

### 580. *Some Observations on the Chemistry of Rhenium in Thionyl Chloride.*

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The action of thionyl chloride on rhenium heptoxide and ammonium per-rhenate produces the sulphuryl chloride complexes,  $(\text{ReO}_3\text{Cl})_2, \text{SO}_2\text{Cl}_2$  and  $(\text{NH}_4)_2\text{ReO}_2\text{Cl}_4, \text{SO}_2\text{Cl}_2$ , respectively. A simple method is reported for preparing rhenium oxytetrachloride,  $\text{ReOCl}_4$ , from which the double chlorides  $(\text{Me}_4\text{N})_2\text{ReCl}_6$  and  $(\text{Et}_4\text{N})_2\text{ReCl}_6$  are easily obtained.

THIONYL chloride has frequently been employed as a chlorinating<sup>1-3</sup> or dehydrating<sup>4,5</sup> agent in the preparation of anhydrous metal chlorides and oxide chlorides. The chlorinations have generally involved reactions between metal oxides and gaseous thionyl chloride, usually in sealed systems. Recent investigations,<sup>6,7</sup> however, have indicated that low-temperature reactions with metal hydroxides are quite feasible; thus the pentachlorides of niobium, tantalum, and protactinium, and rhenium tetrachloride, have been prepared in this manner. Since only three halides or oxide halides of hexavalent and septavalent rhenium are at present known, rhenium hexachloride<sup>8</sup> ( $\text{ReCl}_6$ ), rhenium oxytetrachloride<sup>9</sup> ( $\text{ReOCl}_4$ ), and per-rhenyl chloride<sup>10</sup> ( $\text{ReO}_3\text{Cl}$ ), we have investigated the action of thionyl chloride on rhenium trioxide and heptoxide. No double chlorides of rhenium(VII) are known, and only one<sup>11</sup> ( $\text{K}_2\text{ReOCl}_6$ ) has been claimed for rhenium(VI). We have now examined the reaction between ammonium per-rhenate and thionyl chloride and attempted the preparation of rhenium(VI) double chlorides starting with rhenium oxytetrachloride in thionyl chloride. Other work<sup>6,12,13</sup> has shown that it is possible to obtain salts of the type  $\text{M}^{\text{I}}\text{N}^{\text{V}}\text{Cl}_6$  ( $\text{M}^{\text{I}} = \text{Cs}^+, \text{NH}_4^+, \text{Me}_4\text{N}^+, \text{Et}_4\text{N}^+, \text{and Ph}_4\text{As}^+$ ;  $\text{N}^{\text{V}} = \text{Nb, Ta, W, Pa, and U}$ ) from thionyl chloride solutions, and Adams *et al.*<sup>13</sup> have isolated tetraethylammonium hexachlororhenate(IV) from aqueous solution starting with potassium hexachlororhenate(IV),  $\text{K}_2\text{ReCl}_6$ .

Although rhenium trioxide is inert towards thionyl chloride, either in the cold or under reflux, the heptoxide dissolves readily at room temperature to produce a clear under solution which rapidly darkens and finally turns red. A golden-brown complex of per-rhenyl chloride with sulphuryl chloride,  $(\text{ReO}_3\text{Cl})_2, \text{SO}_2\text{Cl}_2$ , is gradually deposited during the first few hours but on prolonged contact with thionyl chloride this rhenium(VII) complex redissolves, apparently with reduction to rhenium(VI). The per-rhenyl chloride-sulphuryl chloride complex was never obtained in more than 40% yield, the amount isolated varying with the initial time of contact with thionyl chloride.

The complex crystallises as microscopic red needles on sublimation at  $150^\circ$  *in vacuo*; the last traces of impurity are readily removed at lower temperatures during this operation. Hydrolysis with water or aqueous potassium hydroxide gives colourless solutions of per-rhenate without precipitation of rhenium dioxide, indicating the presence of only septavalent rhenium in the complex. Despite the unusual colour for a rhenium(VII) compound, other investigations confirm the results of the hydrolysis; thus, colourless

<sup>1</sup> Gutmann, *Quart. Rev.*, 1956, **10**, 451.

