

Preparation and Isomerisation of Tris(tetrahydrothiophene)chromium(III) Chloride Complexes

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Six co-ordinate complexes of the type $\text{CrCl}_3 \cdot 3\text{L}$ (L = monodentate) with S-bonded donors are much less likely than those of the N- and O-bonded variety¹ and indeed few are known.² The blue-purple *fac*- $\text{CrCl}_3 \cdot 3\text{C}_4\text{H}_8\text{S}$ and lilac *mer*- $\text{CrCl}_3 \cdot 3\text{C}_4\text{H}_8\text{S}$ complexes described in this report add to the list and, moreover, supply a rare instance of a *cis* \rightarrow *trans* isomerisation^{3,4} for this particular class of compounds.

Experimental

Reagent grade tetrahydrothiophene and benzene were dried successively with calcium hydride and molecular sieve and distilled as required. $\text{CrCl}_3 \cdot 2\text{NMe}_3$ was prepared following the procedure described by Fowles *et al.*⁵

Infra red spectra were measured on Perkin Elmer 621 and Fourier FS 720 instruments with samples as nujol and fluorolube mulls. Conductivity measurements were performed using a Wayne Kerr B221 conductance bridge, the conductivity cell used having been calibrated with standard aqueous KCl solutions. Visible and ultra violet spectra were recorded on a Cary 14 spectrophotometer with samples either in 1 cm sealed silica cells or as thin nujol mulls between silica plates and KBr discs. Carbon, hydrogen and sulphur determinations were made by the A. Bernhardt Microanalytical Laboratory, Mülheim, Germany. Chloride was determined by the Volhard method and chromium was estimated spectrophotometrically following oxidation to chromate.

Reactions

(i) Bis(trimethylamine)chromium(III) chloride (~ 3 g) was sealed in a glass ampoule with a twenty-fold excess (for a 1:1 molar ratio) of tetrahydrothiophene and benzene (~ 20 ml) as solvent. The vessel was shaken mechanically for several days, after

which time the excess of ligand, benzene and released trimethylamine were removed by standard techniques using an all-glass vacuum system. The blue-purple solid remaining was thoroughly washed with *n*-pentane and then pumped *in vacuo* at room temperature for several hours. *Anal.* Found: C, 33.8; H, 5.9; S, 22.5; Cr, 12.4; Cl, 24.9. $\text{C}_{12}\text{H}_{24}\text{S}_3\text{CrCl}_3$ requires C, 34.0; H, 5.7; S, 22.7; Cr, 12.3; Cl, 25.1. The infra red spectrum contained bands at 2998 (w), 2930 (sh), 2920 (s), 2900 (sh), 2855 (m), 1455 (w), 1440 (s), 1430 (m), 1305 (m), 1268 (m), 1253 (m), 1205 (w), 1130 (w), 1076 (m), 1022 (w), 958 (m), 881 (m), 817 (m), 722 (w), 668 (m), 512 (w), 471 (w), 368 (s), 340 (s) and 292 (m) cm^{-1} respectively. $\Lambda_M = 0.033 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in CH_2Cl_2 solution at $1 \times 10^{-3} M$ at 295 K.

(ii) Tris(tetrahydrothiophene)chromium(III) chloride (~ 2 g) as prepared in (i) was placed in a small round-bottomed flask and stirred *in vacuo* with benzene (~ 50 ml). The initial blue solution immediately started to deposit a lilac solid. After several days the colour of the solution was clear at which stage the lilac solid was filtered on the vacuum line, washed with *n*-pentane and pumped for several hours. *Anal.* Found: C 34.3; H, 5.2; S, 20.2; Cr, 12.2; Cl, 25.2. $\text{C}_{12}\text{H}_{24}\text{S}_3\text{CrCl}_3$ requires C, 34.0; H, 5.7; S, 22.7; Cr, 12.3; Cl, 25.1. The infra red spectrum contained bands at 2998 (w), 2930 (s), 2920 (s), 2900 (sh), 2858 (m), 1471 (m), 1455 (w), 1435 (m), 1425 (m), 1305 (m), 1268 (m), 1253 (m), 1198 (w), 1078 (m), 956 (m), 878 (m), 804 (m), 721 (w), 696 (m), 668 (m), 510 (w), 471 (w), 380 (s), 351 (s), 292 (m) and 278 (s) cm^{-1} respectively. $\Lambda_M = 0.095 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in CH_2Cl_2 solution at $1 \times 10^{-3} M$ at 295 K.

(iii) Anhydrous chromium(III) chloride (~ 4 g) was sealed in a double ampoule⁵ with a trace of zinc dust and an excess (~ 30 ml) of tetrahydrothiophene. An immediate and vigorous reaction occurred to give a deep blue solution and a blue-purple solid. Extraction of this product by repeated filtration and back-distillation of solvent across the sinter was continued over several days. The resulting blue-purple semi-crystalline material was washed *in vacuo* with *n*-pentane and pumped for six hours. Analysis and spectral measurements confirmed the blue-purple solid to be identical with that described in (i).

