Compounds of Rhenium(vi)

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Three rhenium(vi) compounds have been prepared and characterised. The reactions of $ReOCl_4$ with acetonitrile and with anhydrous liquid ammonia give respectively $ReOCl_4$, MeCN, and oxygen-bridged polymeric $[ReO(NH_2)_4]_n$. The reaction between $[PPh_4]^+Br^-$ and $ReOBr_4$ in anhydrous chloroform gives $[PPh_4]^+[ReOBr_5]^-$.

Knowledge of the chemistry of rhenium(vi) is not extensive. The existence of the hexachloride[1] was doubtful until very recently, although the oxide tetrachlorides, $ReOX_4$ (X = F, Cl, and Br)[2] are well known. The oxopentahalogeno-anions, $[ReOX_5]^-$ (X = F[3] and Cl[4]) have been characterised, but the only published report[5] of a neutral halogeno-complex of rhenium(vi), $ReOCl_4$,$OPCl_3$, is also very recent. Both rhenium oxide tetrachloride and its adduct with $POCl_3$ are reduced by pyridine and by 2,2′-bipyridyl with the formation of oxotrichlororhenium(v) complexes.

We report here the isolation and characterisation of three further compounds of rhenium(vi), namely $ReOCl_4$,MeCN, $[ReO(NH_2)_4]_n$, and $[Ph_4P]^+[ReOBr_5]^-$.

EXPERIMENTAL

Since all the compounds were sensitive to moisture reactions and manipulations were carried out in a vacuum system. The preparation of samples for physical measurements was undertaken in a dry-box. I.r. spectra were measured on Perkin-Elmer 237 and Unicam SP 100 spectrophotometers. Visible spectra were recorded on a Unicam SP 700C spectrophotometer fitted with a reflectance attachment. A Gouy balance was used for room-temperature magnetic measurements. Conductance measurements at 25° were made using a Wayne-Kerr Autobalance bridge and a dip-type cell with platinum electrodes. *X*-Ray powder photographs were obtained using a Debye-Scherrer focussing camera of 11·46 cm. diam. using nickel-filtered Cu-K_α radiation (λ = 1·5418 Å).

Rhenium oxide tetrachloride was prepared as previously described[6] and the oxide tetrabromide by a method to be published. Acetonitrile and chloroform were dried by repeated distillation *in vacuo* from fresh phosphorus pentoxide, and ammonia was similarly dried with sodium.

Rhenium was determined gravimetrically as tetraphenylarsonium perrhenate, halogen gravimetrically as silver halide, and nitrogen by the Kjeldahl procedure.

Oxotetrachloro(acetonitrile)rhenium(vi).—An excess of anhydrous acetonitrile (10 ml) was distilled onto $ReOCl_4$ (1 g). An orange-brown solution and solid formed. After 1 h the excess of acetonitrile was distilled off. The solid remaining was pumped for 1 h at room temperature and then removed to a dry-box under nitrogen (Found: Cl, 36·6; Re, 47·8. $C_2H_3Cl_4NORe$ requires Cl, 36·8; Re, 48·4%).

Reaction of $ReOCl_4$ *with Liquid Ammonia*.—Anhydrous ammonia (30 ml) was distilled onto $ReOCl_4$ (1 g) and allowed to warm to its boiling point. A dark brown solution formed and subsequent filtration revealed a dark brown solid. The ammonia was condensed back onto the solid, allowed to warm to its boiling point, and the solution filtered again. Nine such washes were carried out by which time the filtrate was colourless. The ammonia was then evaporated from the combined filtrates to leave a heterogeneous brown solid. Both the ammonia-soluble and -insoluble products were pumped at room temperature for several hours before analysis. The ratio of ammonia-insoluble to -soluble material could be increased by using larger volumes of liquid ammonia [Found (for the ammonia-insoluble product): Cl, 0·0; N, 21·5; Re, 69·5. H_8N_4ORe requires Cl, 0·0; N, 21·0; Re, 70·0%. Found (for the ammonia-soluble product): Cl, 43·5; N, 24·7; Re, 30·0%].

