

Five- and Six- Coordinate Complexes of Vanadium(III) and Chromium(III) Halides with Dialkylsulphides and with Quinuclidine

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A series of trans-trigonal bipyramidal complexes of vanadium(III) and chromium(III) have been prepared and characterised, in particular by their diffuse reflectance and solution electronic spectra and by their solid and solution infrared spectra in the region 450-200 cm^{-1} . They are $\text{VX}_3 \cdot 2\text{S}(\text{C}_2\text{H}_5)_2$, $\text{VX}_3 \cdot 2\text{Qu}$ and $\text{CrX}_3 \cdot 2\text{Qu}$ ($\text{X} = \text{Cl}$ or Br ; $\text{Qu} = \text{quinuclidine}$). Surprisingly the five-coordinate complexes $\text{VX}_3 \cdot 2\text{S}(\text{C}_2\text{H}_5)_2$ are still present in diethylsulphide solutions, although an equilibrium between these complexes and six-coordinate species is set up. With dimethyl- and diethylsulphides chromium trichloride and tribromide form exclusively six-coordinate species; these are 1:3 adducts in solution in the parent ligand, but 1:2 adducts (dimeric) in solution in benzene. The adducts $\text{CrCl}_3 \cdot 3\text{SR}_2$ ($\text{R} = \text{CH}_3$ or C_2H_5), $[\text{CrCl}_3 \cdot 2\text{S}(\text{CH}_3)_2]_2$, and $[\text{CrBr}_3 \cdot 2\text{SR}_2]_2$ ($\text{R} = \text{CH}_3$ or C_2H_5) have been isolated in the solid state, and their spectroscopic properties studied. Quinuclidine forms a 1:3 adduct $\text{CrCl}_3 \cdot 3\text{Qu}$ with chromium trichloride in addition to the 1:2 five-coordinate species. The usefulness of dialkylsulphide complexes of the early transition elements as intermediates for the preparation of other complexes is discussed.

Introduction

Vanadium(III) and especially chromium(III) complexes are usually six-coordinate,¹ but recently examples of both four- (e.g. VX_4^- ions)² and five-coordination³⁻⁶ (e.g. $\text{VX}_3 \cdot 2\text{N}(\text{CH}_3)_3$, $\text{X} = \text{Cl}$ or Br) have been established.

In the course of an investigation of the applicability of ligand substitution reactions to the preparation of new complexes of the early transition elements, we have established that two further ligands (L), diethylsulphide and quinuclidine ($\text{HC}(\text{C}_2\text{H}_4)_3\text{N}$) form 1:2 complexes of the type $\text{VX}_3 \cdot 2\text{L}$ ($\text{X} = \text{Cl}$ or Br) with vanadium trihalides. These complexes are shown to

be trans-trigonal bipyramidal in both the solid state as well as in solution in non-polar solvents. Similar reactions with the chromium trichloride and tribromide have led to the formation of analogous five-coordinate quinuclidine complexes of chromium(III). Chromium trichloride is shown to form both 1:2 and 1:3 adducts with dimethyl- and diethylsulphides, the species isolated depending on the reaction conditions, but with chromium tribromide only the 1:2 adducts were isolated; the 1:3 species are, however, present in excess ligand solution. All the 1:2 adducts are shown to involve six- rather than five-coordinate chromium(III). The key to the preparation of the quinuclidine complexes appears to be the nucleophilic substitution of coordinated diethylsulphide by the quinuclidine, and the generality of this preparative procedure is discussed. Various spectroscopic properties of the complexes are also presented and discussed.

Experimental Section

Reagents. Diethylsulphide and dimethylsulphide (B.D.H.) were purified by distillation from calcium hydride.

Quinuclidine (Qu) was prepared from the hydrochloride (R.N. Emanuel Ltd.) by the following procedure. $\text{QuHCl}(2\text{g})$ was dissolved in distilled water (10 ml) in a separating funnel (250 ml) and a large excess of sodium hydroxide added in order to precipitate free quinuclidine. The latter was extracted by shaking the suspension with *n*-pentane (3×50 ml) and the resulting solution transferred into a flask (200 ml) to which calcium hydride (5 g) was then added. The suspension was stirred magnetically for several hours in order to eliminate residual traces of water, and then the solution was filtered off under dry nitrogen and the solvent removed *in vacuo*. Free quinuclidine remains as a white solid. It was further purified by vacuum sublimation and stored in a flask of known weight. Solutions of quinuclidine of known concentration were made up by adding a known volume of solvent by syringe through a cap on one neck of the containing flask.

Solvents were rigorously dried by repeated distillation from calcium hydride. Benzene was previously distilled twice from phosphorus pentoxide.

The anhydrous trihalides were supplied by K and

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K Ltd, except for CrCl_3 which was supplied by Light and Co. Owing to their sensitivity to moisture, it was essential to reflux the trichlorides with freshly distilled thionyl chloride for 1 to 2 hours prior to attempting any reaction. The excess of thionyl chloride was then removed *in vacuo*, and the trichloride pumped under vacuum for 1 hour. In the case of chromium trichloride, it is also necessary to heat it under vacuum for 2 to 3 hours at 90° .

Similarly, anhydrous vanadium tribromide was treated with an excess of thionyl bromide (freshly distilled at $70^\circ/62$ mm Hg) for 1 hour at $70^\circ/60$ mm Hg in order to remove the last traces of moisture therefrom. The tribromide was then separated out by filtration and dried *in vacuo* for 1 hour.

Chromium tribromide was treated similarly with thionyl bromide. If the resulting anhydrous material was simply placed under vacuum on a water bath at *ca.* 90° for 3-4 hours, then the product did not appear to react to any extent with dialkylsulphides, even in the presence of zinc. However, if the anhydrous material was dried as above, washed ($\times 4$) with *n*-hexane, and then treated as described below it reacts immediately with dialkylsulphides.

Preparation of complexes $\text{VCl}_3 \cdot 2\text{S}(\text{C}_2\text{H}_5)_2$. The apparatus shown in Fig. 1 was flamed out under vacuum and then filled with oxygen-free nitrogen; a known weight of anhydrous VCl_3 was then added to flask A in a nitrogen-filled dry box. The VCl_3 was refluxed with thionyl chloride *in situ* as described above, the thionyl chloride being injected by syringe through cap C into flask B, and then filtered into flask A. The apparatus in Figure 1 enabled the reflux to be carried out without distillation of the thionyl chloride into flask B. After reflux for 1 to 2 hours, the thionyl chloride was distilled *in vacuo* back into flask B (A at 50° , B at -80°), and removed by syringe through cap C. The whole apparatus was then placed under vacuum for 1 hour to remove the last traces of thionyl chloride, and then a large excess of previously purified diethylsulphide was injected similarly into flask B and filtered into flask A.

