

Synthesis of Oxopentathiocyanato- rhenate(V) from Oxopentachloro- rhenate(VI) & Its Characterisation

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Orange-red or brown compounds, $A_2[ReVO(NCS)_4(SCN)]$ ($A = Ph_4As, Ph_4P$ and Et_4N), have been obtained by reacting $AReOCl_5$ in dichloromethane with $KSCN$ in acetic acid. The compounds have been characterised on the basis of chemical analysis, spectral, magnetic moment and conductivity studies.

Very few thiocyanato complexes of $Re(V)$ have been reported¹⁻⁶, e.g. $[Pt(NH_3)_4]_3 [ReO_2(SCN)_4]_2$, $ReO(SCN)_3L_2$, $ReO(NCS)_2L'L_2$, (Na, NH_4, Ph_4As) $ReO_2(NCS)_2L_2$ ($L = PPh_3, L' = OH, OEt, Cl$), (Cs, Tl, Ag) $Re(NCS)_6$, $(Et_4N)_2 ReOCl_2(NCS)_3$. Salts of $ReO(NCS)_5^{2-}$ reported earlier⁵ have been subsequently found to be contaminated⁷. Among the oxo-rhenium compounds, only $(Ph_4As)_2 ReO(NCS)_5$ has been prepared recently by reducing $KReO_4$ in aqueous solution with $SnCl_2$ in presence of thiocyanate, but the other method employed (ligand exchange in acetonitrile) gives poor yields⁷.

Hence, there is a great need for better synthetic method for preparing different salts of oxopentathiocyanatorhenates(V). We report here the synthesis of $A_2ReVO(NCS)_5^{\dagger}$ ($A = Ph_4As, Ph_4P$ and Et_4N) in good yield from $AReOCl_5$ in non-aqueous medium.

$KReO_4$ (J.M.) was dried at 120°C. $KSCN$ (BDH, AR), Ph_4AsCl , Ph_4PCl and Et_4NCl (Fluka) were dried over P_2O_5 *in vacuo*. All the solvents and other chemicals were thoroughly dried by suitable methods. All experiments were carried out in a glove box under oxygen-free dry nitrogen.

The oxopentachlororhenate(VI) salts $[AReOCl_5]$ ($A = Ph_4As, Ph_4P$ and Et_4N) were prepared by the method already reported⁸.

$A_2ReO(NCS)_5$ — The $AReOCl_5$ salts were prepared from $KReO_4$ (0.5, 0.6 and 1.0 g for $A = Ph_4As, Ph_4P$ and Et_4N respectively), and dissolved in dichloromethane (12 ml). To this was added a solution of potassium thiocyanate (1.0, 1.1 and 1.7 g for $A = Ph_4As, Ph_4P$ and Et_4N respectively) in a mixture of acetic acid (28 ml) and acetic anhydride (2 ml). A yellow precipitate was immediately obtained. This was filtered off on a sintered bed (G-4) and washed several

times with acetic acid. It was then extracted with dichloromethane (12 ml) when $A = Ph_4As$ and Ph_4P and with acetone (15 ml) when $A = Et_4N$; any insoluble part was filtered off. On evaporation of the yellow solution, orange-red crystalline solids were obtained for $A = Ph_4As, Ph_4P$ but brown for $A = Et_4N$, in 50% yield.

The Ph_4P^+ and Ph_4As^+ salts were obtained as yellow powders on precipitation and as tiny orange-red crystals on slow evaporation from solution. On grinding, the crystals of all the three salts turned orange-yellow. The salts do not melt below 230°C and are soluble in dichloromethane, acetone and nitromethane but are insoluble in water, acetic acid and ether.

After alkaline peroxide fusion of the sample, rhenium was determined as $(Ph_4As)ReO_4^{\ddagger}$ and sulphur as $BaSO_4^{10}$. Nitrogen was estimated microanalytically.

