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# Rhenium. Part XIII. An Oxoisothiocyanato Complex of Quinquevalents Rhenium

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*Oxoisothiocyanato complexes of quinquevalent rhenium of the composition $M_2[ReO(NCS)_5]$ (where M = Cs, Tl and $(CH_3)_4N$) have been prepared by heating $Cs_2[ReOCl_5]$ with potassium thiocyanate solution followed by precipitation with the appropriate cation. The salts are very weakly paramagnetic. The molecular conductance of acetone solution of the caesium salt is in agreement with an 1:2 electrolyte. I.r. spectral studies and X-ray powder pattern indicate that the complexes are isothiocyanato ones (N-bonded) and are polymerised through oxide bridge.*

## Introduction

Studies on the thiocyanato complexes of rhenium are very incomplete. Most of the work is restricted to the reduction products of perrhenate with various reducing agents in the presence of thiocyanate and is mainly of analytical interest. The complexes formed under these conditions are generally not well characterised. Nelson and coworkers [1] have described the magnetic properties of a number of hexathiocyanatorhenates(IV), but have given no method of their preparation or any other properties. In recent years Bailey and Kozak [2] and Cotton and coworkers [3] have reported the preparation and characterisation of a few hexathiocyanatorhenates(IV). Bailey and Kozak [4] have also reported the isolation of $Cs[Re(SCN)_6]$. A binuclear complex of Re(III), *viz.*, $[Re_2(NCS)_8]^2$ [3] is known. There is no report of any well characterised oxothiocyanato complex of rhenium, although oxohalo and oxocyano complexes of quinquevalent rhenium are very well known. We present in this communication the isolation and characterisation of an oxoisothiocyanato complex of quinquevalent rhenium.

## Experimental

Potassium perrhenate used was from Degussa (West Germany). Caesium chloride, potassium thiocyanate, tetramethylammonium chloride and thallium(I) nitrate were E. Merck's guaranteed reagents. Hydriodic acid (55%) was of B.D.H. A.R. quality and was distilled before use [5]. Caesium oxopentachlororhenate(V) was prepared by the method of Fergusson and coworkers [6].

Rhenium was estimated gravimetrically as tetraphenylarsonium perrhenate [7, 8]. For the analysis of sulphur the sample was fused with sodium peroxide and the small amount of nitrate formed was removed by repeated evaporation with hydrochloric acid. Sulphate was then determined gravimetrically as barium sulphate. Caesium was estimated gravimetrically as sulphate, after fuming the compounds with sulphuric acid in a platinum crucible. For the analysis of thallium the sample was decomposed by fuming with sulphuric acid and then thallium(I) was determined gravimetrically as thallium(I) chromate. Nitrogen was estimated by Kjeldahl's method and the result was checked by the conventional microanalytical method.

Conductance and magnetic susceptibility measurements were made by the methods described in our previous communication [9]. Infrared spectra were recorded in Nujol mull and in potassium bromide pellet using a Perkin Elmer spectrophotometer (No. 457). Visible and ultraviolet spectra of aqueous solutions were recorded in the range of 250 to 1200 nm with a Carl Zeiss DMR-21 UV-Vis-IR spectrophotometer. Reflectance spectra were recorded in magnesium oxide in the range of 200 to 1000 nm. The X-ray powder diffraction pattern was obtained with a Philips diffractometer (PW 1061) employing $CuK_\alpha$ radiation.

### *Preparation of the Complexes*

#### *Caesium oxopentaisothiocyanatorhenate(V), $Cs_2[ReO(NCS)_5]$*

0.5 g of $Cs_2[ReOCl_5]$ was added to a solution (5 ml) of potassium thiocyanate (1 g) and the mixture was heated on a water bath for an hour. The resulting

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TABLE I. Analytical Data[a] and Magnetic Moment of the Complexes.

| Complex | % Re | % S | % N | % Cs or Tl | $\mu_{eff}$BM at 30 °C |
|---|---|---|---|---|---|
| $Cs_2[ReO(NCS)_5]$ | 24.37<br>(24.55) | 20.50<br>(21.13) | 9.08<br>(9.23) | 34.53<br>(35.03) | 0.79 |
| $Tl_2[ReO(NCS)_5]$ | 20.80<br>(20.66) | 17.11<br>(17.78) | | 44.40<br>(45.36) | 0.69 |
| $[(CH_3)_4N]_2[ReO(NCS)_5]$ | 29.14<br>(29.07) | 25.00<br>(25.03) | 14.91<br>(15.30) | | 0.68 |

[a] The values in parenthesis are the calculated ones.

blood-red solution was filtered hot and the filtrate was collected in a concentrated solution of caesium chloride (1 g). A sticky mass was obtained on stirring. It was kept for three to four hours and the solid was broken to small particles. The residue was washed three to four times with a few drops of cold water and then with methyl alcohol and finally with ether. The dry mass was extracted with acetone and the filtrate was evaporated to dryness. The yield was 0.35 g.

*Tetramethylammonium oxopentaisothiocyanatorhenate(V), $[(CH_3)_4N]_2[ReO(NCS)_5]$*

0.5 g of $Cs_2[ReOCl_5]$ was heated with a solution of potassium thiocyanate (1 g in 10 ml) as before. The solution was filtered after cooling and a concentrated solution of an excess of tetramethylammonium chloride was added to the filtrate. The precipitate was washed with water and then with ethanol. The yield was 0.33 g.