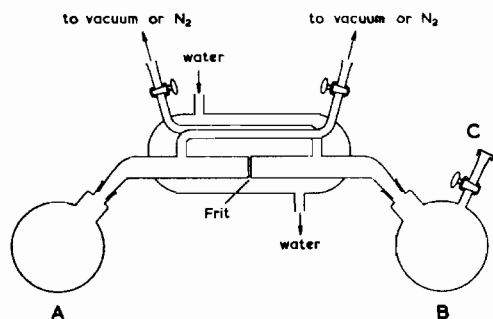


Figure 1. Apparatus for the preparation of the diethylsulphide complexes.

Soon the liquid phase became deep red and after reflux for *ca.* 1 hour all the VCl_3 had dissolved. The solution was then filtered into flask B and the excess of diethylsulphide removed *in vacuo*. The residual dense, dark violet oil, containing some solid mate-

rial, was then dissolved in *n*-hexane giving a violet solution which, on being pumped *in vacuo*, yielded violet crystals of the complex $\text{VCl}_3 \cdot 2\text{S}(\text{C}_2\text{H}_5)_2$.

$\text{VBr}_3 \cdot 2\text{S}(\text{C}_2\text{H}_5)_2$. This complex was prepared similarly, except that the tribromide was dried with thionyl bromide as described above. After refluxing the tribromide with diethylsulphide for *ca.* 1 hour the resulting yellow-brown solution was filtered into flask B, and the excess of the ligand removed *in vacuo*. The resulting yellow-brown oil was recrystallized from *n*-hexane to yield a green-brown complex, which is soluble in benzene as well as in *n*-hexane.

$\text{VCl}_3 \cdot 2\text{Qu}$. This complex was prepared by placing, in a nitrogen-filled dry box, a known weight (0.6 g) of $\text{VCl}_3 \cdot 2\text{S}(\text{C}_2\text{H}_5)_2$ into flask A (Figure 2). *n*-Hexane (30 ml) was added to this flask by syringe through cap D and the resulting deep violet solution was filtered into flask B. The stoichiometric weight of quinuclidine in *n*-hexane was then added to flask B by syringe through cap C. Red-brown crystals of the required complex precipitate; these were filtered off on the frit, washed twice with *n*-hexane, and dried *in vacuo*. The quinuclidine complex is almost insoluble in *n*-hexane, but is soluble in benzene.

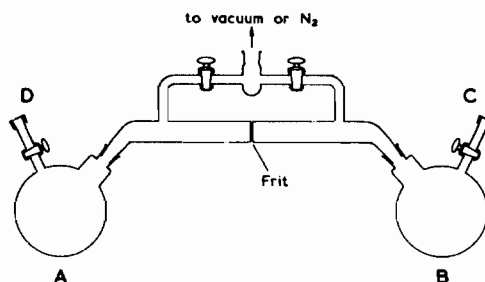


Figure 2. Apparatus for the preparation of the quinuclidine complexes.

The complex can also be prepared similarly using benzene as solvent, from which it can be precipitated with *n*-hexane.

$\text{VBr}_3 \cdot 2\text{Qu}$. This complex was prepared in the same way as the corresponding chloro complex, using *n*-hexane as solvent.

$\text{CrCl}_3 \cdot 3\text{S}(\text{CH}_3)_2$ and $\text{CrCl}_3 \cdot 3\text{S}(\text{C}_2\text{H}_5)_2$. Chromium trichloride reacts instantly and completely with thioethers provided that zinc dust is present in catalytic amounts. The zinc dust was previously heated *in vacuo* under a bunsen flame for *ca.* 30 min. otherwise the reactions are slow. With reference to Figure 2, CrCl_3 (2 g) and the zinc dust (30 mg) were placed in flask A, and the thioether (17 ml) introduced to the same flask by syringe *via* cap D. The CrCl_3 immediately dissolved to form a blue solution. The solution was filtered into flask B, and cooled to -80° . This procedure is essential in order to avoid the formation of an oil. The excess of thioether was removed *in vacuo* to leave a crystalline solid which analyzed as $\text{CrCl}_3 \cdot 3\text{SR}_2$. Both thioether complexes were readily soluble in the parent ligand and also in benzene, but almost insoluble in *n*-hexane. The dimethylsulphide complex, which is the less soluble, could be recrystallized from benzene to yield red-

Table I. Analytical Data

Complex	Colour	% C		% H		% Hal		% N	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
VCl ₃ · 2S(C ₂ H ₅) ₂	violet	28.45	28.6	5.97	5.8	31.50	31.9	—	—
VCl ₃ · 2Qu	red-brown	44.64	44.2	6.96	7.1	28.23	27.8	7.44	7.3
VBr ₃ · 2S(C ₂ H ₅) ₂	green-brown	20.40	20.2	4.28	4.3	50.89	50.5	—	—
VBr ₃ · 2Qu	violet	32.77	32.7	5.11	5.3	46.73	46.5	5.46	5.5
VOBr ₂ · 2Qu	light-green	37.44	37.6	5.83	5.8	35.58	34.1	6.24	6.2
CrCl ₃ · 3S(CH ₃) ₂	violet-blue	20.90	20.2	5.26	4.9	30.85	31.0	—	—
CrCl ₃ · 2S(CH ₃) ₂	red-violet	17.00	16.8	4.28	4.3	37.63	37.9	—	—
CrCl ₃ · 3S(C ₂ H ₅) ₂	violet-blue	33.60	32.6	7.05	6.7	24.80	25.5	—	—
CrBr ₃ · 2S(CH ₃) ₂	deep-green	11.54	11.6	2.91	3.2	57.63	56.6	—	—
CrBr ₃ · 2S(C ₂ H ₅) ₂	deep-green	20.35	20.9	4.27	4.6	50.78	50.0	—	—
CrCl ₃ · 3Qu	pink	51.27	51.8	7.99	8.1	21.62	20.4	8.54	8.4
CrCl ₃ · 2Qu	violet	44.16	43.9	6.88	7.0	27.93	27.6	7.36	7.2
CrBr ₃ · 2Qu	green	32.70	31.5	5.10	5.1	46.63	46.1	5.45	5.7

violet crystals which analyzed as CrCl₃ · 2S(CH₃)₂; the complex has a different diffuse reflectance spectrum, and a slightly different infrared spectrum from the 1:3 complex.