Discussion

Although six co-ordinate chromium(III) chloride complexes of the type $\text{CrCl}_3 \cdot 3\text{L}$ can assume *fac*- and *mer*- arrangements, in practice either one or other configuration is exclusively adopted, e.g. for L = tetrahydrofuran⁶ and pyridine⁷ the *mer*- configuration (C_{2v} symmetry) is favoured. With L = tetrahydrothiophene (THT) the two diastereomers have now been isolated and characterised, the blue-purple *fac*- $\text{CrCl}_3 \cdot 3\text{THT}$ [A] being obtained by a ligand substitution reaction involving the bis-trimethylamine adduct $\text{CrCl}_3 \cdot 2\text{NMe}_3$ and an excess of THT and the lilac *mer*- $\text{CrCl}_3 \cdot 3\text{THT}$ [B] *via* isomerisation of [A] in benzene solution. Direct treatment of the anhydrous metal halide and THT in the presence of a trace of zinc dust also gives [A].

Both compounds are air-moisture sensitive and behave as non-electrolytes in dichloromethane. The infra red spectra of the two complexes in the region $4000 - 400 \text{ cm}^{-1}$ are almost identical and contain bands assignable to co-ordinated tetrahydrothiophene⁵ e.g. the $\nu_{\text{as}}(\text{CSC})$ 819 cm^{-1} and $\nu_{\text{s}}(\text{CSC})$ 685 cm^{-1} modes of the free ligand are both lowered by $\sim 15 \text{ cm}^{-1}$ on coordination. The far infra red spectra ($400 - 200 \text{ cm}^{-1}$) – see Figure 1 – show the characteristically intense bands associated with chromium-chlorine stretching modes and in the present instance allow a clear distinction to be drawn

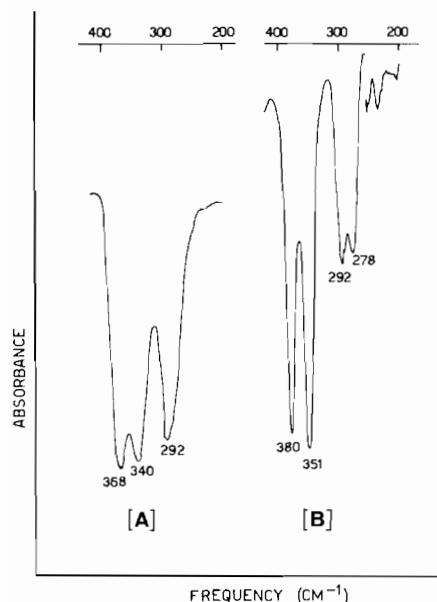


Fig.1. The $(400 - 200) \text{ cm}^{-1}$ region of the infra red spectra of [A] *fac*- $\text{CrCl}_3 \cdot 3\text{THT}$ and [B] *mer*- $\text{CrCl}_3 \cdot 3\text{THT}$.

between the two isomers. The observed triplet [$\nu(\text{CrCl}) \text{ cm}^{-1}$; 380, 351 and 278] and doublet [$\nu(\text{CrCl}) \text{ cm}^{-1}$; 368 and 340] profiles are in accord with theoretical predictions for *mer*- and *fac*- arrangements respectively.⁷ The band at 292 cm^{-1} common to both spectra is assigned to a modified δ (CSC) mode which appears at 283 cm^{-1} in the free ligand. The electronic spectral data – see Table I and Figure 2 – confirms (A) and (B) as octahedral chromium(III) complexes and the bands (solid phase) at $14,600 \text{ cm}^{-1}$ [A] and $14,300 \text{ cm}^{-1}$ [B] and at $20,830 \text{ cm}^{-1}$ [A] and $20,100 \text{ cm}^{-1}$ [B] are assigned (O_h) to the “*d-d*” transitions ${}^4T_{2g} \leftarrow {}^4A_{2g}$ (F) and ${}^4T_{1g} \leftarrow {}^4A_{2g}$ (F) respectively; the remainder, which occur in the $25,000 - 40,000 \text{ cm}^{-1}$ region, are likely to be of the halogen (π) \rightarrow metal (*d*) charge-transfer type. The very weak shoulder at $13,510 \text{ cm}^{-1}$ in the case of (A) is tentatively assigned to the spin-forbidden transition ${}^2E_g \leftarrow {}^4A_{2g}$ (F) and is indicative of some trigonal or lower symmetry distortion of the octahedral environment.⁸

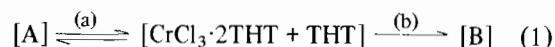
TABLE I. Electronic Spectra

Compound	Medium	Absorption Maxima ^a
<i>fac</i> - $\text{CrCl}_3 \cdot 3\text{THT}$ [A]	nujol	13,510vw (sh), 14,600 20,830 28,570 39,370w (sh)
	THT ^b	8,200 (vw) 13,550vw (sh) 14,350 18,315 (sh) 20,670
	benzene ^b	8,550 (w) 13,520w (sh) 14,336 18,726 19,530w (sh)
<i>mer</i> - $\text{CrCl}_3 \cdot 3\text{THT}$ [B]	nujol	14,300 broad, 20,100 broad, 26,300 38,460 (sh)

^a λ_{max} given as cm^{-1} .

