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The Reaction of Ruthenium(III) Chloride with 1,4,thioxane, 1,4,dithiane, 1,2,dialkyl and 1,2,diphenyl thio ethanes

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Ruthenium(III) chloride reacts with ligands of the type $RSCH_2CH_2SR(L)$ to give complexes $RuCl_3L$ ($R=CH_3$ or C_6H_5) $RuCl_31.5L$ ($R = CH_3$ or C_2H_5) and $RuCl_32L$ ($R = C_6H_5$). I.R. and magnetic measurements were used to propose probable structures for these complexes. The preparation and properties of $RuCl_33L$ ($L = 1,4$ thioxane) and $RuCl_31.5L$ ($L = 1,4$ dithiane) are also described.

Introduction

While the reactivity of ruthenium(III) chloride towards mono and bidentate ligands containing group V donor atoms has been extensively studied[1] there have been very few reports of similar studies with ligands containing group VI donor atoms. Only the diethyl sulphide adducts $RuCl_33Et_2S$ and $[RuCl_32Et_2S]_2$ have been reported.[2] The latter complex has been shown to be dimeric by molecular weight measurements and to have a room temperature magnetic moment of 0.95 BM, this being an indication of considerable magnetic interaction.

The reaction of ruthenium(III) chloride with ligands of the type $RSCH_2CH_2SR$ (where $R=CH_3,C_2H_5$ and C_6H_5) is now reported. These ligands usually adopt the *gauche*-chelating form although some bridging-*trans* examples are known where $R=CH_3$.[3,4,5] According in this study particular attention has been given to the ligand conformation.

Both 1,4 thioxane and 1,4 dithiane adopt the chair form on complex formation. For comparative purposes the complexes these ligands form with ruthenium(III) chloride have been prepared.

Results and Discussion

Cyclic Thioethers. Ruthenium(III) chloride in ethanol reacted with thioxane and dithiane to give $RuCl_3$-$3C_4H_8OS$ and $RuCl_3$ 1.5 $C_4H_8S_2$ respectively. With the simplest thioether tetrahydrothiophen, no characterisable product was isolated.

The infrared spectrum of $RuCl_3$ 3 C_4H_8OS in the region 4000-400 cm^{-1} is typical of sulphur bonded thioxane.[6] The anti-symmetric and symmetric C—O—C frequencies of 1,4 thioxane occur at 1110 and 836 cm^{-1} respectively. The analogous C—S—C frequencies have been assigned[6] to bands at 693 and 667 cm^{-1}. While the oxygen frequencies appear unaltered in the complex the 693 cm^{-1} absorption is absent and that at 667 cm^{-1} is much reduced in intensity.

The complex was quite soluble in a range of organic solvents and was non-conducting in methyl cyanide. The magnetic moment (Table II) was 1.99 BM at 293 K which is typical of spin-paired ruthenium(III).

The evidence suggests a non-bridged octahedral structure and the far infrared (Table I) is similar to the spectrum of $RhCl_33C_4H_8OS$[7] which has been assigned a *cis* octahedral structure. Because of the similarity to the rhodium analogue the bands at 325 and 294 cm^{-1} are assigned to the a_1 and e metal chloride vibrations of a *cis* octahedral configuration.

The postulated structure for $RuCl_33C_4H_8OS$ suggests a similar type of structure for $RuCl_31.5C_4H_8S_2$ where each ruthenium atom would be bonded to three terminal chlorine atoms and three sulphur atoms. Models show that a polymeric structure is possible where each ruthenium atom is linked to three other ruthenium atoms by bridging chair dithian molecules.

The infrared spectrum of the complex between 4000-400 cm^{-1} closely resembles the spectrum of $HgCl_2C_4H_8S_2$[5] where 1,4 dithiane has been shown to be in the chair form with both sulphur atoms co-ordinated. The infrared spectrum in the region 400-200 cm^{-1} shows one broad band centred on 320 cm^{-1} which covers the region assigned to metal chlorine frequencies in the thioxane complex. Thus the evidence from the infrared is not inconsistent with a similar structure to $RuCl_33C_4H_8OS$.