CrBr₃ · 2S(CH₃)₂ and CrBr₃ · 2S(C₂H₅)₂. These complexes were prepared in the same way as the thioether adducts of chromium trichloride. On removal of excess of the ligand from a solution of the tribromide in the thioether, a green product remains which does not have a well-defined composition (it is probably a mixture of 1:2 and 1:3 adducts). However, this solid can be dissolved in benzene to give a green solution from which, after filtration and evaporation, the pure 1:2 adduct can be obtained as a green solid.

CrCl₃ · 3Qu. The complex CrCl₃ · 3S(C₂H₅)₂ was dissolved in benzene and treated with quinuclidine; an instantaneous reaction occurs which was complicated by the fact that two products were formed. In order to prepare the 1:3 adduct, a large excess of quinuclidine and little solvent were essential. CrCl₃ · 3S(C₂H₅)₂ (0.5 g) in benzene (9 ml) was treated with quinuclidine (1.2 g) in benzene (5 ml) by a similar procedure to that used for the corresponding vanadium complex. The solution turns violet and a pink precipitate separates out. This is filtered off, washed twice with *n*-pentane, and dried *in vacuo* for 1 hour.

CrCl₃ · 2Qu. This complex is difficult to obtain free from the 1:3 adduct. However, the latter is less soluble in benzene. CrCl₃ · 3S(C₂H₅)₂ (0.6 g) in benzene (15 ml) was treated with quinuclidine (0.4 g) in benzene (8 ml) (mol. ratio 1:2.5) and stirred. *n*-Pentane (30 ml) was added to the solution, which then precipitated a small amount of CrCl₃ · 3Qu. The residual bright violet solution was filtered from flask A to flask B (Figure 2), cooled to -80° and the solvent removed *in vacuo*. By this procedure a finely divided solid was formed, which was washed twice with *n*-pentane and then dried *in vacuo* for 1 hour. The 1:2 complex was readily soluble in benzene.

CrBr₃ · 2Qu. This complex was prepared in the same way as the corresponding chloro complex; it is green, and readily soluble in benzene.

Analyses. The analyses were performed by the analytical service of this Department. Some of the halogen analyses were also determined gravimetrically. The results are in Table I.

Electronic Spectra. The solution and diffuse reflectance spectra were recorded using a Cary 14 spectrophotometer. As all the complexes are extremely sensitive to moisture, and the vanadium ones also to oxygen, the solution cells were sealed from the air and the solid samples were held between silica plates, in a specially designed cell.

Infrared Spectra. The infrared spectra of the complexes were determined using a Perkin-Elmer 225 spectrometer. The spectra of the solids were determined as Nujol mulls between CsI plates the surfaces of which were protected using a thin film of polythene. Solution spectra were determined using a polythene cell.

Results and Discussion

A. Vanadium Complexes. It is clear from the preparations outlined above that vanadium trichloride and tribromide react with diethylsulphide to form complexes of the type VX₃ · 2S(C₂H₅)₂. Rigorous precautions to exclude moisture and oxygen are essential during all stages of the preparations. The complexes are soluble in benzene, and in *n*-hexane. The diffuse reflectance spectra of the powdered solids are virtually identical with their optical solution spectra in benzene (Figure 3) and likewise the solid and solution (benzene) infrared spectra of the complexes are virtually identical with one another. Analysis of these spectra leads to the conclusion that the complexes are trigonal bipyramidal with *D*_{3h} skeletal symmetry in both the solid and the dissolved states. One dialkylsulphide compound of this composition has been prepared previously, namely VCl₃ · 2S(C₂H₅)₂; however, this was considered⁶ to be a chlorine-bridged dimer in the solid state and a monomer in benzene solution. Surprisingly, the 5-coordinate species is still present in solution in the parent ligand, (Figure 3) although in this case an equilibrium appears to be set up involving a 6-coordinate species (probably a 1:3 adduct). These observations show that vanadium(III) has a marked preference for 5-coordination with diethylsulphide.

The diethylsulphide complexes were prepared as substrates for ligand substitution reactions for two reasons. Firstly, since vanadium(III) and chromium(III) are normally considered to be Class A ions *i.e.*

they form their most stable complexes with the first ligand atom of each group. ($F \gg Cl > Br > I$ and $O \gg S \sim Se \sim Te$),⁷ the coordinated diethylsulphide should be conveniently displaced by oxygen- or nitrogen-donor ligands. Secondly, the diethylsulphide complexes should be sufficiently soluble in non-polar media to permit the ready substitution of the sulphur-ligand. In order to test the facility with which such ligand substitution reactions take place, we have studied the reactions of the complexes $VX_3 \cdot 2S(C_2H_5)_2$ in *n*-hexane with a solution of the bicyclic amine quinuclidine ($HC(C_2H_4)_3N$) in the same solvent. This ligand is of particular interest because of its low steric requirement (compared with that of other tertiary amines)⁸ and high base strength (marginally greater than that of trimethylamine).⁹ Like trimethylamine, quinuclidine might be expected to form *trans*-trigonal bipyramidal complexes $MX_3 \cdot 2Qu$ with D_{3h} symmetry. Moreover, the only complexes of this ligand reported to date appear to be the silver, copper and cobalt derivatives¹⁰ $AgNO_3 \cdot 2Qu$, $CuCl_2 \cdot Qu$ and $CoCl_2 \cdot 2Qu$.

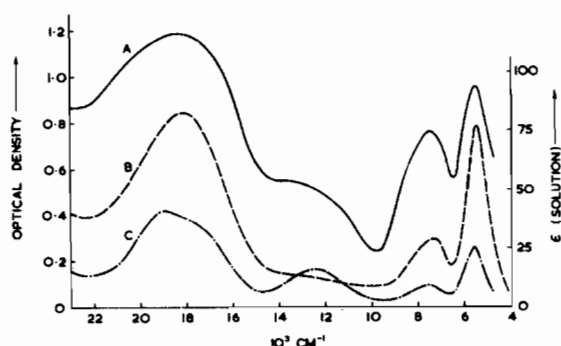


Figure 3. Diffuse reflectance (A) and solution (benzene B, and diethylsulphide C) electronic spectra of $VCl_3 \cdot 2S(C_2H_5)_2$.

The substitution reactions with quinuclidine were found to occur readily in *n*-hexane, complexes of the expected type, $VX_3 \cdot 2Qu$, precipitating immediately and quantitatively from the solvent. The reactions may also be effected in benzene, in which the quinuclidine complexes remain soluble. Optical and infrared spectral studies (see below) show conclusively that the quinuclidine complexes are trigonal bipyramidal with D_{3h} symmetry in both the solid state as well as in solution.

