicative of appreciable metal-ligand covalency. The slightly different properties of the 2-methylpiperidyldithiocarbamate complex have been attributed to the steric requirements of the 2-methyl substituent.

INTRODUCTION

MANY complexes containing the octahedral $Cr(III)S_6$ chromophore are known[1,2] but few systematic studies of their spectral and magnetic properties have been described. Although several chromium(III) trisdithiocarbamate chelates have been reported[3], only-(diethyldithiocarbamato)chromium(III), $Cr(Et_2 dtc)_3$, has been reasonably well-characterized. The present work was undertaken in order to assess the effects of replacing the ethyl groups with piperidyl and methylpiperidyl groups on the properties of the $Cr(III)S_6$ chromophore. I.R., electronic and ESR spectra are reported.

EXPERIMENTAL

Sodium diethyldithiocarbamate, piperidine, 2-, 3-, and 4-methylpiperidine were obtained from Aldrich Chemical Co., Milwaukee Wisc. and used as received. All other chemicals were of reagent or spectroscopic grade. C, H and N analyses (Table 1) were performed by Mr. Daryl G. Sharp of the U.K. Tobacco and Health Laboratory analytical services.

Piperidinium dithiocarbamates, $RNH_2^{\oplus \ominus}S_2CNR$, were prepared via the reaction: $2RNH + CS_2 \rightarrow RNH_2^{\oplus \ominus}S_2$ -CNR, by slowly adding carbon disulfide with stirring to a solution of the amine in absolute methanol. The ligand salts were recrystallized from absolute ethanol. The chromium-(III) tris-chelates were prepared by stirring a stoichiometric mixture of chromium(III) chloride hexahydrate and ligand salt in absolute methanol or ethanol for 24 hr. A small amount of triethylorthoformate or 2,2-dimethoxypropane

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was added to the reaction mixture to remove water. The dark blue-violet chromium(III) chelates were recrystallized several times from chloroform or dichloromethane.

I.R. spectra (4000–200 cm⁻¹) were obtained using Nujol mulls on cesium iodide plates and potassium bromide pellets with a Perkin–Elmer Model 621 recording i.r. spectrophotometer. The i.r. spectra were calibrated with a polystyrene film. Electronic spectrophotometer. ESR spectra were determined with a Magnion Model MVR-12X X-band ESR spectrometer (O.S. Walker Co., Worcester, Mass.) operating at about 9.4 GHz using 6 KHz field modulation and a 12-in electromagnet. The frequency was monitored with a calibrated absorption wavemeter incorporated in the microwave unit. Field calibration was checked using diphenylpicrylhydrazyl (DPPH) free radical for which g = 2.0036. Quartz sample tubes were employed in the measurements of the ESR spectra of powdered solids.

Infrared spectra

The C-N stretching frequency of $Cr(Et_2 dtc)_3$ was originally reported[4] to occur at 1496 cm⁻¹. Table 2 lists the C-N and Cr-S stretching frequencies for the complexes and Fig. 1 presents the i.r. spectra for the region 700-200 cm⁻¹. Normal coordinate analyses of the vibrational spectra of tris-dithiocarbamato complexes have not been reported, so calculations for 1:1 metal-ligand complexes, $Pt(S_2CNH_2)_2[5]$ and $Ni[S_2CN(CH_3)_2]_2[6]$, have been employed to assign i.r. bands. Metal-sulfur stretching frequencies are expected[7] to occur in the region 200-400 cm⁻¹ and to depend mainly on the msss of the metal. Table 2 also allows comparison of the Cr-S stretching frequencies of CrS_6 complexes containing four-membered $CrS_2X(X=C,P)$ chelate rings. From the data in Table

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Compound*	M.P.(°C)	%C	Calculated %C %H %N			Found %C %H %N			
Cr(Et ₂ dtc) ₂		36.27	6.09	8.46	36.31	6.10	8.56		
$Cr(pipdtc)_{3}$	+	40.58	5.68	7.89	40.63	5.71	7.87		
$Cr(2-Menindtc)_{2}$	+	43.87	6.31	7.31	43.97	6.29	7.33		
$Cr(3-Menindtc)_{3}$	155160	43.87	6.31	7.31	43.10	6.34	6.91		
$Cr(4-Mepipdtc)_3$	192-195	43.87	6.31	7.31	43.62	6.33	7.27		

Table 1. Analytical data

* Et₂dtc = diethyldithiocarbamate; pipdtc = piperidyldithiocarbamate; 2-Mepipdtc = 2-methylpiperidyldithiocarbamate; 3-Mepipdtc = 3-methylpiperidyldithiocarbamate; 4-Mepipdtc = 4-methylpiperidyldithiocarbamate.

