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Rhenium.
Part XX. Synthesis and Characterisation of Oxopentakis(isothiocyanato)rhenate(V)

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Abstract

Caesium, tetramethylammonium and a few other salts of $[ReO(NCS)_5]^{2-}$ have been prepared by the electrolytic reduction of ReO_4^- in the presence of SCN^- and H_2SO_4, or by dissolving freshly precipitated ReO_2 in 30% HSCN, or boiling $[ReO_2en_2]Cl$ with 30% HSCN. The complexes are very weakly paramagnetic (μ_{eff} = 0.4 to 0.8 BM at 298 K). The conductivities in acetone are in agreement with those expected for 1:2 type electrolytes. Infrared spectra of the salts give strong Re=O bands and very strong C–N bands at about 930 and 2050 cm^{-1} respectively. The electronic spectra are solvent-dependent and clearly distinguishable from those of $[Re(NCS)_6]^{2-}$. Boiling of $(LH)_2[ReO(NCS)_5]$ in water gave the non-electrolytic complexes $[ReO(NCS)_3L]$ (L = 1,10-phenanthroline and 2,2′-bipyridine).

Introduction

Among the few isothiocyanato complexes of rhenium reported to date, the species $[Re(NCS)_6]^{2-}$ is firmly established [1–5]. Isolation of salts of a few other ions, viz. $[Re_2(NCS)_8]^{2-}$, $[Re(NCS)_6]^-$, $[Re_2(NCS)_{12}]^{4-}$ and $[Re_2(NCS)_{10}]^{3-}$ has been reported recently [3–6]. Only very few oxoisothiocyanato complexes of Re(V) can be claimed to have been established beyond doubt. The existence of the product formulated as $[Pt(NH_3)_4][ReO_2(NCS)_4]$ [7, 8] is doubtful. Only a few mixed ligand oxoisothiocyanato complexes, viz. $[ReO(NCS)_3(Ph_3P)_2]$ and $[ReO(OEt)py_2(NCS)_2]$ have been reported [9, 10]. On the other hand, oxohalo complexes of Re(V) of the types $[ReOX_3L_2]$ and $[ReO(OEt)X_2L_2]$ are abundant [11]. In the same way, while complexes of the type $[ReOX_5]^{2-}$ (X = Cl, or Br) have been studied [11] extensively, only two papers on the analogous isothiocyanato complex have appeared recently. We first synthesised $Cs_2[ReO(NCS)_5]$ and other salts from the reaction of $Cs_2[ReOCl_5]$ and KSCN in hot water [12]. More recently, Davison and coworkers [13] have synthesised the Ph_4As^+ and $(n\text{-}Bu_4N)^+$ salts of $[ReO(NCS)_5]^{2-}$ by ligand substitution of $[ReOCl_5]^{2-}$ or $[ReOBr_4{\cdot}CH_3CN]^-$ by SCN^- in acetonitrile, and by the reduction of ReO_4^- (with $SnCl_2$ or electrolytically) in the presence of HCl and SCN^-. Depending on the method of crystallisation the authors have obtained two crystalline forms of $(Ph_4As)_2[ReO(NCS)_5]$ which gave similar electronic spectra and almost similar IR spectra. The tetrabutylammonium salt, however, gave only one form. The two forms of the tetraphenylarsonium salts differ remarkably in their magnetic property. While the yellow–orange form has been stated to have μ_{eff} = 2.0–2.8 BM, the yellow–green form has μ_{eff} = 1.2–2.0 BM at 298 K. The magnetic moment of the other salt has not been reported. No reason has been given for the large difference in the magnetic moments. In fact the large range of μ_{eff} for a crystalline salt at the same temperature is surprising. In acetonitrile medium the two forms are diamagnetic. Oxorhenium(V) complexes are by and large diamagnetic or very weakly paramagnetic [11]. The various samples of $[ReOCl_5]^{2-}$ and $[ReOBr_5]^{2-}$ were at one time reported to have μ_{eff} ranging from 0.8 to 2.8 BM depending on the method of preparation [11]. This has been ascribed to the presence of $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$ in the samples and pure $Cs_2[ReOCl_5]$ has been shown [14] to have μ_{eff} = 0.41 BM at room temperature. More recently, an orange–red compound formulated as $(Ph_4As)_2[ReO(NCS)_4(SCN)]$ has been reported by Yatirajam and Kantam [15, 16]. The electronic spectra of the complex do not agree fully with those reported for $[ReO(NCS)_5]^{2-}$ and no convincing proof has been put forward in favour of both N- and S-coordination of SCN^-. In view of this, we have undertaken a detailed study of the oxopentakis(isothiocyanato) complex.

Experimental

Potassisum perrhenate used was supplied by Johnson Matthey & Co. Ltd. Other chemicals were B.D.H. or E. Merck's Analar or G.R. quality. Solvents

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were dried before use. $[ReO_2en_2]Cl$ and $K_2[ReCl_6]$ were prepared by the literature methods [17, 18]. Thiocyanic acid was prepared [19] from $Ba(NCS)_2 \cdot 3H_2O$ and H_2SO_4. The methods of analysis of rhenium anc caesium were the same as described earlier [12, 20]. Nitrogen was determined by the standard microchemical method. Sulphur was determined gravimetrically as $BaSO_4$ after decomposing the complexes with HNO_3 [21].