The UV and visible spectra of solutions were recorded on a Beckman DU-2 spectrophotometer using 1 cm silica cells. Infrared spectra were recorded in the region 4000-400 cm^{-1} with a Beckman IR-20 in nujol and up to 100 cm^{-1} with Brucker IFS 113 as polyethylene discs. Magnetic susceptibilities were determined by the Gouy method, packing the tubes under dry nitrogen in a glove box. Molar conductances were measured with a Philips bridge PR9500/90 using a dip type micro cell having a cell constant of 0.14 cm^{-1} .

Addition of thiocyanate to $Ph_4AsReOCl_5$ in dichloromethane gave an impure yellow precipitate of the thiocyanate complex¹¹. The present method enables preparation of Ph_4As^+ , Ph_4P^+ and Et_4N^+ salts of oxopentathiocyanatorhenate(V) in a very pure form. Their molar conductances [$150-180 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$] in nitromethane support their formulations as 2:1 electrolytes¹². Their chemical analyses and other physical data are presented in Table 1. Their colours are different from the yellow and green

Table 1 — Analytical and Magnetic Data of Oxopentathiocyanatorhenate(V) Complexes

Compound (Colour)	Found (Calc.), %			μ_{eff} (B.M.)
	Re	S	N	
$(Ph_4As)_2ReO(\overline{NCS})_5$ (Orange-red)	14.06 (14.80)	11.88 (12.74)	5.82 (5.56)	0.75
$(Ph_4P)_2ReO(NCS)_5$ (Orange-red)	14.84 (15.90)	12.83 (13.67)	5.80 (5.98)	0.28
$(Et_4N)_2ReO(\overline{NCS})_5$ (Brown)	24.03 (24.74)	20.04 (21.30)	13.07 (13.02)	0.48

[†] NCS includes thiocyanato groups bonding through N and S.

reported for the isopentathiocyanates⁷. The magnetic moments of the present complexes (0.28-0.75 B.M.) are within the expected range for oxopentachlororhenates(V) but different from those (1.2-2.8 B.M.) reported by other workers^{5,7} for the salts of $\text{ReO}(\text{NCS})_5^{2-}$ ion.

The electronic spectra of the present complexes show three bands in dichloromethane at 32258, 27000, 10869 cm^{-1} ($\text{A} = \text{Ph}_4\text{As}$); 32258, 27397, 10869 cm^{-1} ($\text{A} = \text{Ph}_4\text{P}$); and 31746, 27397, 11111 cm^{-1} ($\text{A} = \text{Et}_4\text{N}$) respectively. The spectra of the $\text{ReO}(\overline{\text{NCS}})_5^{2-}$ salts are very similar to that¹³ of ReOCl_5^{2-} but a single band at 10869 cm^{-1} appears at the mean position of the two lower energy bands of the latter ion. The ϵ value of this band (127.7) is of the right order for a ligand field type of transition and its shift is consistent with the higher position of $-\text{NCS}$ compared to that of Cl^- in the spectrochemical series. The ϵ values of the other two bands (1.22×10^4 and 2.39×10^4) indicate their charge-transfer nature.

The IR spectra of $\text{A}_2\text{ReO}(\overline{\text{NCS}})_5$ show a strong sharp band at 960 cm^{-1} (950 cm^{-1} when $\text{A} = \text{Ph}_4\text{P}$) characteristic of terminal¹³ $\text{Re}=\text{O}$. The weak νCS and δNCS modes are obscured by cation bands. In the νCN region, there are three bands at 2100, 2040 and 2010 cm^{-1} which are also shown in nitromethane solution indicating absence of solid state effects. The νCN at 2100 cm^{-1} , which is very sharp, is characteristic of S-bonded thiocyanates¹⁴ and is 20 cm^{-1} higher than the highest (2080 cm^{-1}) reported so far for N-bonded non-bridging thiocyanato groups in rhenium complexes¹⁵. The other two are broader and in the right region for N-bonded thiocyanato groups, which for known hexathiocyanatorhenium complexes is 2022-2086 cm^{-1} (refs. 3, 16, 17). The bridged thiocyanato $\text{Re}(\text{III})$ complexes^{18,19} show νCN at 2110 or 2120 cm^{-1} , well above 2100 cm^{-1} (ref. 15), hence the $\overline{\text{NCS}}$ groups in the present complexes are non-bridging. Accordingly, these complexes are monooxopentathiocyanatorhenates(V) with both $-\text{NCS}$ and $-\text{SCN}$ groups. N-bonding is further confirmed by the presence of νReN^{20} at 295 cm^{-1} . Only Ph_4P^+ salt could be got analysed by far IR. This shows a band at 179 cm^{-1} assignable to νReS confirming the presence of S-bonding monodentate thiocyanate²¹. This should not be surprising as rhenium is on the border line of metals forming S-bonded thiocyanato complexes. Further, the

