

## Preparation of Oxopentachloro-, Oxopentathiocyanato- & Oxochlorotetra-thiocyanato-rhenates(V) from $H_2ReOCl_5$ in Non-aqueous Medium

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A new method, which does not involve special handling techniques, is reported for the preparation of oxorhenium(V) complexes. A ketonic extract of  $H_2ReOCl_5$  is prepared by shaking  $KReO_4$  and hydroquinone in conc. HCl with methyl ethyl ketone and saturated magnesium chloride solution. Salts of the ions  $[ReOCl_5]^{2-}$ ,  $[ReO(NCS)_4(SCN)]^{2-}$  and  $[ReOCl(NCS)_4]^{2-}$  have been prepared starting from  $H_2ReOCl_5$ . These have been characterised on the basis of their chemical analyses and physical data.

Although oxopentachlororhenates(V) have been prepared by a variety of methods<sup>1-5</sup>, many of the reported methods are not satisfactory due to impure nature of the product obtained and low yields. Very few thiocyanato and mixed ligand thiocyanato complexes of monooxorhenium(V) are known<sup>6-8</sup>. Almost all of the mixed ligand thiocyanato complexes contain two  $Ph_3P$  moieties and one (OH) or (OEt) or Cl besides two (NCS) groups because of their synthesis from a corresponding complex by exchange.

We report in this note the preparation and characterisation of some monooxorhenates(V) from a non-aqueous solution of  $H_2ReOCl_5$  obtained by hydroquinone reduction of perrhenate in hydrochloric acid.

### (a) Preparation of ketonic extract of $H_2ReOCl_5$

Potassium perrhenate (0.450 g) in conc. HCl (15 ml) was reduced by hydroquinone (0.171 g) to oxopentachlororhenate(V). After mixing with saturated magnesium chloride solution (42 ml), the complex ion was extracted into methyl ethyl ketone (48 ml).

### (b) Transfer of $H_2ReOCl_5$ from ketone to acetic acid

The ketonic extract was mixed well immediately with acetic acid (10 ml) and acetic anhydride (9 ml) under cooling, set aside for 30 min and shaken well with petroleum ether (50 ml). Taking the lower layer, this step was repeated with 50 ml petroleum ether. The yellow viscous layer obtained was a concentrate of  $H_2ReOCl_5$ .

### (c) Preparation of $H_2ReO(NCS)_5$

Ketonic extract of  $H_2ReOCl_5$  was prepared as in (a) above, taking  $KReO_4$  (0.300 g) and hydroquinone (0.114 g). To the ketonic extract a solution of KSCN (0.704 g) in acetone (7 ml) was added. The green solution was filtered off and kept over molecular sieves for 20 hr. The upper layer was separated, filtered and the solution was reduced in volume by evaporation to about 5 ml.

### Preparation of $Rb_2ReOCl_5$

The  $H_2ReOCl_5$  concentrate prepared as in (b) above, was dissolved in acetic acid-HCl (30 ml) and acetic anhydride (3 ml). To this was added rubidium chloride (0.460 g) refluxed 2 hr in acetic acid (24 ml) and acetic anhydride (2 ml). Yellow precipitate of  $Rb_2ReOCl_5$  was formed. The precipitate was washed with acetic acid, then with petroleum ether and dried *in vacuo* for 6 hr over sodium hydroxide, yield 75%.

Other oxopentachlororhenates(V) were similarly prepared from the  $H_2ReOCl_5$  concentrate.

### Preparation of $(Ph_4As)_2ReO(NCS)_4(SCN)$

To the concentrate obtained as in (c) above,  $Ph_4AsCl$  (0.900 g) dissolved in acetic acid (30 ml) was added. Orange-yellow precipitate was formed immediately. It was filtered, washed with acetic acid, petroleum ether and recrystallised from dichloromethane, yield 75%.

Tetraphenylphosphonium and tetraethylammonium salts were also prepared similarly (yield, 80%).

### Preparation of $(Ph_4As)_2ReOCl(NCS)_4$

The green solution prepared as in (c) above from  $KReO_4$  (0.300 g) and hydroquinone (0.120 g), was mixed with acidified saturated magnesium chloride solution and shaken with methyl ethyl ketone. The ketone extract was evaporated to about 5 ml. The orange-red concentrate was diluted with acetic acid (30 ml) and mixed with  $Ph_4AsCl$  (1.0 g) in acetic acid (10 ml). A dirty orange-red precipitate was formed, filtered, washed with acetic acid, then with petroleum ether, and recrystallized from dichloromethane, yield 80%.

Cetylpyridinium salt was also prepared similarly, but it was recrystallised from acetone in which it is more soluble than in dichloromethane, yield 75%.

Spectra were recorded on Beckman DU-2, Beckman IR-20 and Brucker IFS 113 spectrophotometers. Magnetic susceptibilities were determined by the Gouy method, and conductivities were measured on a Philips

bridge PR 9500/90. TGA scans were made with a Stanton Redcroft TG-750 instrument. After peroxide decomposition, rhenium<sup>9</sup> was determined as  $\text{Ph}_4\text{AsReO}_4$ , chloride<sup>10a</sup> as  $\text{AgCl}$  and sulphur<sup>10b</sup> as  $\text{BaSO}_4$ .

KSCN (BDH, AR),  $\text{Ph}_4\text{AsCl}$  (Fluka, p.a.) cetylpyridinium chloride (CpCl) (SISCO) were dried over  $\text{P}_2\text{O}_5$  *in vacuo*. Petroleum ether (60-80°C), other solvents and chemicals were of high purity and were dried thoroughly. Acetic acid-HCl was prepared by passing HCl gas to saturation into acetic acid.