All four complexes, but especially the bromo ones, are extremely sensitive to oxygen, forming oxovanadium(IV) complexes of the type $VOX_2 \cdot 2L$. One of these, $VOBr_2 \cdot 2Qu$ has been characterised by elemental analyses (Table I) and by its infrared spectrum ($\nu(VO)=994$ vs, $\nu(VBr)=354$ vs and 307 s, cm^{-1}). It is thus analogous to the many other com-

plexes of this type,¹ although these are normally prepared from oxovanadium(IV) species. In particular, it is probably analogous to the trigonal bipyramidal molecule¹¹ $VOCl_2 \cdot 2N(CH_3)_3$.

Optical spectra. The band maxima in the solution and diffuse reflectance spectra of the vanadium complexes are listed in Table II. As indicated above, the solid and solution spectra are essentially identical, (Figure 3) and hence all the complexes are considered to have the same structure in both states of matter. Moreover, the spectra are closely similar to those for the corresponding trimethylamine complexes which are known to have the *trans*-trigonal bipyramidal structure.³ The assignments for the various bands follow immediately from a comparison with those made for the trimethylamine complexes¹² on the basis of D_{3h} symmetry and the ground-state configuration (e'').² The values of the ligand field parameters D_s , D_t , B , $D_{q_{eq}}$ and $D_{q_{ax}}$ derived¹² for the trimethylamine and dimethylsulphide complexes describe equally adequately the spectra of the quinuclidine and diethylsulphide complexes (respectively) reported herein.

Infrared spectra. The infrared spectra of the complexes in the metal-halogen and metal-ligand stretching region are given in Table III. The VX stretching frequencies, which are higher than those typical of six-coordinate vanadium(III) complexes,¹³ are clearly assignable as $\nu(VCl)=422-425$ cm^{-1} and $\nu(VBr)=339-345$ cm^{-1} cf. for $VX_3 \cdot 2N(CH_3)_3$ the corresponding bands are at 409 and 345 cm^{-1} respectively.¹⁴ There is no significant difference between the solid state and solution data. The occurrence of only a single infrared-active VX stretching frequency for these four complexes is consistent only with their possessing D_{3h} skeletal symmetry, for which this mode is of the e' species. More complicated infrared spectra would be expected for either a trigonal bipyramidal complex in which both neutral ligands were not on the threefold axis or for a tetragonal pyramidal complex. A further band occurs in the spectra of the complexes near 240 cm^{-1} which may be the vanadium-ligand stretching frequency of a_2' symmetry.

B. Chromium Complexes with Dialkylsulphides. Considerable difficulty was experienced in obtaining reaction between chromium trichloride or chromium tribromide and dimethyl- or diethylsulphide, even in the presence of zinc. It was discovered that, in order to get immediate reaction, it is essential (a) to reflux the trihalide with the appropriate thionyl halide, (b) after removing excess of the thionyl halide from the chromium trihalide, to pump the latter under vacuum for some hours at ca 90° and (c) in the case of the tribromide to wash the resulting product several times with *n*-hexane. With this treatment and in the presence of catalytic amounts of zinc (see Experimental section) chromium trichloride reacts immediately with dimethyl- and diethylsulphide to form violet complexes of the type $CrCl_3 \cdot 3SR_2$ which can be isolated by removal of excess of ligand. Spectroscopic data

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Table II. Electronic Spectra of the Complexes $VX_3 \cdot 2L$ ($X = Cl$ or Br) in cm^{-1} Ground State $^3A_2'$

Complex		$^3A_1''$, $^3A_2''$	$^3E''$	$^1A_2'(D)?$	$^1E''(D)$	$^3E'$, $^3A_2'(P)$, $^3E''(P)$
$VCl_3 \cdot 2S(C_2H_5)_2$	DR	5,500(s)	7,450(ms)	12,350(wm, sh)		18,350(s)
	Bz	5,500(76)	7,400(29)	12,200(w, sh)		18,350(82)
	$S(C_2H_5)_2$	5,530(25)	7,450(9)	12,500(16)		~ 18,400(br, as, 39)
$VBr_3 \cdot 2S(C_2H_5)_2$	DR	4,670(s)	6,330(m)			17,800(s)
	Bz	4,670(s)				18,200(s)
	$S(C_2H_5)_2^a$	4,700(m)	6,500(w)			
$VCl_3 \cdot 2Qu$	DR	4,520(s)	6,850(m)	11,500(w) $b?$	16,000(w)	19,800(s)
	Bz	4,370(58)	6,730(27)	11,500(vw) $b?$	16,000(w)	19,920(77)
$VBr_3 \cdot 2Qu$	DR		5,950(m)	12,560(w)		18,700(s)
	Bz a			13,420(w)		18,500(s)

DR = diffuse reflectance, Bz = benzene solution, $S(C_2H_5)_2$ = diethylsulphide solution. s, strong; m, medium; w, weak; br, broad; as, asymmetric; sh, shoulder; these designations are only relative within each spectrum. Extinction coefficients are in parentheses. a These complexes are extremely sensitive to oxygen and moisture, and their spectra contain bands in the visible which are indicative of oxovanadium(IV) species as impurities. b This band may arise from decomposition products.

Table III. Infrared Spectra of the Five-Coordinate Complexes and the Free Ligands ($450-200\text{ cm}^{-1}$)

Assignment	$VCl_3 \cdot 2S(C_2H_5)_2$		$VBr_3 \cdot 2S(C_2H_5)_2$		$S(C_2H_5)_2$ Liquid	$VCl_3 \cdot 2Qu$		$VBr_3 \cdot 2Qu$		$CrCl_3 \cdot 2Qu$ Nujol	$CrBr_3 \cdot 2Qu$ Nujol	Qu Nujol
	Nujol	Bz	Nujol	Bz		Nujol	Bz	Nujol	Bz			
$\nu(MX)$	422 vs, br	425 vs	344 vs	345 vs, br		423 vs	423 vs	340 ms	339 m	383 vs	330 s	
$\nu(ML)$	242 s	241 m	237 wm	236 wm		232 s	227 s	232 wm	232 m	257 s	235 ms	
Ligand	380 vw, sh	380 w, sh	391 vw	392 vw	382 m	395 s	396 s	407 m	407 m	416 s	407 m	403 w
	335 w	327 w			343 m	321 vw	320 vw					
	312 w				304 m	308 w	308 w, sh	308 wm	308 wm	308 w?	302 m	303 m
	293 vw	290 vw	291 w, br	284 m		299 wm	298 wm	300 m	294 m			

