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Co-ordination Studies of Cyclic Polythioethers: Complexes of Au(III), Nb(V), Sb(V), Sn(IV), Ta(V) and Ti(IV) Halides with 1,4-Dithiane and 1,3,5-Trithiane

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Reactions of the S-donor ligands 1,4-dithiane (DT) and 1,3,5-trithiane (TT) with a series of covalent metal halides have been studied. We report the preparation and characterisation of the 1:1 complexes $AuCl_3\cdot(TT)$, $MCl_5\cdot(TT)$ *(M = Sb, Ta),* $TiCl_4\cdot(TT)$, $MX_4\cdot(DT)$ *(M = Sn, X = Cl, Br),* $MCl_5\cdot(DT)$ *(M = Nb, Ta), the 1:2 complexes* $MX_4\cdot 2(TT)$ *(M = Ti, Sn, X = Cl; M = Sn, X = Br) and the 2:1 complexes* $2MCl_5\cdot(DT)$ *(M = Nb, Ta). Structural assignments in terms of metal geometry and coordination number and of ligand binding as either monodentate or bidentate bridging between separate metal atoms are based on infrared data. Variable temperature* ^1H *NMR measurements of* $SnCl_4\cdot 2(TT)$ *indicate fluxional rearrangements of the six-membered sulphur-containing rings.*

Introduction

1,4-dithiane $\overline{SCH_2CH_2SCH_2CH_2}$ and 1,3,5-trithiane $\overline{SCH_2SCH_2SCH_2}$ form complexes with, typically, class B or 'soft' metals *e.g.*, Ag(I) [1], Hg(II) [2], with more borderline cases, *e.g.*, Sb(III) [3–6], Sn(II) [7] and with class A or 'hard' metals, *e.g.*: Ti(IV) [8], Mo(II) [9]. For complexes where X-ray structural information is available it appears that (a) full utilisation of *S*-donor sites in normal bidentate (1,4-dithiane) and terdentate (1,3,5-trithiane) chelation is never realised; as a general rule, ligand involvement is in the form of a bridging mode linking two or more separate metal centres and (b) both 1,4-dithiane and 1,3,5-trithiane normally retain the chair form that each shows in the uncomplexed state [10, 11]. One exception is $[(Me_3PtCl)_2(\overline{SCH_2SCH_2SCH_2})]$ where the six-membered ring adopts a somewhat distorted boat conformation [12]. Another aspect of these organosulphur ligands that has aroused recent interest concerns the several fluxional processes (ring reversal, pyramidal *S* inversion *etc.*) shown by *e.g.* Pt(II), Pt(IV), Pd(II), Sn(IV) complexes as discussed by Abel *et al.* [12–16] in their elegant dynamic NMR spectral studies.

We have investigated complex formation of 1,4-dithiane and 1,3,5-trithiane with both 'soft' and 'hard' metal halides with a view to subsequent structural investigations of their metal–sulphur binding characteristics. Herein we report the preparation and. spectral characterisation of a representative series.

Experimental

Manipulations of materials were carried out using an all-glass vacuum line and standard Schlenk systems. Infrared samples were prepared as nujol mulls held between CsI plates and their spectra recorded on a Perkin Elmer 580B grating spectrophotometer. ^1H NMR spectra were recorded on a Perkin Elmer R34 (220 MHz) and Brüker WH400 (400 MHz) instruments with TMS as an internal standard. Carbon and hydrogen analyses were obtained commercially and chlorine was determined by the Volhard method.

All complexes were prepared by direct reactions between the ligand and the appropriate metal halide in $CHCl_3$ or CH_2Cl_2 solutions. As a typical example: $TiCl_4$ (1 cm^3, 9.1 mmol) in $CHCl_3$ (150 cm^3) was added dropwise to a solution of $(\overline{SCH_2SCH_2SCH_2})$ (2.5 g, 18.2 mmol) in $CHCl_3$ (300 cm^3) to give an orange solution and an orange precipitate. The solution was decanted *in vacuo* whereupon the resultant orange solid was washed first with benzene (50 cm^3) and then n-hexane (2 × 50 cm^3) and finally pumped *in vacuo* for several hours at room temperature. The *product* $TiCl_4\cdot 2(\overline{SCH_2SCH_2SCH_2})$ (3.8 g, 89.6%) was stored in glass ampoules under an N_2 atmosphere.