† No well-defined m.p. or decomposition temperature.

2 the Cr-S bond orders in the tris-chelates can be seen to follow the order: dithiocarbamate > xanthate > dithiophosphinate \cong dithiophosphate. The spectrochemical series of these ligands follows [2, 9] the order: xanthate > dithiocarbamate > dithiophosphate \cong dithiophosphinate, while the nephelauxetic series is: dithiocarbamate > dithiophosphate \cong dithiophosphinate > xanthate. Unfortunately, limited optical spectral data are available on which to base correlations and the Cr-S stretching frequencies are functions of several variables[5,6,8]. Thus, correlations of optical and vibrational spectra at this time are rather premature. The lowering of the Cr-S stretching frequencies on going from Nujol mulls to potassium bromide pellets is indicative of some sort of interaction of the tris-chelates with the potassium bromide matrix. The broad bands at about 520 cm^{-1} are due [5,6] to molecular vibrations which are combinations of Cr-S stretching, chelate ring deformations and C'-N-C' (where C' comes from substituents on nitrogen) bending modes. The bands appearing at about 600 cm⁻¹ can be attributed [5,6] to vibrations arising from combinations of Cr-S stretch-

Table 2. Infrared stretching frequencies

Complex	$v(Cr-S)(cm^{-1})^*$	$v(C-N)^{\dagger}(cm^{-1})$		
Cr(Et_dtc)_t	372 [365]†	1485		
$Cr(pipdtc)_{2}^{\dagger}$	359 [350]†	1470		
$Cr(2-Mepipdtc)_{2}$	345 [335]†	1450		
$Cr(3-Menipdtc)_{3}$	355 [346]†	1464		
$Cr(4-Mepipdtc)_3$	350 [335]†	1466		
Cr(mexn) ₂ §	388*			
Cr(etxn) ₃ §	340*			
Cr[S_P(CH_2)_]_¶	313*			
$Cr[S_2P(C_4H_4)_2]_3$	305			
$Cr[S_P(OC_1H_5)_2]_3$	315*			
$Cr[S_{2}P(CF_{2})_{2}]_{3}$	307*			
$Cr[S_2PF_2]_3$ ¶	316*			

* Nujol mulls. All values ± 2 cm⁻¹.

† KBr pellets. All values ± 2 cm⁻¹.

 $\ddagger Et_2dtc = diethyldithiocarbamate; pipdtc = piperidyl$ dithiocarbamate; 2-Mepipdtc = 2-methylpiperidyldithiocarbamate; 3-Mepipdtc = 3-methylpiperidyldithiocarbamate; 4-Mepipdtc = 4-methylpiperidyldithiocarbamate.

 $\{[8]; mexn = methyl xanthate; extn = ethyl xanthate.$ <math>[9] ing and chelate ring deformations as well as combinations of C–S stretching, C'–N–C' bending and C'–N stretching modes. More extensive band analyses will require complete normal coordinate analyses, isotopic substitution for both ligand atoms and the metal[10], and more complete i.r. and Raman spectral data.

Electronic spectra

The electronic spectral data for tris(dithiocarbamato)chromium(III) complexes are summarized in Table 3. The complexes exhibit two strong absorption bands in the visible region at about 15 and 21 kK (1 kK = 1000 cm^{-1}) which are assigned to the ${}^{4}T_{2g} \leftarrow {}^{4}A_{2g}(v_1)$ and ${}^{4}T_{1g}(F) \leftarrow {}^{4}A_{2g}(v_2)$ transitions, respectively, octahedral geometry being assumed. The ${}^{4}T_{1g}(P) \leftarrow {}^{4}A_{2g}$ transition, expected to appear at about 31 kK, is not observed due to intense charge-transfer bands in the ultraviolet region. The positions and oscillator strengths of the bands are consistent with those reported [1,2,9,11–13] for other complexes containing the Cr(III)S₆ chromophore. The data for Cr(pipdtc)₃ is in fair agreement with the recent low temperature crystal data of Schreiner and Hauser[13]. They performed an extensive analysis of the optical and magnetic circular



Fig. 1. Infrared spectra of chromium(III) dithiocarbamates.