Table IV. Electronic Spectra of Six-Coordinate Chromium(III) Complexes (band maxima in cm^{-1})

Complex		Assignment		Charge transfer
		$^4T_{1g} \leftarrow ^4A_{1g}$	$^4T_{1g}(F) \leftarrow ^4A_{1g}$	
$CrCl_3 \cdot 3S(CH_3)_2$	DR	14,500(s)	17,570(m) 20,580(ms)	27,000(vs)
	Bz	13,470(vw, sh)	14,350(116)	
	$S(CH_3)_2$	13,380(vw, sh)	14,500(112)	
$[CrCl_3 \cdot 2S(CH_3)_2]_2$	DR	13,400(w, sh)	14,300(s)	
	Bz	13,470(vw, sh)	14,300(103)	
	$S(CH_3)_2$	13,380(vw, sh)	14,500(112)	
$CrCl_3 \cdot 3S(C_2H_5)_2$	DR	14,290(s)	17,540(m), 20,660(ms)	26,800(vs)
	Bz	13,370(vw, sh)	14,080(98)	
	$S(C_2H_5)_2$	13,240(vw, sh)	14,160(102)	
$[CrBr_3 \cdot 2S(CH_3)_2]_2$	Bz	13,440(120)	17,540(145) 19,230(vw, sh)	
	$S(CH_3)_2$	13,890(118)	17,000(81) 19,300(86)	
	DR	13,330(s)	17,540(s) 19,230(vw, sh)	
$[CrBr_3 \cdot 2S(C_2H_5)_2]_2$	Bz	13,160(113)	17,420(126) 19,120(vw, sh)	26,600(vs)
	$S(C_2H_5)_2$	13,640(110)	16,670(76) 19,050(84)	
	DR	13,330(m)	14,500(w, sh)	
$CrCl_3 \cdot 3Qu$	DR	13,600(53)	14,500(w, sh)	35,350(vs)
	Bz		18,970(m) 21,980(wm)	
			18,870(56) 22,200(38)	

DR = diffuse reflectance; Bz, $S(CH_3)_2$ and $S(C_2H_5)_2$ = benzene, dimethyl- and diethylsulphide solutions. Extinction coefficients are in parentheses.

(see below) indicate that these are pseudo-octahedral complexes in the solid state and also in excess dialkylsulphide solution. However in an inert solvent like benzene they lose a molecule of ligand giving 1:2 adducts which are 6-coordinate dimers. The pure 1:2 adduct with $S(CH_3)_2$ was isolated by recrystallization of the 1:3 adduct $CrCl_3 \cdot 3S(CH_3)_2$ from hot benzene.

Chromium tribromide also forms 1:3 adducts with dimethyl- and diethylsulphide, but by removal of excess of the ligands, products with mole-ratios less than 1:3 were isolated; by dissolving these products in benzene, and then removing the solvent, pure 1:2 adducts were isolated which are considered to be six-coordinate dimers like the corresponding chloro-complexes.

Two points of interest arise from this part of the work. Firstly, the reactions of the chromium trihalides with dialkylsulphides are instantaneous only if the halide is prepared properly. This suggests that the halides as commonly used contain some impurities which act as anticatalysts. The rapid reactions of the chromium trihalides with the dialkylsulphides is surprising in comparison with the long reaction times quoted for their reactions with stronger ligands e.g. $CrCl_3/THF$, 10-15 hours,¹⁵ $CrCl_3/N(CH_3)_3$, 12 hours.⁶ Further investigation of the catalytic action of zinc is called for.

Secondly, the formation of six coordinate complexes of the chromium trihalides where the vanadium trihalides form exclusively five coordinate complexes

(15) W. Herwig and H. H. Zeiss, *J. Org. Chem.*, 23, 1404 (1958).

emphasises the very marked preference of chromium(III) for six-coordination.

It is appropriate now to discuss in detail the spectra of the dialkylsulphide complexes.

Electronic Spectra. The band maxima in the electronic spectra of the chromium(III) complexes are listed in Table IV. In particular, it is important to note that the 1:2 adducts have electronic spectra (Figure 4) typical of six-coordinate, *not* of five-coordinate adducts (for which, see below, a band at ca 10,000 cm^{-1} is characteristic). It is concluded, therefore, that the complexes are dimeric $[\text{CrX}_3 \cdot 2\text{SR}_2]_2$, probably with halogen bridges as suggested for the analogous phosphine complexes¹⁷ $[\text{CrX}_3 \cdot 2\text{PR}_3]_2$. The frequency of ν_1 for $[\text{CrCl}_3 \cdot 2\text{SR}_2]_2$ is almost identical with that for $\text{CrCl}_3 \cdot 3\text{SR}_2$; ν_2 however, occurs as a single band for the former but as two bands of comparable intensities for the latter, the splitting being ca 3000 cm^{-1} .

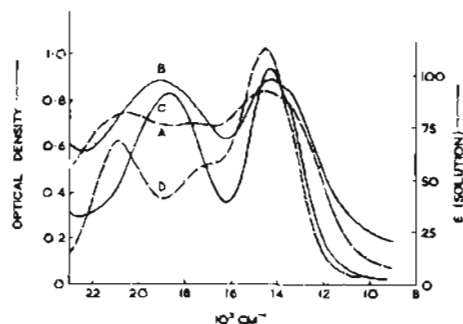
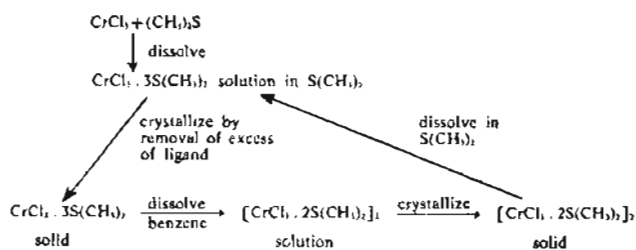


Figure 4. Diffuse reflectance spectra of (A) $\text{CrCl}_3 \cdot 3\text{S}(\text{CH}_3)_2$ and (B) $[\text{CrCl}_3 \cdot 2\text{S}(\text{CH}_3)_2]_2$. Solution spectra of either $\text{CrCl}_3 \cdot 3\text{S}(\text{CH}_3)_2$ or $[\text{CrCl}_3 \cdot 2\text{S}(\text{C}_2\text{H}_5)_2]_2$ in (C) benzene or (D) dimethylsulphide.