<sup>2</sup> Hecht, Jander, and Schlappmann, *Z. anorg. Chem.*, 1947, **254**, 255.

<sup>3</sup> Bradley, Chakravarti, and Chatterjee, *J. Inorg. Nuclear Chem.*, 1957, **3**, 367.

<sup>4</sup> Hecht, *Z. anorg. Chem.*, 1947, **254**, 37.

<sup>5</sup> Freeman and Smith, *J. Inorg. Nuclear Chem.*, 1958, **7**, 244.

<sup>6</sup> Bagnall and Brown, *J.*, following Paper.

<sup>7</sup> Brown and Colton, *Nature*, 1963, **198**, 1300; *J.*, 1964, 714.

<sup>8</sup> Colton, *Nature*, 1962, **194**, 374.

<sup>9</sup> Woolf, *Quart. Rev.*, 1961, **15**, 372.

<sup>10</sup> Wulf and Clifford, *J. Amer. Chem. Soc.*, 1957, **79**, 4257.

<sup>11</sup> Brukl and Ziegler, *Ber.*, 1932, **65**, 916.

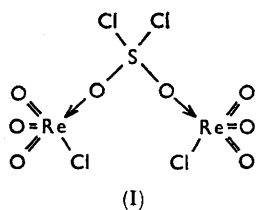
<sup>12</sup> Bagnall, Brown, and du Preez, *J.*, 1964, 2603.

<sup>13</sup> Adams, Chatt, Davidson, and Gerratt, *J.*, 1963, 2189.

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solutions are obtained in acetone, methyl cyanide, and nitromethane, boiling ceric sulphate solution is unaffected, and magnetic susceptibility measurements show the complex to be essentially diamagnetic ( $\chi_m \sim 70 \times 10^{-6}$  c.g.s. units).

The presence of sulphuryl chloride rather than the expected thionyl chloride in the complex is indicated by its behaviour on hydrolysis and by its infrared spectrum. Barium sulphate is precipitated directly from the acidified solutions obtained on hydrolysis, indicating the presence of sulphuryl chloride, since thionyl chloride on hydrolysis would produce sulphite which requires oxidation (*e.g.*, by bromine water) before precipitation occurs with barium in acid media. The infrared spectrum shows no absorption around  $1230 \text{ cm}^{-1}$  where the S=O stretching vibration occurs in thionyl chloride,<sup>14</sup> but there is a



very broad intense band with indications of peaks at  $1157$ ,  $1117$ , and  $1080 \text{ cm}^{-1}$  (the sulphur–oxygen stretching vibration occurs at  $1182 \text{ cm}^{-1}$  in sulphuryl chloride<sup>14</sup>), and the presence of such a band is characteristic of the bridging sulphato-group.<sup>15</sup> Peaks at  $983$ ,  $963$ , and  $948 \text{ cm}^{-1}$  can be assigned to the Re=O stretching frequencies with possibly some contribution from S–O vibrations. (Re=O vibrations in per-rhenyl chloride<sup>16</sup> occur at  $1001$  and  $960 \text{ cm}^{-1}$ .)

As there is no indication of vibrations arising from oxygen bridges between rhenium atoms, expected around  $770 \text{ cm}^{-1}$ , it appears reasonable to formulate the per-rhenyl chloride–sulphuryl chloride complex as (I).

On vacuum evaporation of the thionyl chloride supernatant, or of the final solution after redissolution of the per-rhenyl chloride–sulphuryl chloride complex, the dark red, low melting, rhenium oxytetrachloride,  $\text{ReOCl}_4$ , is obtained, but repeated vacuum sublimation of this compound is necessary to remove all traces of thionyl chloride. Clearly, the observed colour changes (green to red) are an indication of the reduction of rhenium(VII) to rhenium(VI) with accompanying formation of sulphuryl chloride. The rhenium–oxygen vibrations in the infrared spectrum are observed at  $1028$  and  $1017 \text{ cm}^{-1}$ .