Tetraphenylphosphonium Oxopentabromorhenate(vi).—Solutions of $ReOBr_4$ (1 g) dissolved in anhydrous chloroform (15 ml), and $[PPh_4]^+Br^-$ dried at 100° *in vacuo* and then dissolved in anhydrous chloroform were mixed, to yield a maroon precipitate. This was filtered off, washed with chloroform, and dried *in vacuo* (Found: C, 30·1; H, 2·3; Br, 42·6; Re, 19·6. $C_{24}H_{20}Br_5OPRe$ requires C, 30·6; H, 2·25; Br, 42·4; Re, 19·8%).

RESULTS AND DISCUSSION

The reaction between rhenium oxide tetrachloride and acetonitrile at room temperature leads to the

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[5] A. Guest and C. J. L. Lock, *Canad. J. Chem.*, 1971, **49**, 603.

[6] D. A. Edwards and A. A. Woolf, *J. Chem. Soc.* (*A*), 1966, 91.

adduct $ReOCl_4$,MeCN. The halogeno-anions $[ReOX_4L]^-$ ($X = Cl$ and Br, $L = H_2O$ and MeCN) have C_{4v} local symmetry.[7] The oxygen atom is *trans* to the ligand, which is bonded weakly to the metal. $ReOCl_4$,MeCN presumably has a similar structure, and indeed the acetonitrile may be removed by heating the complex at 100° *in vacuo*.

The i.r. spectrum of a Nujol mull of the complex (Table) shows a band at 1000 cm.$^{-1}$ attributable to ν(Re=O), with ν(C≡N) at 2295 cm.$^{-1}$ indicating the presence of σ-bonded nitrile. The visible reflectance spectrum of the adduct is reminiscent of that of $[Ph_4As]^+[ReOCl_5]^-$. By analogy with the assignment [4] of the visible spectrum of the latter, the band at 12,500 cm.$^{-1}$ may be of *d–d* origin, the further bands being due to halogen → metal charge-transfer. The magnetic moment at room temperature is similar to those of $ReOCl_4$,[5] $ReOCl_4$,$OPCl_3$,[5] and $[Ph_4As]^+[ReOCl_5]^-$.[4] The approach of this value to that expected for a spin-only d^1 system is presumably due to reduction of the free-ion spin-orbit coupling constant on complex formation and to the lack of degeneracy of the $^2T_{2g}$ ground term in the non-octahedral environment.

Physical data

Compound	ν(ReO) (cm.$^{-1}$)	μ (B.M.) at 295 K	Λ_M (Ω^{-1} cm^2) (10^{-3}M soln.) Nitromethane	Reflectance spectra (10^3 cm.$^{-1}$)
$ReOCl_4$	1033s, 1016s [a]	1·7 [b]		12·3v,br, 18·1, 23·9
$ReOCl_4$,MeCN	1000s	1·67		12·5, 17·9, 22·7
$[ReO(NH_2)_4]_n$	830s,br	*c*	Insoluble	*d*
$[AsPh_4]^+[ReOCl_5]^-$ [a]	968s	1·65	78	11·8v,br, 18·1, 23·0
$[PPh_4]^+[ReOBr_5]^-$	950s	1·50	66	11·2br, 16·1, 20·0

[a] Ref. 4. [b] Ref. 5. [c] $10^6\chi'_m = 20$ c.g.s.u. [d] Highly absorbing throughout visible region.

Tetraphenylphosphonium oxopentabromorhenate(VI) is formed from the reaction between the oxide tetrabromide and tetraphenylphosphonium bromide in chloroform. The molar conductivity of the salt in nitromethane (Table), is indicative of a uni-univalent electrolyte and the room-temperature magnetic moment is again of the order expected for a d^1 C_{4v} complex with strong metal–oxygen multiple bonding. The visible reflectance spectrum is closely similar to that of the $ReOCl_5^-$ anion,[4] so the band at 11,200 cm.$^{-1}$ probably relates to a *d–d* transition, the two bands of higher wavenumber probably being halogen → metal rather than oxygen → metal charge-transfer transitions on the basis of the frequency shifts when compared to the analogous bands of $ReOCl_5^-$.