The diffuse reflectance spectrum of $[\text{CrCl}_3 \cdot 2\text{S}(\text{CH}_3)_2]_2$ is essentially identical with the solution spectrum of this complex in benzene (Figure 4); this indicates that there is no structural change in this complex on its dissolving in benzene. There is, however, a difference between the diffuse reflectance spectrum of $[\text{CrCl}_3 \cdot 2\text{S}(\text{CH}_3)_2]_2$ and its solution spectrum in excess of ligand; the latter spectrum is identical with both the dimethylsulphide solution spectrum and the diffuse reflectance spectrum of $\text{CrCl}_3 \cdot 3\text{S}(\text{CH}_3)_2$, and it is concluded that a structural change *does* occur in this case. The various reactions are best understood from a consideration of the block diagram below:



The diethylsulphide system is analogous, except that the complex $[\text{CrCl}_3 \cdot 2\text{S}(\text{C}_2\text{H}_5)_2]_2$ was not isolated. For the $\text{CrBr}_3/\text{SR}_2$ systems, the behaviour is similar

(Figure 5) except that the species $\text{CrBr}_3 \cdot 3\text{SR}_2$ could not be isolated.

The spectra of the dialkylsulphide complexes are typical of six-coordinate chromium(III) and yield, by the standard treatment,¹⁶ values for the ligand field parameters Dq , B and β . Data for other complexes of the type $\text{CrCl}_3 \cdot 3\text{Ligand}$ have been calculated and are included in Table V for comparison. The parameter Dq lies in the typical order, with respect to the donor atoms, of $\text{P} \sim \text{N} \sim \text{As} > \text{O} \sim \text{S} > \text{Cl}$. The phosphorus, arsenic- and sulphur-donor ligands have uniformly low values for β , in comparison with those for oxygen- and nitrogen-donor ligands. The phosphorus- and arsenic-donor ligands give rise to the highest extinction coefficients.

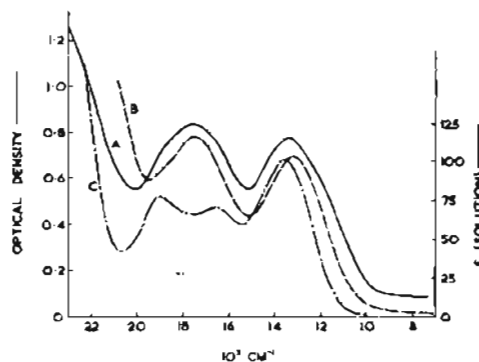


Figure 5. Diffuse reflectance (A) and solution (benzene B, and diethylsulphide C) electronic spectra of $\text{CrBr}_3 \cdot 2\text{S}(\text{C}_2\text{H}_5)_2$.

Infrared Spectra. The band maxima in the infrared spectra of the six-coordinate chromium(III) complexes in the range 450-200 cm^{-1} are in Table VI. By comparison with the corresponding infrared spectra of other complexes of the type $\text{MCl}_3 \cdot 3\text{ligand}$ ($\text{M} = \text{Ti}, \text{V}, \text{or Cr}$)^{13,17} the strong bands in the range 307-380 cm^{-1} are attributed to the CrCl stretching frequencies. The two dialkylsulphide complexes $\text{CrCl}_3 \cdot 3\text{S}(\text{CH}_3)_2$ and $\text{CrCl}_3 \cdot 3\text{S}(\text{C}_2\text{H}_5)_2$ both give rise to three such bands; accordingly, these complexes are considered to have the *mer*-configuration (C_{2v} symmetry) like $\text{CrCl}_3 \cdot 3\text{py}$ and $\text{CrCl}_3 \cdot 3\text{THF}$ ¹⁷ for which the three CrCl stretching modes, $2a_1 + b_1$, are active. For the *fac*-configuration only two CrCl stretching modes are infrared active ($a_1 + e$ of C_{3v}). The complexes possibly adopt the *mer*-configuration for steric reasons, as the *fac*-isomer would be expected to have the greater steric hindrance.

Dimethylsulphide gives rise to no infrared-active bands in the 300-400 cm^{-1} region.¹⁸ Free diethylsulphide, however, does show three medium bands at 382, 343 and 304 cm^{-1} .¹⁹ On coordination of the ligand, however, these bands invariably become very weak. One band near 280 cm^{-1} , attributable to the dialkylsulphide, $\delta(\text{CSC})$, does occur in the spectra of these complexes; however, this is lower than is typically found for Cr-Cl stretching modes, and thus it

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 (17) M. A. Bennett, R. J. H. Clark, and A. D. I. Goodwin, *J. Chem. Soc. (A)*, 541 (1970).

(18) I. R. Atkins and P. I. Heitdra, *J. Chem. Soc. (A)*, 1325 (1967).
 (19) R. J. H. Clark, G. Natile, U. Belluco, L. Cattalini, and C. Filippin, *J. Chem. Soc. (A)*, 659 (1970).

Table V. Electronic Spectra of Chromium(III) Complexes of the Type $\text{CrCl}_3 \cdot 3$ ligand (band maxima in cm^{-1})

Complex		ν_1	ν_2	Dq	B'	β	Ref.
$\text{CrCl}_3 \cdot \text{TP}$	Soln	16,500(1210)	21,000(490)	1650	414	0.45	<i>a</i>
$\text{CrCl}_3 \cdot \text{QP}$	Soln	16,300(1060)	21,200(520)	1630	457	0.50	<i>a</i>
$\text{CrCl}_3 \cdot o\text{-TAS}$	Soln	15,650(670)	20,000(220)	1565	424	0.46	<i>b</i>
$\text{CrCl}_3 \cdot \nu\text{-TAS}$	Soln	15,450(~ 200)	19,850(~ 100)	1545	407	0.44	<i>b</i>
$\text{CrCl}_3 \cdot 3\text{py}$	DR	16,250	22,200				<i>c, d</i>
	py Soln	16,300(29)	22,050(58)	1630	764	0.83	<i>d</i>
$\text{CrCl}_3 \cdot 3\text{THF}$	DR	14,200	19,500				<i>d</i>
	THF Soln	14,800(28)	20,250(40)	1480	532	0.58	<i>d</i>
$\text{CrCl}_3 \cdot 3\text{S}(\text{CH}_3)_2$	DR	14,500	$\sim 19,100$				<i>e</i>
	$\text{S}(\text{CH}_3)_2$ Soln	14,500(112)	$\sim 19,100$ (~ 68)	1450	434	0.47	<i>e</i>
$\text{CrCl}_3 \cdot 3\text{S}(\text{C}_2\text{H}_5)_2$	DR	14,290	$\sim 19,100$				<i>e</i>
	$\text{S}(\text{C}_2\text{H}_5)_2$ Soln	14,160(102)	$\sim 18,900$ (77)	1416	452	0.49	<i>e</i>
$\text{CrCl}_3 \cdot 3\text{TU}$	DR	14,700	19,600	1470	467	0.51	<i>f</i>
CrCl_3^{3-}	DR	13,180	18,700	1320	561	0.61	<i>g</i>