*Thallium(I) oxopentaisothiocyanatorhenate(V), $Tl_2[ReO(NCS)_5]$*

This was prepared by precipitating a concentrated solution of $Cs_2[ReO(NCS)_5]$ with slight excess of a concentrated solution of thallium(I) nitrate. The precipitate was washed as in the case of the tetramethylammonium salt. The yield was almost quantitative.

All the salts were dried over sulphuric acid. The analytical data of the compounds are given in Table I.

## Results and Discussion

The three salts are deep brown (almost black) in colour. The caesium salt is moderately soluble in water and highly soluble in many organic solvents like methanol, ethanol, acetone, dioxan, nitrobenzene, acetonitrile, dimethyl sulphoxide, *etc.* The thallium(I) and the tetramethylammonium salts are practically insoluble in water and ethanol, but soluble in acetone, acetonitrile, nitrobenzene and dimethyl sulphoxide.

On boiling an alkaline solution of the caesium salt in absence of air Re(V) underwent disproportionation giving perrhenate and a black precipitate of rhenium dioxide. The amounts of rhenium in the filtrate and the residue were in the ratio of 1:2.

The molecular conductance of an $1 \times 10^{-3}$ *M* aqueous solution of the caesium salt was 360 $ohm^{-1}$ $mol^{-1}$ $cm^2$ at 25 °C which indicates that the complex ion is considerably dissociated. The molecular conductance of an acetone solution ($1 \times 10^{-3}$ *M*) of the complex was, however, 185 $ohm^{-1}$ $mol^{-1}$ $cm^2$, which is in agreement with an 1:2 electrolyte.

All the three salts are very weakly paramagnetic (Table I) which agrees with the similar properties of Re(V) oxo complexes [9–11].

In the infrared spectra of the complexes the thiocyanate C–N stretching frequency was observed as a very strong band at about 2050 $cm^{-1}$ (Table II). Its position and rather broad nature are characteristic [12, 13] of isothiocyanates (M–NCS). The precise location of the C–S band in the spectra of the complexes is difficult due to their presumably polymeric nature involving oxo bridge (*vide infra*). The rhenium–oxygen vibrational band in oxo bridged complexes is likely to appear between 900–700 $cm^{-1}$. From the positions of $\nu$(C–N) and $\delta$(N–C–S) in the spectra of $[(C_6H_5)_4As]_2[Re(NCS)_6]$ and $[(C_4H_9)_4N]_2[Re(NCS)_6]$ Cotton and coworkers [3] concluded that the complexes have Re–N bonding. They, however, have not observed with certainty the C–S vibrations because of cation absorption in this range. Bailey and Kozak [4] who observed the C–S stretch in $Cs_2[Re(NCS)_6]$ and $Cs[Re(NCS)_6]$ at about 700 $cm^{-1}$, also favour N-coordination in view of the high value of the integrated intensity of the cyanide bond [14]. It has been pointed out that for diagnostic purposes the C–S frequency is less reliable than the C–N frequency, because of the weak or medium intensity of the band and the appearance of bands due to many other ligands in the same region [15].

A very intriguing feature in the i.r. spectra of the caesium and the thallium salts is the weak intensity of the bands assignable to Re=O vibrations. Several

TABLE II. I. R. Spectral Bands ($\nu$, cm$^{-1}$) of the Complexes.

| Complex | Medium | $\nu$(C≡N) | $\nu$(Re=O) | $\nu$(C–S) and $\delta$(Re–O–Re) | Other Bands |
|---|---|---|---|---|---|
| $Cs_2[ReO(NCS)_5]$ | KBr | 2050vs | 960w, 910w | 840w, 730m | 600w, 560w, 460w |
| | Nujol | 2055vs | 960w, 910w | 835w, 720m | 600w, 560w, 460w |
| $[(CH_3)_4N]_2[ReO(NCS)_5]$ | Nujol | 2050vs | 970sh, 940s (overlapped with cation band)<br>900w | 840w, 740m | 2300w, 1270w, 560w, 470m, 410m |
| $Tl_2[ReO(NCS)_5]$ | KBr | 2060vs | 960w, 915w | 840w, 730w | 610w, 560w, 480w |

medium to weak intensity bands appear in the spectra between 1000 to 700 cm$^{-1}$ (Table II). The positions of the bands lying in the ranges of 1000 to 900 and 900 to 700 cm$^{-1}$ indicate that the complexes contain both terminal and bridged Re=O grouping. The assignment of $\nu$(Re=O) in the spectrum of the tetramethylammonium salt is difficult due to cation absorption in this range. It is believed that the complexes are polymerised. The caesium salt gave a very simple X-ray powder diffraction pattern with only one line ($d$ = 3.00 Å).

The reflectance spectrum of the caesium salt gave a group of bands around 17,000 cm$^{-1}$ (18,000 sh, 16,700 and 15,600 sh) and a very broad band around 11,800 cm$^{-1}$. These are attributed to charge transfer and ligand field transitions, respectively. The electronic spectrum of the aqueous solution was, however, different and gave two very intense charge transfer bands at 31,200 ($\epsilon = 9.8 \times 10^3$) and 23,000 ($\epsilon = 1.3 \times 10^4$) cm$^{-1}$. This difference may be due to the breaking up of the polymeric complex in solution.

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