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TABLE I. Analytical Data.

Compound	Colour	Calculated (%)			Found %		
		C	H	Halogen	C	H	Halogen
1,3,5-trithiane (TT)							
$TiCl_4 \cdot 2TT$	orange	15.5	2.6	30.4	15.2	2.6	30.3
$SnCl_4 \cdot 2TT$	white	13.4	2.3	26.4	13.6	2.3	26.4
$SnBr_4 \cdot 2TT$	pale yellow	10.0	1.7	44.7	10.3	1.8	44.3
$SbCl_5 \cdot TT$	pale yellow	8.2	1.4	40.5	9.2	1.7	39.9
$TaCl_5 \cdot TT$	yellow	7.3	1.2	35.7	7.1	1.3	36.9
$AuCl_3 \cdot TT$	brown	8.2	1.4	24.1	8.1	1.3	23.9
$TiCl_4 \cdot TT$	yellow	11.0	1.8	43.3	10.7	1.9	43.5
1,4-dithiane (DT)							
$SnCl_4 \cdot DT$	white	12.6	2.1	37.2	12.7	2.2	37.0
$SnBr_4 \cdot DT$	pale yellow	8.6	1.4	57.2	8.7	1.5	56.9
$TaCl_5 \cdot DT$	yellow	10.0	1.7	37.0	10.4	1.6	36.6
$NbCl_5 \cdot DT$	red	12.3	2.1	45.4	12.2	2.0	45.4
$2NbCl_5 \cdot DT$	yellow	7.3	1.2	53.7	7.5	1.3	53.5

Results and Discussion

Complexes of 1,3,5-Trithiane

Direct addition of chlorocarbon solutions of $\overline{SCH_2SCH_2SCH_2}$(TT) and the appropriate metal halide gave immediate precipitation of the 1:1 [$AuCl_3 \cdot$(TT), $MCl_5 \cdot$(TT) (M = Sb, Ta), $TiCl_4 \cdot$(TT)] and 1:2 [$MX_4 \cdot 2$(TT) where M = Ti, Sn, X = Cl, M = Sn, X = Br] adducts (Table I). Apart from $AuCl_3 \cdot$(TT), which could be handled on the bench without any trace of decomposition, the complexes were air–moisture sensitive, insoluble in the common organic solvents, and invariably underwent ligand displacement reactions when subjected to coordinating solvents. $TiCl_4 \cdot 2$(TT) was particularly sensitive and showed ligand exchange even in weak donor solvents such as Et_2O. The successful isolation of $TiBr_4 \cdot 2$(TT) [8] using Et_2O as solvent is possibly a reflection of the more pronounced class B character of $TiBr_4$ *wrt* $TiCl_4$ leading to a greater stability.

No products were isolated from the reactions with $AsCl_3$, $AlCl_3$ and $GeCl_4$. As an alternative route to complex formation, treatment of $MCl_3 \cdot 3L$ (M = Ti, V; L = MeCN, THF), $ZrCl_4 \cdot 2NMe_3$ and $Mo(CO)_3(MeCN)_3$ respectively with an excess of (TT) failed to bring about effective ligand exchange even after prolonged heating at reflux. Reactions with $MoCl_5$, $NbCl_5$ and $VOCl_3$ each gave a mixture of products with the dominant reaction being ring degradation.