DR = diffuse reflectance; extinction coefficients are in parentheses. ^a I. V. Howell, L. M. Venanzi, and D. C. Goodall, *J. Chem. Soc. (A)*, 395 (1967). ^b R. J. H. Clark and M. L. Greenfield, *J. Chem. Soc., (A)*, 409 (1967). ^c E. König and H. L. Schäfer, *Z. Phys. Chem. (Frankfurt)*, 26, 371 (1960). ^d A. D. J. Goodwin, Ph. D Thesis, London, 1969. ^e This work; ν_2 is split, see Table IV, and hence its average value has been taken. ^f E. Cavone, P. Cancellieri, and C. Furlani, *J. Inorg. Nucl. Chem.*, 30, 2431 (1968). ^g W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Amer. Chem. Soc.*, 85, 265 (1963). TP = bis(*o*-diphenylphosphinophenyl)phenylphosphine; QP = tris(*o*-diphenylphosphinophenyl)phosphine; *o*-TAS = bis(*o*-dimethylarsinophenyl)methylarsine; ν -TAS = tris-1,1,1-(dimethylarsinomethyl)ethane; TU = thiourea; Py = pyridine.

Table VI. Infrared Spectra of Six-Coordinate Chromium Trihalide Complexes

Assignment	$\text{CrCl}_3 \cdot 3\text{S}(\text{CH}_3)_2$ Nujol	$[\text{CrCl}_3 \cdot 2\text{S}(\text{CH}_3)_2]_2$ Nujol	Bz	$\text{CrCl}_3 \cdot 3\text{S}(\text{C}_2\text{H}_5)_2$ Nujol	$[\text{CrCl}_3 \cdot 2\text{S}(\text{C}_2\text{H}_5)_2]_2$ Bz	$[\text{CrBr}_3 \cdot 2\text{S}(\text{CH}_3)_2]_2$ Nujol	$[\text{CrBr}_3 \cdot 2\text{S}(\text{C}_2\text{H}_5)_2]_2$ Nujol	$\text{CrCl}_3 \cdot 3\text{Qu}$ Nujol
Ligand	403 w, sh			411 w, sh		395 w, br	398 w, br	407 w 396 vw, sh
$\nu(\text{CrX})$	{ 375 vs 346 vs 317 s	381 s 350 s 316 m	379 s 349 s 316 s	368 vs, br 345 m, sh 307 s	372 s 350 sh 307 s	316 s 290 s	311 s 287 s	369 w 344 vs 324 w, sh 308 m
SR_2	{ 303 vw, sh 280 s	303 w, sh 280 s	298 vw, sh 275 s	297 m, sh 268 m	260 s	275 m	274 m, sh	
$\nu(\text{CrL})?$	{ 256 vw 234 w 210 w?	257 w, sh 235 w	255 ms 233 w	250 sh		244 w	245 m	242 w 222 w

does not confuse the assignment. The assignment of the metal-sulphur stretching frequencies is only tentative, owing principally to the weak absorption which is typically associated with such modes.¹⁹

The complex $[\text{CrCl}_3 \cdot 2(\text{CH}_3)_2]_2$ has an infrared spectrum very similar to that of $\text{CrCl}_3 \cdot 3\text{S}(\text{CH}_3)_2$, which suggests that the chromium is six-coordinate. Its spectrum is also very similar, in the CrCl stretching region, to that of the known dimer¹⁷ $[\text{CrCl}_3 \cdot 2\text{P}(\text{C}_2\text{H}_5)_3]_2$, viz $\nu(\text{CrCl})$ for the former are at 379 and 349 cm^{-1} and for the latter at 370 and 345 cm^{-1} . The known data on this and related complexes can thus be plausibly assigned, but they are not sufficiently detailed to establish the precise structures of the absorbing species.

Chromium Complexes with Quinuclidine. Most six-coordinate complexes of chromium(III) are kinetically rather inert. However, the dialkylsulphide ligands in the complexes $\text{CrCl}_3 \cdot 3\text{SR}_2$ and $[\text{CrBr}_3 \cdot 2\text{SR}_2]_2$ are immediately displaced by quinuclidine. Presumably the first step in the substitution reaction is a slight dissociation of the dialkylsulphide complex to form some five-coordinate species, which can then react with free quinuclidine to form a new six-coordinate species. Further steps of this sort would lead to complete displacement of the coordinated dialkylsulphide.

Of interest is the fact that two different adducts of CrCl_3 can be formed, $\text{CrCl}_3 \cdot 3\text{Qu}$ and $\text{CrCl}_3 \cdot 2\text{Qu}$,

which can be separated owing to the lower solubility of the former in benzene. Analysis of the spectroscopic properties of these two complexes (see below) suggests that the former is octahedral whereas the latter is a *trans*-trigonal bipyramidal molecule, directly analogous to the corresponding vanadium(III) complex, and to $\text{CrCl}_3 \cdot 2\text{N}(\text{CH}_3)_3$. Only the five-coordinate species $\text{CrBr}_3 \cdot 2\text{Qu}$ could be isolated with chromium tribromide.

$\text{CrCl}_3 \cdot 3\text{Qu}$. The electronic spectrum of the complex $\text{CrCl}_3 \cdot 3\text{Qu}$ is consistent with six-coordination for the chromium(III), but the band maxima suggest that there is considerable distortion from octahedral. The diffuse reflectance spectrum of the complex is virtually identical with its benzene solution spectrum, and hence no dissociation occurs such as was observed in benzene with the corresponding dialkylsulphide complexes. The position of the first band (${}^4T_{2g} \leftarrow {}^4A_{2g}$) is lower than expected for a Cl_3N_3 chromophore on Cr^{III} , and the second band (${}^4T_{1g}(\text{F}) \leftarrow {}^4A_{2g}$) is split in the same way as found for the 1:3 dialkylsulphide complexes. The precise stereochemistry of this complex cannot be deduced. In its infrared spectrum, the pattern of the bands associated with the CrCl stretching modes (Table V) is different from that typical of *mer*-octahedral complexes of the type, and may imply that the complex is *fac*-octahedral. The bands at 222 and 242 cm^{-1} are assigned tentatively to CrN stretching frequencies *c.f.* for $\text{CrCl}_3 \cdot 3\text{py}$ the CrN stretching fre-