Infrared spectra were recorded in the range 4000–250 cm^{-1} using a Perkin-Elmer (Model 577) grating spectrophotometer. Electronic spectra were obtained with a Cary 17D spectrophotometer. Magnetic susceptibility measurements were made with a Gouy balance using $Hg[Co(NCS)_4]$ as calibrant. Diamagnetic corrections were taken from a standard source [22].

Syntheses

$M_2[ReO(NCS)_5]$ where $M^+ = Cs^+, Me_4N^+$, $phenH^+$ and $bipyH^+$ (Method A)

$KReO_4$ (0.3 g) was dissolved in hot water (10 ml) in a 50 ml beaker and then 0.8 g NaNCS was added. Dilute H_2SO_4 was added to make the acidity 0.5 M. Then a rubber stopper carrying two platinum electrodes and gas input/exit tubes was fitted in the mouth of the beaker. Electrolysis of the solution was carried out at about 60 °C in N_2 atmosphere for 1 h applying 10 V which gave 1.0 amp current. After cooling, the dark brown solution was filtered free from the small amount of residue. The concentrated aqueous solutions of CsCl, $(CH_3)_4NCl$, 2,2'-bipyridine or 1,10-phenanthroline (the latter two were dissolved in 2 M acetic acid) were added. The products were separated by filtration and washed with water and diethyl ether. The yields were about 20% for the caesium salt and 40% for the rest.

$M_2[ReO(NCS)_5]$ where $M^+ = Cs^+$ and Me_4N^+ (Method B)

Hydrated ReO_2 was prepared by the hydrolysis of $K_2[ReCl_6]$ (0.8 g) in alkaline medium. The precipitate was thoroughly washed and then 3 ml of HSCN (30%) was added to it. The precipitate readily dissolved to give a dark brown solution. A concentrated solution of CsCl or $(CH_3)_4NCl$ was added and the precipitates were filtered and washed with water and diethyl ether. The yields were about 25% for the caesium salt and 40% for the other.

$M_2[ReO(NCS)_5]$ where $M^+ = Cs^+$ and Me_4N^+ (Method C)

$[ReO_2en_2]Cl$ (0.4 g) was mixed with 4 ml of 30% HSCN and heated under reflux for 4 h. After cooling, the dark brown solution was filtered and precipitated with a concentrated solution of CsCl or $(CH_3)_4NCl$. The salts were washed with water and diethyl ether. The yields were about 25% and 45% respectively.

$[ReO(NCS)_3L]$ where L = 1,10-phenanthroline and 2,2'-bipyridine

A suspension of 0.3 g of $(phenH)_2[ReO(NCS)_5]$ or $(bipyH)_2[ReO(NCS)_5]$ in water was boiled for half an hour until the issuing vapour was neutral to litmus. The residues were filtered and washed several times with water and 2–3 times with ethanol. The yields were about 90%.

Results and Discussion

All the complexes are deep brown to black. The caesium salt is moderately soluble in water, while the other salts are sparingly soluble in water. All the salts are highly soluble in acetone and acetonitrile and sparingly soluble in ethanol and methanol. The complexes of the type $[ReO(NCS)_3L]$ where L = 1,10-phenanthroline and 2,2'-bipyridine are insoluble in water, ethanol and methanol, but soluble in acetone and acetonitrile.

All the complexes of the types $[ReO(NCS)_5]^{2-}$ and $[ReO(NCS)_3L]$ prepared by us are very weakly paramagnetic (μ_{eff} = 0.4 to 0.8 BM at 298 K) (Table 1) which is in agreement with the magnetic property of other oxorhenium(V) complexes [11].

The molecular conductances of acetone solutions (1×10^{-3} M) of the caesium and tetramethylammonium salts of $[ReO(NCS)_5]^{2-}$ are 210 and 212 $ohm^{-1}\ cm^2\ mol^{-1}$ respectively (Table 1) which are in agreement with those expected for a 1:2 type electrolyte [23]. The very low molecular conductances of $[ReO(NCS)_3(phen)]$ and $[ReO(NCS)_3(bipy)]$ in acetone indicate that they are non-electrolytes.

The IR spectra of all the salts of $[ReO(NCS)_5]^{2-}$ are characterised by strong Re=O bands at about 930 cm^{-1}. Very strong thiocyanato C–N stretching frequencies occurred at about 2050 cm^{-1} (Table 2) indicating that the complexes are isothiocyanato ones. Although rather broad, the cyanide band in the solid state spectra showed distinct splitting. In acetonitrile medium however, the bands were sharp and split into three components. The spectra of the complexes $[ReO(NCS)_3L]$ also gave strong Re=O bands at about 920 cm^{-1} and very strong and broad CN bands at about 2040 cm^{-1}.