^b exclusive examination of the spectral region of each absorption was made using an increased instrument sensitivity ($\times 10$) and maximised solution concentrations.

The isomerisation (A) \rightarrow (B) in benzene solution can occur in a formal sense⁹ either *via* a bond rupture mechanism involving a five co-ordinate $[\text{CrCl}_3 \cdot 2\text{THT}]$ intermediate or by means of a bond twist mechanism. Our preference for the former, *viz.*,



is supported in some measure by the solution spectral data – see Figure 2. By analogy with the solid phase

spectrum, the bands observed at $14,336\text{ cm}^{-1}$ and $19,530\text{ (sh) cm}^{-1}$ in the benzene solution spectrum of (A) can be assigned to the “*d-d*” transitions ${}^4T_{2g} \leftarrow {}^4A_{2g}\text{ (F)}$ and ${}^4T_{1g}\text{ (F)} \leftarrow {}^4A_{2g}\text{ (F)}$ respectively; the remainder, clearly superfluous to an octahedral

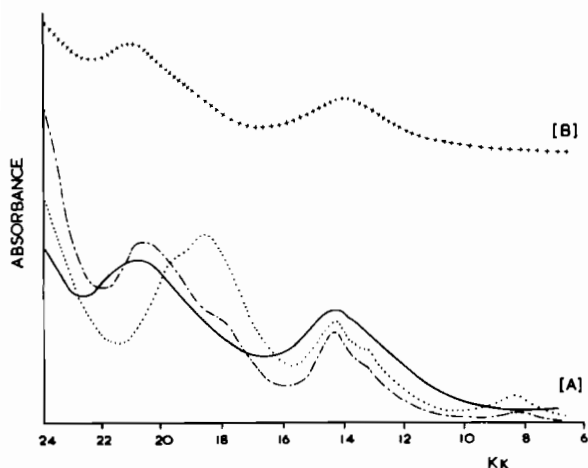


Fig. 2. Electronic spectra of [A] *fac*- $\text{CrCl}_3 \cdot 3\text{THT}$ in: — solid phase (nujol mull), - - - tetrahydrothiophene solution, . . . benzene solution and of [B] *mer*- $\text{CrCl}_3 \cdot 3\text{THT}$ in the solid phase (nujol mull) xxxxx.

model, can be accommodated on the basis of a five co-ordinate chromium(III) species and, following a comparison with the spectral analyses of $\text{CrCl}_3 \cdot 2\text{NMe}_3$ ¹⁰ and $\text{CrCl}_3 \cdot 2\text{Qu}$ ^{2b} [Qu = $\text{HC}(\text{C}_2\text{H}_4)_3\text{N}$] can be assigned (D_{3h} symmetry), *viz.*, $8,500\text{ cm}^{-1} {}^4E''\text{ (F)} \leftarrow {}^4E'\text{ (}\nu_1\text{)}$, $18,726\text{ cm}^{-1} {}^4A_2'\text{ (P)}$, ${}^4E''\text{ (P)}$, ${}^4A_2' \leftarrow {}^4E'\text{ (}\nu_3\text{)}$ and $13,520\text{ cm}^{-1}$ (shoulder) ${}^4A_1'$, ${}^4A_2' \leftarrow {}^4E'\text{ (}\nu_2\text{)}$. Equally, the latter may well include the spin-forbidden ${}^2E_g \leftarrow {}^4A_{2g}$ transition as suggested for the solid phase spectrum. The presence of both five- and six-co-ordinate chromium(III) species in benzene solution when coupled with the complete insolubility of (B) in benzene is consistent with step (a) in equation (1) being in fact an equilibrium stage. Since solvent molecules are unlikely to be involved *via* metal co-ordination in a mechanistic role¹¹ the formation of (B) *via* isomerisation of (A) in benzene is assured with a *mer*- configuration now being favoured on steric grounds.

Interestingly, in addition to the two bands at $14,350\text{ cm}^{-1}$ [${}^4T_{2g} \leftarrow {}^4A_{2g}\text{ (F)}$] and at $20,670\text{ cm}^{-1}$ [${}^4T_{1g}\text{ (F)} \leftarrow {}^4A_{2g}\text{ (F)}$] as expected, very weak bands

at $8,200\text{ cm}^{-1}$, $13,550\text{ cm}^{-1}$ and $18,315\text{ cm}^{-1}$ are discernible in the tetrahydrothiophene solution spectrum of (A). With a surfeit of donor solvent molecules forcing the equilibrium stage (a) to the LHS — hence the successful preparation of (A) — the implication here is that the bis-tetrahydrothiophene adduct $\text{CrCl}_3 \cdot 2\text{C}_4\text{H}_8\text{S}$ does possess an inherent stability.

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References

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