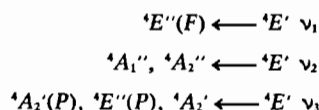
Table VII. Electronic Spectra of Trigonal Bipyramidal Complexes of Chromium Trichloride ^a

Complex		Band Maxima (cm ⁻¹)				
		ν_1	ν_2	ν_3	ν_4	ν_5
CrCl ₃ · 2Qu	DR	9,850(m)	13,000(w, sh)	17,640(s)	29,850(vs)	35,700(vs)
	Bz	9,980(22)	13,070(w, sh)	18,020(163)	—	—
CrBr ₃ · 2Qu	DR	9,010(m)	12,200(w, sh)	16,400(s)	broad absorption	
	Bz	9,070(31)	12,500(w, sh)	16,600(235)	—	—
CrCl ₃ · 2N(CH ₃) ₃	Soln ^b	10,100(23)	13,000(w, sh)	17,600(130)	—	—

^a The numbers in parentheses refer to the extinction coefficients for solution spectra. Bz = benzene solution; DR = diffuse reflectance. ^b Ref. 12.

quencies likewise occur²⁰ near 220 cm⁻¹.

CrCl₃ · 2Qu and CrBr₃ · 2Qu. The second quinuclidine complex of chromium chloride is undoubtedly *trans*-trigonal bipyramidal and exactly analogous to the corresponding complex of vanadium trichloride. The diffuse reflectance spectrum of the powdered solid is virtually identical with its solution spectrum in benzene (Figure 6), and also with the corresponding spectra of the complex CrCl₃ · 2N(CH₃)₃ (Table VII). The band assignments follow immediately, in terms of the ground-state configuration (*e''*)²(*e'*) of *D*_{3h} symmetry, from the discussion of Wood,¹² in which the first three ligand field transitions are assigned as follows:



The infrared spectrum of the complex (450-200 cm⁻¹ Table III, Figure 7) is also closely similar to that of the corresponding vanadium complex, and is fully consistent with the molecule's having *D*_{3h} symmetry. The bromo complex is entirely analogous.

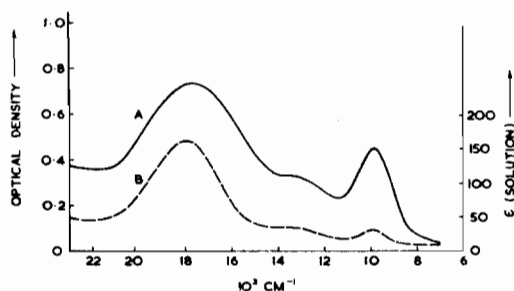


Figure 6. Diffuse reflectance (A) and solution (benzene B) electronic spectra of CrCl₃ · 2Qu.

The quinuclidine peak at 416 cm⁻¹ tends to complicate the assignment of the *e'* CrCl stretching mode; however, the 383 cm⁻¹ band is so assigned on account of its large intensity and breadth, and owing to its close proximity to the frequency of the corresponding mode of CrCl₃ · 2N(CH₃)₃ (392 cm⁻¹);⁶ moreover, the corresponding quinuclidine peak in the spectrum of the bromo complex is at 407 cm⁻¹.

The complex CrCl₃ · 2Qu appears to be only the se-

cond adduct of chromium trichloride to be shown to involve five-coordinate chromium(III), the other being CrCl₃ · 2N(CH₃)₃; the complex CrBr₃ · 2Qu is the first established five-coordinate adduct of chromium tribromide. Most other neutral ligands give rise to complexes of the types CrCl₃ · 3L, (CrCl₂ · L₄)⁺Cl⁻, (CrCl · L₅)²⁺2Cl⁻ or CrL₆³⁺3Cl⁻, and even structurally similar ligands such as triethylphosphine give rise to complexes in which chromium is six-coordinate.²¹

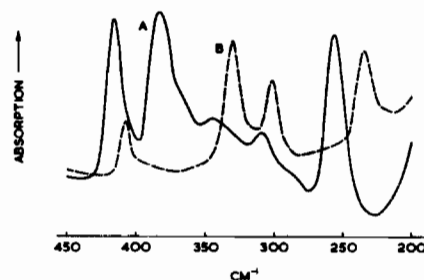
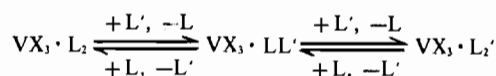


Figure 7. Infrared spectra of CrCl₃ · 2Qu (A) and CrBr₃ · 2Qu (B) as Nujol mulls.

D. Concluding Remarks. The present work has led to the preparation and characterization of a number of *trans*-trigonal bipyramidal complexes with quinuclidine and dialkylsulphides of VCl₃, VBr₃, and with quinuclidine of CrCl₃ and CrBr₃. The electronic and infrared spectra of the complexes are fully consistent with this formulation. Chromium(III) gives rise exclusively to six-coordinate complexes with dimethyl- and diethylsulphide. These occur as two different series, CrX₃ · 3SR₂ and [CrX₃ · 2SR₂]₂. The latter are probably dimeric with halogen bridging. Chromium trichloride also gives rise to a 1:3 adduct with quinuclidine; the preference of chromium(III) for six-coordination is clear.

The replacement of a coordinated sulphide(L) by another ligand (L') may be regarded as a nucleophilic substitution reaction, *viz*:



For the successful production of pure VX₃L₂', the equilibrium above must lie well to the right. The preparative procedure has the advantage that reaction in solution is very rapid and it may be used in instan-

(20) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

(21) K. Issleib and G. Bohn, *Z. Anorg. Allgem. Chem.*, **301**, 188 (1959).

ces where direct reaction between a metal halide and a ligand is inconvenient or impossible. Although other ligand/solvent systems have been used previously in this connection (*e.g.* acetonitrile or tetrahydrofuran), the dialkylsulphide system appears to be extremely useful for preparations involving the early transition elements, owing to the weakness of the $M^{III}-S$ bonds and consequently the ready displacement of the coordinated dialkylsulphide. The high solubility of the

dialkylsulphide complexes in non-polar solvents such as benzene and, in the case of vanadium(III) species, also in *n*-hexane, is a further valuable preparative feature.

Acknowledgement. One of us (G.N.) thanks N.A. T.O. (Grant No. 341) for financial support, and for leave of absence from the University of Padova. We also thank Dr. A.J. McAlees for valuable discussions.