electronic effects of an almost triple bond²² between rhenium and the terminal oxide, make the *trans* position soft²³ and favourable to S-bonding with thiocyanate. The four *cis* positions are expected to show the same bonding behaviour and, in view of νCN at 2040 and 2010 cm^{-1} , all the positions should be taken as occupied by N-bonding thiocyanate. Thus, the physicochemical data support the formulation of present complexes as $\text{A}_2[\text{ReO}(\text{NCS})_4(\text{SCN})]$.

This seems to be the first instance of a monooxopentathiocyanatorhenate(V) complex containing both N- and S-bonding thiocyanates.

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References

- 1 Ryabchikov D I & Nazerenko I I, *Zh neorg Khim*, **7** (1962) 931.
- 2 Fergusson J E, *Coord chem Rev*, **1** (1966) 459.
- 3 Bailey R A & Kozak S L, *Inorg Chem*, **6** (1967) 2155.
- 4 Freni M, Guisto D & Romiti P, *Gazz chim ital*, **99** (1969) 641.
- 5 Chakravarti M C & Das C K, *Inorg chim Acta*, **27** (1978) 249.
- 6 Bol'shakov A M, Glushkova M A & Busalaev Yu A, *Koord Khim*, **4**(7) (1978) 1075.
- 7 Davison A, Jones A G, Muller L, Tatz R & Trop H S, *Inorg Chem*, **20** (1981) 1160.
- 8 Yatirajam V & Harjinder Singh, *J inorg nucl Chem*, **37** (1976) 2006.
- 9 Willard H H & Smith G M, *Ind Engng Chem Anal Edn*, **11** (1939) 305.
- 10 Vogel A I, *A text-book of quantitative inorganic analysis* (Longman, New York), 1975, 554.
- 11 Harjinder Singh, *Chemistry of rhenium*, Ph D Thesis, Kurukshetra University, 1976.
- 12 Geary W J, *Coord chem Rev*, **7** (1971) 81.
- 13 Grove D E & Wilkinson G, *J chem Soc A*, (1966) 1224.
- 14 Sabatini A & Bertini I, *Inorg Chem*, **4** (1965) 1665, 959.
- 15 Nakamoto K, *Infrared and Raman spectra of inorganic and coordination compounds* (John Wiley, New York), 1977, 270.
- 16 Bailey R A & Kozak S L, *Inorg Chem*, **6** (1967) 419.
- 17 Bailey R A, Michelsen T W & Mills W N, *J inorg nucl Chem*, **33** (1971) 3206.
- 18 Nimry T & Walton R A, *Inorg Chem*, **16** (1977) 2829.
- 19 Cotton F A & Robinson W R, Walton R A & Whyman R, *Inorg Chem*, **6** (1967) 929.
- 20 Ferraro J R, *Low frequency vibrations of inorganic and coordination compounds* (Plenum Press, New York), 1971, 227.
- 21 Ferraro J R, *Low frequency vibrations of inorganic and coordination compounds* (Plenum Press, New York), 1971, 249.
- 22 Cotton F A, *Advanced inorganic chemistry* (Wiley Eastern, New Delhi), 1972, 975.
- 23 Emeleus H J & Sharpe A G, *Adv Inorg Chem & Radiochem*, **17** (1975) 262.