1,2 Dialkyl and 1,2 Diphenyl Thioethane Complexes. a) *1:1 Complexes.* The infrared spectrum of 1,2 dimethylthioethane has been fully assigned[8] and thus it is possible to identify infrared absorption bands due to specifically the *trans* or *gauche* isomers. In the complex $RuCl_3$DTH only bands due to the *gauche* form of the ligand appear in the infrared. Although

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(1) W.P. Griffith, « The Chemistry of the Rarer Platinum Metals », p. 206, pub. Interscience (1967).
(2) J.E. Fergusson, J.D. Karran, and S. Seevaratnan, *J. Chem. Soc.*, 2627 (1965).
(3) F.A. Cotton, R.A. Walton, *Inorg. Chem.*, *5*, 1802 (1966).
(4) R.A. Walton, D.A. Edwards, *Spectrochim. Acta*, *24A*, 833 (1968).
(5) D.A. Rice, R.A. Walton, *Spectrochim. Acta*, *27A*, 279 (1971).
(6) R.A. Walton, *Inorg. Chem.*, *5*, 643 (1966).
(7) R.A. Walton, *J. Chem. Soc.* *(A)*, 1852 (1967).
(8) H. Hayashi, Y. Shiro, T. Oshima, M. Murata, *Bull. Chem. Soc. Japan*, *39*, 118 (1966).

Table I. *I*.R. (400→200 cm^{-1}).

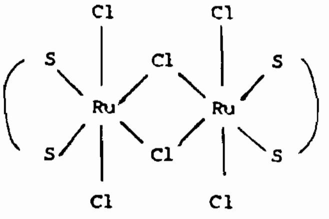
Complex	Peak maxima (cm^{-1})
$RuCl_33C_4H_8OS$	400 (m), 383 (m), 325 (vs), 294 (m), 270 (sh), 262 (m-s), 253 (m-s), 253 (m-s), 222 (w,br).
$RuCl_31.5\ C_4H_8S_2$	320 (vs, br), 300 (sh).
$RuCl_3DTH$	310 (vs, br), 282 (m-s, br), 225 (w,br).
$RuCl_31.5$ DTH	330 (vs, br), 290 (sh).
$RuCl_30.6$ ETH	320 (vs, br), 285 (sh).
$RuCl_31.5$ ETH	330 (vs, br), 302 (sh).
$RuCl_3DPTE$	310 (vs, br), 282 (m-s,br), 245 (w,br).
$RuCl_32DPTE$	365 (m), 348 (m), 295 (s), 260 (m), 221 (w).
DPTE	235 (w).

Table II. Magnetic Measurements.

Complex	χ (x 10^6c.g.s.units)	μ_{eff}(B.M.)
$RuCl_33C_4H_8OS$	1,682 (293 K)	1.99
$RuCl_31.5C_4H_8S_2$	676 (292 K), 1,930 (85 K)	1.26 (293 K), 1.15 (85 K)
$RuCl_3DTH$	685 (294 K)	1.25
RuCl 1.5 DTH	652 (296)	1.25
$RuCl_3$ 1.5 ETH	701 (292 K)	1.29
$RuCl_3$ DPTE	620 (296 K), 1,780 (84 K)	1.23 (296 K), 1.10 (84 K)
$RuCl_32DPTE$	360 (293 K)	0.95

no full studies have been made of the infrared of 1,2 diphenylthioethane (DPTE) and 1,2 diethylthioethane (ETH) a band which appears in the spectra of both ligands at 1208 cm^{-1} does not appear in the spectra of $RuCl_3DPTE$ or the species $RuCl_30.6ETH$. Clarke and Errington[9] have reported the disappearance of this 1208 cm^{-1} band on the formation of DPTE complexes and this has been attributed to the presence of the *gauche* chelating ligand. Accordingly we assume that the *gauche* conformer is present in both complexes.

The infrared spectra between 400-200 cm^{-1} (Table I) of $RuCl_3DPTE$ and $RuCl_3DTH$ show two broad bands at 310 and 282 cm^{-1} which can be attributed to bridging and terminal metal chlorine frequencies of a structure such as I. The extremely broad nature of the absorptions may be caused by the presence of a number of isomers of I or by the coincidence with the metal-chlorine vibrations of metal-sulphur frequencies.



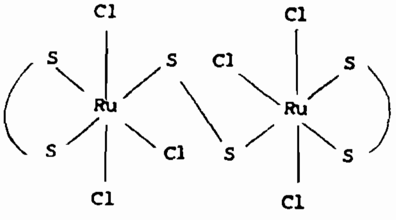
I

The magnetic properties of both 1:1 complexes (Table II) show that considerable magnetic interaction is occurring at room temperature in agreement with measurements made on $[RuCl_32Et_2S]_2$.[2]

Attempts were made to prove the chlorine bridged nature of $RuCl_3DTH$ by reacting the complex with various nitrogen donors. Pyridine completely replaced the sulphur ligand to give $RuCl_33py$. A range of weaker donors yielded non-stoichiometric products.

b) *1:1.5 Complexes.* The complexes of stoichiometry $RuCl_31.5L$ (L = DTH or ETH) which slowly formed from a solution of the halide and ligand in ethanol are interesting because their infrared spectra (4000-400 cm^{-1}) resemble closely the spectra of the free ligands where both *gauche* and *trans* ligand are present. Most complexes formed with DTH contain the ligand in its *gauche* chelating form as was observed with $RuCl_3DTH$. Recently a few examples of complexes containing the *trans* ligand have been prepared.[3,4,5] In the spectrum of $RuCl_31.5DTH$ the bands characteristic of *trans* ligand which occur at 1208 cm^{-1} and 1138 cm^{-1} are observed as well as the weak *gauche* band at 840 cm^{-1}.