No attempt has been made to confirm the work of Brukl and Ziegler<sup>11</sup> but the possibility of preparing double chlorides of rhenium oxytetrachloride from thionyl chloride solution has been explored. The addition of tetraethyl- or tetramethyl-ammonium chloride to solutions of the oxytetrachloride causes no immediately apparent reaction, but on standing for several days the dark red solutions slowly deposit large pale green and buff crystals, respectively, and in the presence of excess alkylammonium chloride the solutions finally become colourless. The crystalline products are tetraethylammonium and tetramethylammonium hexachlororhenate(IV),  $(\text{Et}_4\text{N})_2\text{ReCl}_6$  and  $(\text{Me}_4\text{N})_2\text{ReCl}_6$ , respectively, and, since rhenium oxytetrachloride is indefinitely stable in thionyl chloride, the reduction of rhenium(VI) to rhenium(IV) must be due to impurities in the alkylammonium chlorides or to some decomposition product formed by its reaction with the thionyl chloride. A similar reduction of tungsten hexachloride has also been observed.<sup>12,13</sup> The salts are only slightly soluble in cold water but are hydrolysed readily by aqueous potassium hydroxide, giving rhenium dioxide. The infrared spectra show only those peaks due to the vibrations of the alkylammonium cations. Magnetic susceptibility measurements between  $94$  and  $305^\circ\text{K}$  (Table 1) indicate the presence of three unpaired electrons; both compounds obey the Curie–Weiss law very closely over the whole temperature range, with small Weiss constants,  $\theta = -1$  and  $-20^\circ$  for the tetraethyl and tetramethyl salts, respectively. The calculated moments,  $3.62$  and  $3.66 \text{ B.M.}$ , are close to the spin-only value of  $3.87 \text{ B.M.}$  and agree with the values previously reported for hexachlororhenate(IV) compounds.<sup>13,17,18</sup> X-Ray powder diffraction patterns for the

<sup>14</sup> Nakamoto, "Infra-red Spectra of Inorganic Co-ordination Compounds," Wiley, New York, 1963.

<sup>15</sup> Nakamoto, Fujita, Tanaka, and Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.

<sup>16</sup> Miller and Carlson, *Spectrochim. Acta*, 1960, **16**, 1148.

<sup>17</sup> Figgis, Lewis, Nyholm, and Peacock, *Discuss. Faraday Soc.*, 1958, **26**, 103.

<sup>18</sup> Nelson, Boyd, and Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 348.

TABLE 1.

Magnetic susceptibility data ( $\chi_m \times 10^6$  in c.g.s. units; temp. in  $^\circ\text{K}$ ).

$(\text{Me}_4\text{N})_2\text{ReCl}_6$ .....	294 $^\circ$	249 $^\circ$	229 $^\circ$	194 $^\circ$	178 $^\circ$	155 $^\circ$	118 $^\circ$	96	80
	5402	6193	6728	7779	8270	9208	11,492	13,240	14,712
$(\text{Et}_4\text{N})_2\text{ReCl}_6$ .....	305 $^\circ$	265 $^\circ$	232 $^\circ$	196 $^\circ$	155 $^\circ$	118 $^\circ$	101 $^\circ$	94 $^\circ$	
	5407	6107	7008	8374	10,238	13,795	15,871	17,241	
$(\text{NH}_4)_2\text{ReO}_2\text{Cl}_4 \cdot \text{SO}_2\text{Cl}_2$ .....	296 $^\circ$	259 $^\circ$	243 $^\circ$	224 $^\circ$	193 $^\circ$	170 $^\circ$	128 $^\circ$	113 $^\circ$	98
	934	1034	1050	1092	1167	1258	1424	1499	1565

TABLE 2.

X-Ray diffraction data.