 Table 3. Electronic spectral data

Compound*	$v_1 ({\rm cm}^{-1})$	$\varepsilon_{m_1}^{\dagger}$ †	10 ⁵ f ₁ ‡	$v_2 ({\rm cm}^{-1})$	£ _{m2}	10 ⁵ ₂	$v_2 - v_1 (\text{cm}^{-1})$	f_2/f_1
Cr(Et ₂ dtc) ₃	15,540	335	464	20,280	318	470	4740	1.01
Cr(pipdtc) ₃	14,820	270	454	20,780	240	383	5960	0.84
Cr(2-Mepipdtc),	14,750	273	460	20,960	246	392	6210	0.85
Cr(3-Mepipdtc) ₃	14,940	274	459	20,630	252	388	5690	0.84
Cr(4-Mepipdtc) ₃	15,120	283	458	20,680	258	405	5560	0.88

* For abbreviations for ligands see Table 1. The spectra were obtained for N,N-dimethylformamide solutions. The spectrum of $Cr(Et_2dtc)_3$ was obtained in nitrobenzene.

† Molar absorptivity.

[‡] Oscillator strengths, f, were calculated using the expression $f = 4.60 \times 10^{-9} \varepsilon_{\text{max}} v_{1/2}$ where ε_{max} is the molar absorptivity of the band maximum and $v_{1/2}$ is the band width at half-height expressed in wave numbers: C. J. Ballahusen, *Prog. Inorg. Chem.* 2, 251 (1960).

dichroism spectra of the $Cr(pipdtc)_3$ and related compounds using trigonal (D_3) crystal field theory and ground state semi-empirical LCAO-MO calculations. The present data is not of sufficient resolution to warrant such detailed interpretation. Interestingly, Schreiner and Hauser's[13] MO calculation for $Cr(S_2C-NH_2)_3$ led to the conclusion of a significant anti-bonding *trans*-annular Cr-C interaction.

Except for the 2-methylpiperidine derivative, which probably suffers from steric distortion due to the methyl substitutent, the electronic spectra of the complexes are very similar. The slightly anomalous nature of the 2-Mepipdtc complex is also apparent in the infrared data (Table 2) where the v(Cr-S) and v(C-N) frequencies are lower than for the other compounds.

The appreciable oscillator strengths of the electronic absorption bands are indicative of appreciable metalligand covalency which is in agreement with the various covalency parameters collected in Table 4. The nephelauxetic parameters, β_{35} , are readily obtained using the relation $\beta_{35} = B(\text{complex})/B(\text{free ion})$ where $B = (2v_1^2 - 3v_1v_2 + v_2^2)/(15v_2 - 27v_1)$ and B(free ion) = 0.918 kK. The β_{35} values are a measure of the strong covalency in the metal-ligand σ bonds. The nephelauxetic parameters, β_{55} , obtained from a consideration of lowenergy quartet-doublet transitions[1,11] are also consistent with appreciable Cr–S π bonding in compounds containing Cr(III)S₆ chromophores. Jørgensen[14] has demonstrated that decreasing values of β_{35} are associated with a reduction in the effective positive charge of the cation and with an increasing tendency to be reduced to the next lower oxidation state. In later work Jørgensen showed[15] that for the 3d transition metals the variation of the Racah interelectronic repulsion parameter with cationic charge, Z, and q, the occupation number of the d^q shell, is well-expressed by the relation :

$$B(cm^{-1}) = 384 + 58q + 124(z+1) - 540/(z+1).$$

From a plot of B vs Z the effective ionic charges of the complexes of interest here have been found (Table 4) to lie in the range 0.67–1.41, considerably below the formal + 3 oxidation state of chromium. Chromium(III) complexes with oxygen and nitrogen donors have effective charges[16] in the ranges 0.8–1.94 and 1.12–2.57, respectively. A survey[16] of compounds with Cr(III)S₆ chromophores shows that the effective metal charges calculated using Jørgensen's approach[15] lie in the range $\pm 0.52 \pm 1.10$. These ranges of effective metal charges agree reasonably well with charges calculated using Sanderson's electronegativity method [17]. The appreciable metal–ligand covalency in Cr(III)S₆ compounds is also found in electron delocalization parameters obtained from ESR spectra.