The most probable type of structure to explain the ligand conformation is of the type shown in II where there are bridging and chelating ligand molecules together with terminal metal-chlorine bonds. The infrared spectra in the range 400-200 cm^{-1} of both $RuCl_31.5DTH$ and $RuCl_31.5ETH$ (Table I) resemble closely the spectrum of $RuCl_31.5C_4H_8S_2$ for which a structure involving only terminal metal-chlorine bonds has been proposed. An alternative structure for the $RuCl_3L_{1.5}$ is similar to that propesd for $RuCl_3L$ with unco-ordinated ligand molecules in the lattice. This suggestion would account for the similarity in the magnetic properties of $RuCl_3L$ and $RuCl_3L_{1.5}$ and for the close resemblance of the infrared spectrum in the



II

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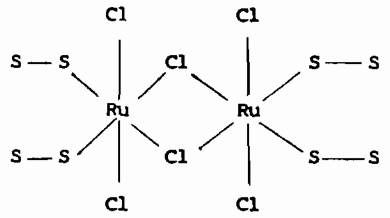
[9] R.J.H. Clark, W. Errington, *Inorg. Chem.*, 5, 650 (1966).

region 4000-500 cm^{-1} of $RuCl_3L_{1.5}$ and the free ligand. The magnetic properties (Table II) of both 1:1.5 complexes reveal the presence of considerable interaction as seen in $RuCl_31.5C_4H_8S_2$.

c) *1:2 Complexes.* The conditions which produced 1:1.5 adducts with DTH and ETH yield a 1:2 adduct with DPTE. The infrared spectrum of the compound is markedly different to the spectra of the free ligand and the 1:1 complex. There is no band at 1208 cm^{-1} indicative of *trans* ligand and the bands which appear at 740 and 480 cm^{-1} in the free ligand are split into triplets. The compound is non conducting in dimethyl formamide. Exchange reactions were attempted with sodium tetraphenyl boron and potassium hexafluoro phosphate but only unchanged starting material was isolated. A possible structure (III)



III

which explains the observations is a chlorine bridged dimer with mono dentate ligand molecules.

The magnetic properties (Table II) show considerable lowering of the moment below the spin only value which is not inconsistent with the proposed structure.

Although a similar 1:2 adduct was not obtained with DTH, by boiling with sodium tetraphenyl boron the solution from which $RuCl_31.5DTH$ had been isolated, a complex having the analysis $[RuCl_22DTH]BPh_4$ was obtained. The infrared shows that the ligand is in the *gauche* chelating form. The infrared spectrum in the region 400-200 cm^{-1} was so poor that it was impossible to determine whether the cation was a *cis* or *trans* species.

This study has shown that the stoichiometry of the product obtained by reacting ruthenium(III) chloride with ligands of the type $RSCH_2CH_2SR$ is dependent on the nature of the alkyl or aryl group which in turn alters the bulk of the ligand and its donor properties.[10,11] Also we obtained no evidence for the reduction of ethanolic ruthenium(III) chloride by thioethers.

Experimental Section

1,2 diphenylthioethane (DPTE) was prepared as previously reported.[12] 1,2 dimethylthioethane (DTH), 1,4 thioxane and 1,2 diethylthioethane (ETH) that were obtained commercially were purified by vacuum distillation. 1,4 dithiane was purified by recrystallisation from benzene. Hydrated ruthenium trichloride was loaned by International Nicked Ltd.

Physical Measurements. I.R. spectra were recorded as mulls on P.E. 457 (4000-250 cm^{-1}) and Grubb Parsons D.M. 4 (400-200 cm^{-1}) spectrophotometers. Magnetic measurements were made using a Newport Instruments variable temperature Gouy balance. Conductance measurements were obtained with a Pye 11700 conductance bridge.

Carbon and hydrogen analyses were obtained in our own microanalytical laboratory. Ruthenium was determined by reducing a weighed sample of the complex to the metal with a hydrogen flame. Many methods were attempted to determine the chloride analyses but none of these methods proved satisfactory for the complexes studied.

Preparations. All the preparations were carried out using an ethanolic ruthenium(III) chloride solution which had been vigorously shaken with mercury to reduce any ruthenium(IV) present, and then filtered.