$(\text{Me}_4\text{N})_2\text{ReCl}_6$				$(\text{Et}_4\text{N})_2\text{ReCl}_6$			
$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	$h, k, l$	$I$ (obs.)	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	$h, k, l$	$I$ (obs.)
0.0110	0.0110	1, 1, 1	100	0.0092	0.0092	1, 1, 1	100
0.0146	0.0146	2, 0, 0	80	0.0115	0.0115	0, 2, 0	30
0.0292	0.0292	2, 2, 0	90	0.0119	0.0120	2, 0, 0	30
0.0403	0.0402	3, 1, 1	90	0.0132	0.0130	0, 0, 2	10
0.0585	0.0585	4, 0, 0	70	0.0235	0.0236	2, 2, 0	50
0.0691	0.0694	3, 3, 1	30	0.0250	0.0250	2, 0, 2	60
0.0732	0.0731	4, 2, 0	70	0.0324	0.0322	1, 3, 1	60
0.0878	0.0877	4, 2, 2	30	0.0329	0.0333	3, 1, 1	30
0.0988	0.0987	{ 5, 1, 1 3, 3, 3	70	0.0363	0.0365	2, 2, 2	30
0.1171	0.1169	4, 4, 0	50	0.0461	0.0461	0, 4, 0	10
0.1280	0.1279	5, 3, 1	60	0.0484	0.0482	4, 0, 0	10
0.1318	0.1315	{ 4, 4, 2 6, 0, 0	50	0.0547	0.0550	0, 3, 3	5
0.1462	0.1462	6, 2, 0	40	0.0581	0.0581	2, 4, 0	5
0.1572	0.1571	5, 3, 3	5	0.0598	0.0597	4, 2, 0	10
0.1609	0.1608	6, 2, 2	10	0.0610	0.0611	4, 0, 2	10
0.1749	0.1753	4, 4, 4	5	0.0726	0.0726	4, 2, 2	5
0.1862	0.1863	{ 5, 5, 1 7, 1, 1	20	0.0787	0.0786	5, 0, 1	20
0.1899	0.1900	6, 4, 0	10	0.0813	0.1814	5, 1, 1	20
0.2045	0.2045	6, 4, 2	30	0.0939	0.0942	4, 4, 0	5
0.2152	0.2156	{ 5, 5, 3 7, 3, 1	30	0.1038	0.1036	0, 6, 0	10
0.2483	0.2483	8, 2, 0	5				
0.2632	0.2630	8, 2, 2	5				

compounds indicate that the tetramethylammonium compound is face-centred cubic ( $a_0 = 12.74 \pm 0.01 \text{ \AA}$ ) and the tetraethylammonium salt is orthorhombic ( $a_0 = 14.04$ ,  $b_0 = 14.35$ ,  $c_0 = 13.51 \pm 0.01 \text{ \AA}$ ) like the uranium(IV) analogues,<sup>19</sup> the space groups being  $O_h^5Fm3m$  and  $Fmmm$ , respectively. Observed and calculated  $\sin^2\theta$  values together with visually estimated intensities are provided in Table 2. The tetraethylammonium compound gives poor powder patterns but the similarity to those of the uranium(IV) analogue is sufficiently pronounced to permit them to be indexed satisfactorily.

The reaction between ammonium per-rhenate and thionyl chloride proceeds only slowly at room temperature, again with reduction to rhenium(VI), the final product being the ammonium di-oxy-tetrachlororhenate(VI)-sulphuryl chloride complex,  $(\text{NH}_4)_2\text{ReO}_2\text{Cl}_4 \cdot \text{SO}_2\text{Cl}_2$ . The dark red, crystalline complex is sensitive to moisture, the alkaline hydrolysis proceeding as expected for a rhenium(VI) compound, *i.e.*,  $3\text{Re(VI)} \rightarrow \text{Re(IV)} + 2\text{Re(VII)}$ , and barium sulphate is precipitated from the acidified supernatant on the addition of barium chloride. The infrared spectrum shows the rhenium-oxygen vibration at  $997 \text{ cm}^{-1}$ , with a shoulder at  $960 \text{ cm}^{-1}$ , and a broad band at  $1040 \text{ cm}^{-1}$  which we assigned to the sulphur-oxygen stretching frequency. This is a negative shift of  $142 \text{ cm}^{-1}$  indicating co-ordination through oxygen, but the splitting to be expected on co-ordination of sulphuryl chloride was not observed. There may also be some contribution from sulphur-oxygen vibrations around  $960 \text{ cm}^{-1}$ . Magnetic susceptibility

<sup>19</sup> Staritzky and Singer, *Acta Cryst.*, 1952, 5, 536.

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measurements show Curie–Weiss dependence between 98 and 300°K, with a rather large Weiss constant,  $\theta$ , of  $-184^\circ$ , so that the calculated moment of 2.03 B.M. is probably of little significance. This value is higher than the spin-only moment for a  $d^1$  system (1.73 B.M.) but is close to those reported for rhenium hexachloride<sup>7</sup> (2.07 B.M.) and the octacyanorhenates(vi)<sup>20</sup> (2.0 B.M.).