The reaction between anhydrous liquid ammonia and rhenium oxide tetrachloride at —33° leads to scission of all the rhenium–chlorine bonds of the oxohalide, leaving $[ReO(NH_2)_4]_n$ as an ammonia-insoluble product. This product is insoluble in organic solvents such as benzene, iso-octane, acetonitrile, ethanol, and nitromethane. However, a considerable portion of the total rhenium used is found in the ammonia-soluble product, suggesting that partial breakdown of the $[ReO(NH_2)_4]_n$ occurs, to give an ammonia-soluble complex anion in the presence of the ammonium chloride formed by solvolysis *i.e.*

$$n\,ReOCl_4 + 8n\,NH_3 \longrightarrow [ReO(NH_2)_4]_n + 4n\,NH_4Cl$$
$$[ReO(NH_2)_4]_n + n\,NH_4Cl \longrightarrow n[NH_4]^+[ReO(NH_2)_4Cl]^-$$

The formation of anionic species to account for the solubility of ammoniolysis products of metal halides on the addition of ammonium salts and their subsequent instability on evaporation of the ammonia, is well documented.[8] Such anion formation will also account for the observation that the ratio of insoluble to soluble material is increased when larger volumes of ammonia are used. The formation of complex ammonio-acids will be favoured by a high concentration of ammonium chloride arising from ammoniolysis. Indeed, with our experimental conditions most of the ammonium chloride is removed in the first filtration so breakdown of the ammoniolysis product will be incomplete.

The i.r. spectrum of the ammonia-insoluble product shows bands attributable to co-ordinated amido-groups (*ca.* 3100s,br; 1605m; 1050s,br cm.$^{-1}$), but no band which could be assigned to a terminal rhenium–oxygen stretching mode was evident. However, a strong, very broad, band centred at 830 cm.$^{-1}$ points to the presence of a $\cdots ReOReO \cdots$ chain system. For comparison the antisymmetric Re–O–Re stretching frequencies of several rhenium-(IV) and -(V) complexes are found in the 700—860 cm.$^{-1}$ range.[9] The products of the ammoniolysis of $MoOCl_4$ and $WOCl_4$ also have strong, very broad bands in this region of the infrared,[10,11] which have been similarly assigned. Two weak bands at 480 and 500 cm.$^{-1}$ may be Re–N stretching frequencies, the corresponding frequencies for $[ReO_2(NH_3)_4]^+$ appearing [9] at 510 and 443 cm.$^{-1}$. $[ReO(NH_2)_4]_n$ shows (Table) only very weak paramagnetism and must be magnetically concentrated with spin–spin coupling occurring through the proposed rhenium–oxygen chain system. Rhenium(VI) oxide shows similar magnetic behaviour,[12] as does the ammoniolysis product of

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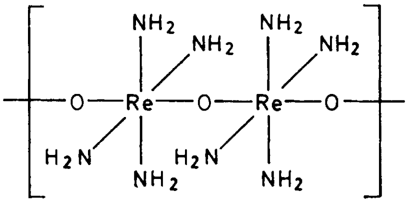
molybdenum(V) oxide tribromide, $[MoOBr(NH_2)_2]_n$,[13] also a d^1 system. A proposed structure, such as (I),



(I)

or a related structure with *cis*-oxygen atoms, is an idealised formulation, since although the i.r. spectrum appears to exclude formulations such as $[ReO(=NH)(NH_2)_2(NH_3)]_n$ or $[ReO(=NH)_2(NH_3)_2]_n$, the polymeric chain terminator may well be a co-ordinated ammonia molecule.

The i.r. spectrum of the ammonia-soluble portion is very similar to that of the insoluble product with the addition of characteristic ammonium ion absorptions (1710 and 1405 cm.$^{-1}$). The presence of ammonium chloride was established by *X*-ray powder photography, $[ReO(NH_2)_4]_n$ apparently being amorphous to *X*-rays. Examination of the analytical figures shows that if all the rhenium is assumed to be present as $[ReO(NH_2)_4]_n$, the proportion of remaining nitrogen and chlorine is close to 1 : 1, as expected if ammonium chloride is the only other product.

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