The infrared spectra of the adducts show a marked similarity to that of the free ligand indicating that the centrosymmetric chair form of the six-membered ring persists on complexation. A general slight lowering of the CS stretching and CH_2 group frequencies is in accord with *S* donation [17]. In some instances multiplet ν(CS) bands are observed *e.g.*, the strong ring stretch at 725 cm^{-1} appears as a triplet in $TiCl_4 \cdot 2$(TT) (749, 730, 722 cm^{-1}), perhaps a hint that complexation is accompanied by a lowering in the symmetry of the ring [18]. For complexes which are coordinatively unsaturated intermolecular association in the solid state can cause the reverse effect. Typically $SbCl_3 \cdot (\overline{SCH_2SCH_2SCH_2})$, the crystal structure of which shows each ligand molecule symmetrically placed between three separate $SbCl_3$ moieties [6], exhibits no such ν(CS) band splitting. Metal halogen vibrational profiles in the far infrared region are interpreted as follows: (i) $MX_4 \cdot 2$(TT): A single intense ν(MX) band *viz.*, M = Ti, X = Cl 391 cm^{-1}, M = Sn, X = Cl 322 cm^{-1}, M = Sn, X = Br 276 cm^{-1} is in accord with a *trans*-octahedral (D_{4h}) arrangement of ligands. (ii) $AuCl_3 \cdot$(TT): The presence of three ($2a_1 + b_1$) gold–chlorine vibrations (ν(AuCl)365(b_1), 340, 326 cm^{-1}) is consistent with a square planar (C_{2v}) metal environment. The asymmetric AuCl vibration appears at ~360 cm^{-1} for a variety of such $AuCl_3 \cdot L$ complexes with little variation [19]. (iii) $MCl_5 \cdot$(TT): With a three-band pattern ($2a_1$ + e) (M = Ta, ν(TaCl) 408, 378, 335 cm^{-1} and M = Sb, ν(SbCl) 391, 343,

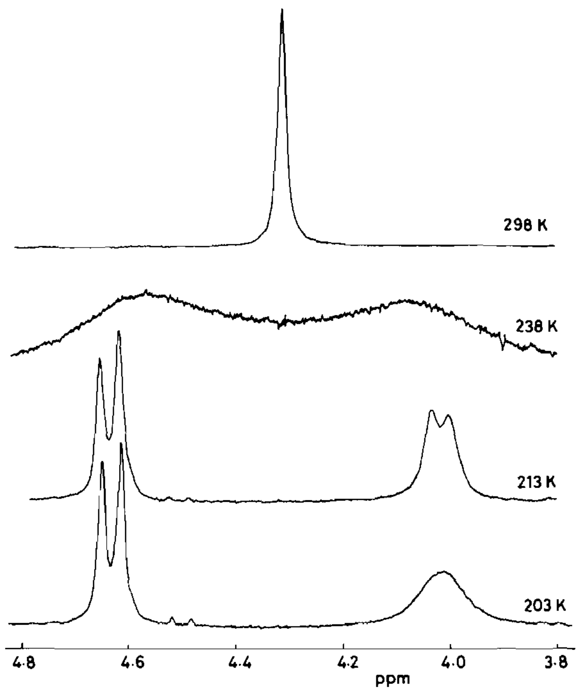

Fig. 1. Variable temperature ^{1}H NMR spectrum of $SnCl_4 \cdot 2(TT)$.

285 cm^{-1}) these complexes are considered to involve six coordinate octahedral structures (C_{4v}). (iv) $TiCl_4 \cdot (TT)$: With both $\nu(TiCl)_{terminal}$ 417, 405, 380 cm^{-1} and $\nu(TiCl)_{bridging}$ 320, 275 cm^{-1} vibrations present a dimeric halogen-bridged structure involving six co-ordinate titanium is proposed.