Electron spin resonance spectra

The ESR spectra of powdered samples of the tris-(dithiocarbamato) chromium(III) complexes consisted in each case of a single broad line with a peak-to-peak separation of about 300 G. A typical spectrum is shown in Fig. 2. The g-values are listed in Table 4 along with related spectroscopic data. The spin-Hamiltonian for S = 3/2 chromium(III) complexes generally takes the form

$$\hat{H} = g\beta S \cdot H + D[\hat{S}_z^2 - 5/4] + E(\hat{S}_x^2 - \hat{S}_y^2).$$

Compound	$Dq ({\rm cm}^{-1})$	$B(cm^{-1})$	β_{35}	Z*	$\langle g \rangle (\pm 0.005)$	λ' (cm ⁻¹)	γt	γ′‡
Cr(Et ₂ dtc) ₃	1540	444	0.48	+ 0.67	1.9873	29.1	0-32	0.50
Cr(pipdtc) ₃	1482	596	0.65	+1.24	1.9876	27.2	0.30	0.65
Cr(2-Mepipdtc),	1475	632	0.69	+1.41	1.9784	44.0	0-49	0.68
Cr(3-Mepipdtc) ₃	1494	591	0.61	+1.11	1.9873	27.9	0.31	0.61
$Cr(4-Mepipdtc)_3$	1512	542	0.59	+1.02	1.9810	40.2	0.45	0.59

Table 4. Spectroscopic and covalency parameters

* Effective ionic charge on metal.

 $\dagger \gamma = \lambda'/(90 \,\mathrm{cm}^{-1}).$

 $\ddagger \gamma'$ calculated from $\lambda = 0.0110 (\mathbf{B} + 1.080)^3 + 0.0062$.



Fig. 2. Electron spin resonance spectrum of a powdered sample of tris(2-methylpiperidyldithiocarbamato)chromium(III).

The g-values are essentially isotropic and the zero-field splitting terms D and E indicate the symmetry of the ligand field. E gives a measure of the axial distortion. The actual point symmetry of the dithiocarbamate complexes is closer to D_3 than O_h and it can be anticipated that the zero-field splitting parameters will be non-zero. A study[18] of tris (dibutyldithiocarbamato)chromium(III) yielded an almost isotropic g value of 1.981 with D and E being $\pm 0.5662 \pm 0.003$ and ± 0.0695 ± 0.0002 cm⁻¹, respectively. However, the present results even for the 2-Mepipdtc complex (Fig. 2), indicate that the magnitude of the zero-field splitting parameter D is on the order of 0.03 cm^{-1} or less with E being still smaller. This assessment concurs with that made for the Et_2 dtc complex by Garif'yanov et al. [19]. It is noted that for trigonal tris(ethylenediamine)chromium(III) chloride[20] |D| = 0.036 cm⁻¹. The powder ESR spectra of the di-n-butyl- and dibenzyl-dtc complexes exhibit the effects of appreciable zero-field splitting[21]. Apparently, the zero-field splitting in tris(dithiocarbamato)chromium(III) complexes is dominated by the steric requirements of the organic groups bound to the nitrogen atoms.

The g-values of effectively octahedral chromium(III)

$$g = 2.0023 (1 - 4\lambda'/10 Dq)$$

where λ' is the effective spin-orbit coupling constant for the metal ion in the complex. Owen[23] noted that the reduction of the spin-orbit coupling constant from the free ion value ($\lambda = 90 \text{ cm}^{-1}$ for Cr(III)) can be employed as a measure of metal-ligand covalency. It is possible to define[16] a covalency parameter, γ , analogous to nephelauxetic parameters which is the ratio of λ' to λ for the free ion. The values of γ for the dithiocarbamate complexes are also listed in Table 4. This measure of covalency is in accord with electronic transition strengths and nephelauxetic parameters discussed above. The dithiocarbamate compounds exhibit γ values lower than the related dithiophosphate complexes which were found[2] to have values of about 0.56 indicating a greater degree of σ -covalency in the dithiocarbamate complexes.

From the work of Cole and Garrett[24] on spin-orbit coupling constants the empirical relation

$$\lambda = 0.0110(B + 1.080)^3 + 0.0062$$

connecting the Racah interelectronic repulsion parameter B (in kK) to λ (in kK) may be obtained [16] for chromium(III) complexes. γ values calculated using this relation are also listed in Table 4. It is observed that γ values evaluated using the empirical relation are consistently higher than those obtained from ESR data. Changing the sign of the constant term in the empirical relation results in more satisfactory agreement with experiment. The real value of the empirical relation of λ and B is in its ability to allow reasonable estimates of λ or B if either cannot be determined by experiment.

In summary, the electronic and ESR spectra of piperidyldithiocarbamate complexes of chromium(III) provide independent, but nevertheless related, measures of the appreciable metal-ligand covalency in these compounds. The 2-Mepipdtc complex exhibits anomalies in the infrared and optical spectra which can be attributed to steric requirements of the 2-methyl substituent. Zero-field splitting in chromium(III) dithiocarbamate complexes is probably controlled by steric effects of organic substituents rather than the trigonal (D_3) geometry associated with the chelate rings.

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