Oxochlorotetraisothiocyanatorhenates(V) are soluble in acetone, dichloromethane and nitromethane. The chemical analyses and other physical data are presented in Table 1. The magnetic moments of the complexes are within the expected range for Re(V) complexes. The molar conductances of oxopentathiocyanato- and oxochlorotetraisothiocyanato-rhenates(V) in nitromethane support their formulations as 2:1 electrolytes<sup>11</sup>.

The present methods give high yields of the already known<sup>3,8</sup> oxopentachlororhenates(V) and oxopentathiocyanato-rhenates(V). Their identities have been confirmed by their IR and electronic spectra.

Oxochlorotetraisothiocyanatorhenates(V) have been prepared for the first time by the method given above. Their IR spectra show the presence of  $\nu(\text{Re}=\text{O})$  band and the  $\nu(\text{CN})$  band of isothiocyanate<sup>12</sup>. The far IR spectrum of the cetylpyridinium salt shows  $\nu(\text{ReN})$  at  $297\text{ cm}^{-1}$ . Two bands obtained at  $320$  and  $222\text{ cm}^{-1}$  are probably due to  $\nu(\text{ReCl})$  and  $\delta(\text{ReCl})$  modes respectively<sup>12</sup>. These data support the formulation of these compounds as oxochlorotetraisothiocyanatorhenates(V).

The electronic spectra of oxochlorotetraisothiocyanatorhenates(V) are similar to that of oxopentathiocyanatorhenate(V).

The TGA scan of the cetylpyridinium salt is shown in Fig. 1. The mass losses correspond to a two-step

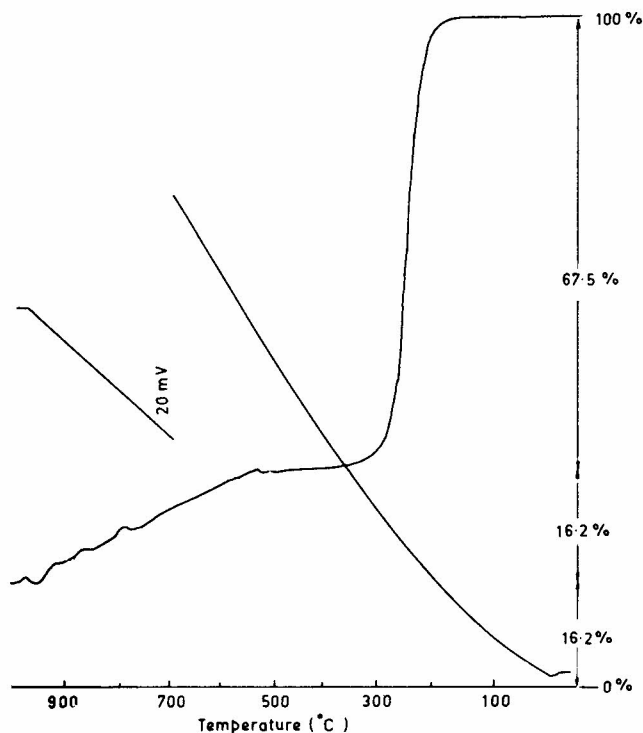
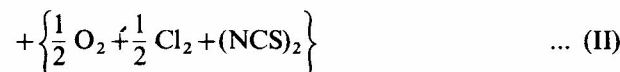
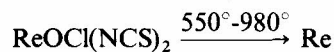


Fig. 1—TG curve of  $(\text{Cp})_2[\text{ReOCl}(\text{NCS})_4]$

decomposition to rhenium,



The calculated losses are 67.2% for the step I and 15.6% for the step II. These accord well with the values of 67.5 and 16.2% actually found. The rhenium residue is 16.2% against the calculated 17.3%. These data further confirm the stoichiometry of cetylpyridinium

Table 1—Analytical, Spectral and Magnetic Data of Oxorhenates(V)

Compound (Colour)	Found (Calc.), %			$\lambda_{\text{max}}$ (nm)	$\Lambda_M^\dagger$	IR ( $\text{cm}^{-1}$ )		$\mu_{\text{eff}}^\ddagger$ (B.M.)
	Re	S	N			$\nu(\text{ReO})$	$\nu(\text{CN})$	
$\text{Rb}_2\text{ReOCl}_5$ (Yellow)	32.30* (33.78)	—	—	415, 482, 800, 1110 (in conc. HCl)	—	950	—	0.96
$(\text{Ph}_4\text{As})_2\text{ReO}(\text{NCS})_4(\text{SCN})$ (Orange-red)	14.00 (14.80)	11.72 (12.74)	5.80 (5.56)	310, 370, 920 (in $\text{CH}_2\text{Cl}_2$ )	145	960 945	2100 2040 2010	0.50
$(\text{Ph}_4\text{As})_2\text{ReOCl}(\text{NCS})_4$ (Dirty orange-yellow)	14.60 (15.06)	10.35 (10.40)	4.85 (4.53)	370, 880 (in $\text{CH}_2\text{Cl}_2$ )	142	948	2040	0.73
$(\text{Cp})_2\text{ReOCl}(\text{NCS})_4$ (Yellow)	16.79 (17.27)	11.52 (11.88)	7.60 (7.79)	370, 910 (in acetone)	141	948	2040 2010	0.54

\*Satisfactory analysis for Cl was also obtained.

†in nitromethane, ‡at room temperature.

salt. Also,  $\text{ReOCl}(\text{NCS})_2$  would be a new compound if confirmed by product analysis. As it exhibits stability over a wide temperature range, it can be easily prepared by heating the cetylpyridinium salt.

The present methods start from perrhenate and do not require special handling techniques. They can be extended to the synthesis of various oxorhenium(V) complexes.

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