One complex *trans*-$SnCl_4 \cdot 2(TT)$ showed sufficient solubility and stability in $CDCl_3$ to allow limited variable temperature ^{1}H NMR spectral measurements (Fig. 1). The room temperature spectrum exhibits a single sharp resonance at δ 4.31; uncomplexed ligand gives a sharp singlet at δ 4.14. On lowering the temperature this signal broadens and at 238 K has split into a humped doublet as a consequence of a slower rate of ligand ring reversal. The ring reversal energy for free ligand is $\Delta G^{\neq}_{266} \cong$ 46 kJ mol^{-1} [20] and is not expected to change radically on metal complexation [13]. At 213 K the $H_{axial} \sim H_{equatorial}$ geminal coupling results in a twin doublet profile of intensity ratio 1:1. The energy barrier $\Delta G^{\neq}$ for sulphur inversion is expected to be significantly higher than that for ring reversal for this particular ligand both in the uncomplexed and complexed forms [15] and the absence of further splitting suggests that the fluxional sulphur inversion process is still rapid at this lower temperature. The simplicity of the spectrum also denies the presence of *cis–trans* isomers as found, for example, in the complexes $SnX_4 \cdot (R_2E)_2$, R = CH_3, C_2H_5; E = S, Se; X = Cl, Br [16, 21]. At the much lower temperature of 203 °K, whereas the downfield doublet, assigned axial, remains sharply defined there is a pronounced broadening of the equatorial signal. This may well be the consequence of a slowed rate of the sulphur inversion fluxional process resulting in long range coupling between equatorial protons [15].

Complexes of 1,4-Dithiane

Slow addition of dichloromethane solutions of $\overline{SCH_2CH_2SCH_2CH_2}$ (DT) and the appropriate metal halide results in the formation of $MX_4 \cdot (DT)$ (M = Sn, X = Cl, Br), $MCl_5 \cdot (DT)$ (M = Nb, Ta) and $2MCl_5 \cdot (DT)$ (M = Nb, Ta) (Table I). Repeated reactions involving the M(IV) halides confirmed that these 1:1 adducts were the sole products being independent of both reagent stoichiometry and initial concentrations.

The $MCl_5 \sim (DT)$ (M = Nb, Ta) systems have been previously investigated by Wilkins [22] who obtained 2:1 complexes respectively but failed to isolate any 1:1 adducts. Our results match those published for white $2TaCl_5 \cdot (DT)$ (ν(TaCl) 409, 376, 333 cm^{-1}); the reported orange $2NbCl_5 \cdot (DT)$ (ν(NbCl) 375 cm^{-1} (s, v,br); Cl_{found} 55.4, Cl_{calc} 53.7) is possibly a mixture of the red (1:1) and yellow (2:1) complexes obtained here (?). The infrared spectral data support ligand attachment as monodentate (1:1) or as bridging bidentate (2:1) with retention of the centrosymmetric chair conformation [23]. Three strong metal–chloride stretching bands ($2a_1$ + e) for $NbCl_5 \cdot (DT)$ (395, 375, 356 cm^{-1}), $TaCl_5 \cdot (DT)$ (391, 376, 337 cm^{-1}) and $2NbCl_5 \cdot (DT)$ (417, 385, 355 cm^{-1}) typify an octahedral six coordinate metal environment and the ν(CS) ligand band at 663 cm^{-1} remains essentially unchanged (±10 cm^{-1}) throughout [24]. The ^{1}H NMR spectra (CD_3NO_2) for these M(V) species show a single broad resonance, *e.g.* $NbCl_5 \cdot (DT)$ (δ 3.09), $TaCl_5 \cdot (DT)$ (δ 3.12) and $2NbCl_5 \cdot (DT)$ (δ 2.98) shifted downfield from that of the free ligand (δ 2.84) to confirm the equivalence of methylene protons at room temperature. Addition of a further mol equivalent of (DT) gives retention of the broad singlet in each case with a shift intermediate between free and bound ligand signifying fast ligand exchange. The broadening phenomenon is most likely due to the onset of ring reversal [25] but was not further pursued (disproportionation ~ decomposition was clearly evident over a very short time period).

For the $MCl_4 \cdot (DT)$ complexes a polymeric structure utilising a bidentate bridging situation is intuitively favoured [3, 4, 26]. However, the appearance of multiplet ν(MX) bands, *e.g.* $SnCl_4 \cdot (DT)$ (348, 325, 289 cm^{-1}), $SnBr_4 \cdot (DT)$ (235, 225 cm^{-1}) and $TiCl_4 \cdot (DT)$ (402, 381, 318 cm^{-1}) tends towards a *cis*-octahedral arrangement, *i.e.* discrete bidentate chelation. All show multiple ν(CS) bands, *e.g.* $SnBr_4\cdot$(DT) (675, 666, 655 cm^{-1}).

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