The electronic spectra of the salts of $[ReO(NCS)_5]^{2-}$ are solvent dependent (Table 3) which may be due to interaction with the solvent. Two to three intense charge transfer bands are present in the region of 33000 to 22000 cm^{-1}. The spectra of $Cs_2[ReO(NCS)_5]$ in acetonitrile give three intense bands at 235000, 27400 and 32700 cm^{-1}. The tetrabutylammonium and the tetraphenylarsonium

TABLE 1. Analytical data, magnetic moments and molecular conductances of the complexes

Complex	Found(calc.) (%)				μ_{eff} (BM) at 298 K	Molecular conductance (ohm^{-1} cm^2 mol^{-1})
	Re	S	N	Cs		
$Cs_2[ReO(NCS)_5]$	24.0 (24.5)	21.3 (21.1)	9.2 (9.2)	34.9 (35.1)	0.78	210
$(Me_4N)_2[ReO(NCS)_5]$	28.8 (29.0)	24.9 (25.0)	15.2 (15.3)		0.56	212
$(phenH)_2]ReO(NCS)_5]$	21.6 (21.7)	18.6 (18.7)	14.7 (14.7)		0.75	
$(bipyH)_2[ReO(NCS)_5]$	23.0 (23.1)	19.7 (19.8)	15.7 (15.6)		0.59	
$[ReO(NCS)_3(phen)]$	33.1 (33.4)	16.9 (17.2)	12.5 (12.6)		0.43	13
$[ReO(NCS)_3(bipy)]$	34.7 (34.9)	18.0 (18.0)	13.2 (13.1)		0.40	12

TABLE 2. IR spectral bands (ν, cm^{-1}) of the complexes

Complex	Medium	ν(C–N)	ν(Re=O)	ν(C–S)	δ(NCS)
$Cs_2[ReO(NCS)_5]$	KBr	2135vs, 2020vs	930s	700m	490w
	CH_3CN	2090vs, 2070vs, 2040m			
$(Me_4N)_2[ReO(NCS)_5]$	KBr	2100vs, 2060vs, 2000vs	940s[a]		480w
	CH_3CN	2060vs, 2000vs, 1990m			
$(phenH)_2[ReO(NCS)_5]$	CsI	2040vs, 2000vs	910s	700m	470w
$(bipyH)_2[ReO(NCS)_5]$	CsI	2040vs, 2000vs	940s, 920s	720w	470w
$[ReO(NCS)_3(phen)]$	KBr	2040vs, 2000vs	920s, 900sh		
$[ReO(NCS)_3(bipy)]$	KBr	2040vs, 2020sh	920sh, 910s		

[a] Overlapped with cation band.

TABLE 3. Electronic spectral data

Complex	Medium	λ_{max} (cm^{-1})
$Cs_2[ReO(NCS)_5]$	water	30700, 23200
	ethanol	32700, 28100, 23200
	acetone	29400, 22700
	acetronitrile	32700, 27400, 23500
$(Me_4N)_2[ReO(NCS)_5]$	water	30700, 23200
	ethanol	32800, 28100, 23200
	acetone	29400, 22800
$(phenH)_2[ReO(NCS)_5]$	ethanol	32700, 28200, 23200
	acetone	29400, 22700
$Cs_2[Re(NCS)_6]$	ethanol	38300, 23800[a, b]
	acetone	23700[a]
	acetonitrile	37700, 23800[a]

[a] Ref. 5. [b] Ref. 2.

salts (both forms) reported by Davison and coworkers [13] gave bands at 27 400 and 32 700 cm^{-1} in acetonitrile. They have not reported the spectra in any other solvent. On the other hand, the spectra reported by us [12] earlier for $Cs_2[ReO(NCS)_5]$ in water agree with the spectra of the caesium salt reported in this communication. The spectral band positions of $Cs_2[Re(NCS)_6]$ are also recorded in Table 3 for comparison. It is evident that the spectra of the two complexes $[ReO(NCS)_5]^{2-}$ and $[Re(NCS)_6]^{2-}$ are different. Although both give an intense band at about 23 000 cm^{-1} there is a recognisable difference in the position.

Conclusions

The magnetic moment and the IR spectra of our complex $[ReO(NCS)_5]^{2-}$ agree nicely with the expected ones. The electronic spectra are also clearly distinguishable from those of $[Re(NCS)_6]^{2-}$. The salts prepared by the three different methods gave identical spectra and magnetic moments. Method C used for the preparation of $[ReO(NCS)_5]^{2-}$ involves a reaction which is similar to the reaction of [Re-

O_2en_2]Cl with boiling 5 M HCl [24, 25]. The formation of the non-electrolytes $[ReO(NCS)_3L]$ from $(LH)_2[ReO(NCS)_5]$ almost quantitatively can also be explained as

$$(LH)_2[ReO(NCS)_5] \longrightarrow [ReO(NCS)_3L] + L + 2HSCN$$

Judging from the above it is concluded that the salts prepared by us are pure oxopentakis(isothiocyanato)rhenates(V).

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