$RuCl_33C_4H_8OS$. To an ethanolic solution of ruthenium(III) chloride a solution of thioxane in ethanol was added (mole ratio 1:5). The mixture was filtered and the filtrate heated for 30 minutes on a steam bath. On cooling the solution orange needle-shaped crystals separated These were filtered, washed with ethanol and ether and pumped for 24 hours.

Analysis. Found C, 27.7; H, 4.7; Ru, 19.5%. Calcd for $RuCl_33C_4H_8OS$: C, 27.7; H, 4.6, Ru, 19.5 per cent.

The complex was soluble in acetone, nitromethane and methylcyanide. A freshly prepared methyl cyanide solution of $RuCl_33C_4H_8OS$ was non-conducting and had a U.V.-visible spectrum identical with that of the solid complex.

$RuCl_31.5C_4H_8S_2$. An ethanolic solution of ruthenium(III) chloride was added dropwise with stirring to a solution of dithiane in ethanol (mole ratio 1:3).

The red-brown insoluble product that slowly separated was filtered, washed with ethanol and ether and dried in vacuo.

Analysis. Found: C 18.6, H 3.4, Ru 26.6%, $RuCl_3$ 1.5 $C_4H_8S_2$ requires C 18.6, H 3.1, Ru 26.2%. The complex was insoluble in methyl cyanide and nitromethane.

$RuCl_3DPTE$. Ethanolic solutions of ruthenium(III) chloride and 1,2 diphenylthioethane were mixed in the mole ratio 1:3. The solution was left for 12 hours when a deep brown precipitate was formed. The precipitate was filtered washed with ethanol and ether.

Analysis. Found: C, 36.5; H, 3.4; Ru, 22.4%. $RuCl_3DPTE$ requires C, 37.1; H, 3.1; Ru, 22.3%. The complex was fairly soluble and non-conducting in methyl cyanide and nitromethane.

$RuCl_32DPTE$. When the filtrate from the preparation of $RuCl_3DPTE$ was allowed to evaporate a yellow powdery solid slowly separated. This product was filtered, washed with ethanol, Soxhlet extracted with ether and dried in vacuo.

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(10) R.L. Carlie and E. Weissberger, *Inorg. Chem.*, 3, 611 (1964).
(11) C.D. Flint and M. Goodgame, *J. Chem. Soc. (A)*, 2178 (1968).
(12) E.V. Bell and G.M. Bennett, *J. Chem. Soc.*, 3190 (1928).

Analysis. Found: C, 48.7; H, 4.1; Ru, 15.1%. $RuCl_3$2DPTE requires C, 48.0; H, 4.0; Ru, 14.5%. The complex was virtually insoluble in methyl cyanide and a solution in dimethyl formamide was non-conducting.

Reactions of ruthenium(III) chloride with 1,2 dimethylthioethane (DTH) and 1,2 diethylthioethane (ETH). An excess (3:1 mole ratio) of an ethanolic solution of the appropriate ligand was added with stirring to ethanolic solution of ruthenium(III) chloride. With both ligands brown precipitates were formed within five minutes which were filtered, washed with ethanol and ether, and finally dried in vacuo.

Analysis. a) DTH adduct: Found C, 14.7; H, 3.2; Ru, 31.4%. $RuCl_3$DTH requires C, 14.6; H, 3.0; Ru, 30.7%. b) ETH adduct: Found C, 14.3; H, 3.4; Ru, 34.0%. $RuCl_3$0.6ETH requires C, 14.5; H, 2.8; Ru, 34.0%. The ETH adduct may contain excess ligand although the product was washed well and pumped at 10^{-3} mm Hg for 24 hours. The preparation with ETH was repeated a number of times and all the products had the same unusual analysis.

After the above precipitates had been filtered off dark brown solids were slowly precipitated over a period of 48 hours. The complexes were filtered, washed with ethanol and ether and dried in vacuo.

Analysis. a) DTH adduct: Found C, 18.4; H, 3.9; Ru, 25.2%. $RuCl_3$1.5DTH requires C, 18.4; H, 3.9; Ru, 25.8%. b) ETH adduct: Found C, 24.6; H, 4.9; Ru, 23.4%, requires $RuCl_3$1.5ETH C, 24.9; H, 4.9; Ru, 23.4%.

($RuCl_3$2DTH)BPh_4. If the filtrate from the preparation of $RuCl_3$1.5DTH was refluxed with sodium tetraphenyl boron a yellow-green powder slowly precipitated. This product was isolated by filtration and thoroughly washed with water, ethanol and ether. *Analysis.* Found C, 53.8; H, 6.2; Ru, 13.2%. ($RuCl_3$2DTH)BPh_4 requires C, 52.4; H,5.5; Ru, 13.8%.