## EXPERIMENTAL

Reactions were carried out in the open laboratory since thionyl chloride afforded protection from atmospheric moisture. After isolation, however, the moisture-sensitive sulphuryl chloride complexes and rhenium oxytetrachloride were handled in a dry-box, in which samples were prepared for magnetic susceptibility, infrared, and X-ray diffraction studies.

*Per-rhenyl Chloride–Sulphuryl Chloride Complex.*—Commercial rhenium heptoxide (3 g.) was finely ground and dissolved in the minimum volume of thionyl chloride (~3 ml.) at room temperature. The initially green solution rapidly darkened and overnight produced a brown deposit, which, on further standing, redissolved. The brown deposit was isolated by centrifugation, washed with carbon tetrachloride containing 2% (v/v) of thionyl chloride and vacuum-dried at 90°, and the product further purified by vacuum-sublimation at ~150° [Found: Re, 55.2; Cl, 21.45; S, 4.6. (ReO<sub>3</sub>Cl)<sub>2</sub>.SO<sub>2</sub>Cl<sub>2</sub> requires Re, 55.2; Cl, 21.05; S, 4.7%].

*Rhenium Oxytetrachloride.*—The supernatant thionyl chloride from the above reaction was slowly evaporated under a vacuum, and the dark red-brown residue purified by repeated sublimations at about 50° (Found: Re, 53.8; Cl, 40.8. Calc. for ReOCl<sub>4</sub>: Re, 54.1; Cl, 41.2%). A trace (<1%) of sulphur was usually detected in the final product.

*Ammonium Di-oxy-tetrachlororhenate(vi)–Sulphuryl Chloride Complex.*—Finely-ground, oven-dried ammonium per-rhenate was treated with an excess of thionyl chloride at room temperature, the mixture being allowed to stand in a stoppered vessel for several days, with repeated grinding of the dark red crystals which formed in order to ensure complete reaction. The product was washed with thionyl chloride several times and vacuum-dried at room temperature [Found: Re, 35.2; Cl, 40.3; N, 5.25; S, 6.1. (NH<sub>4</sub>)<sub>2</sub>ReO<sub>2</sub>Cl<sub>4</sub>.SO<sub>2</sub>Cl<sub>2</sub> requires Re, 35.05; Cl, 40.05; N, 5.25; S, 6.05%].

*Tetraethylammonium and Tetramethylammonium Hexachlororhenate(iv).*—Solutions of alkyl-ammonium chloride and rhenium oxytetrachloride in thionyl chloride were mixed and allowed to stand for several days in a stoppered vessel. The crystals, which formed slowly with accompanying decoloration of the dark red solution, were washed with cold thionyl chloride and vacuum-dried at room temperature [Found: Re, 28.1; Cl, 32.15. (Et<sub>4</sub>N)<sub>2</sub>ReCl<sub>6</sub> requires Re, 28.25; Cl, 32.25%] [Found: Re, 34.0; Cl, 38.75. (Me<sub>4</sub>N)<sub>2</sub>ReCl<sub>6</sub> requires Re, 34.05; Cl, 38.9%].

*Analysis.*—Rhenium was estimated colorimetrically with furil  $\alpha$ -dioxime<sup>21</sup> after alkaline hydrolysis of the complexes, chlorine potentiometrically against silver nitrate solution, and nitrogen by the Kjeldahl method.<sup>22a</sup> Sulphur was weighed, after hydrolysis of the complex, as barium sulphate.<sup>22b</sup>

*Physical Measurements.*—Magnetic susceptibilities were measured by the Gouy Method over the temperature range 80–300°K, on a balance constructed by one of us<sup>23</sup> and described elsewhere.<sup>7</sup> Previously calibrated tubes were packed in a dry atmosphere and sealed with Polythene bungs to exclude atmospheric moisture during measurements. Infrared spectral samples were mounted as Nujol mulls between silver chloride plates, and spectra were recorded with a Hilger H800 spectrometer in the range 2–15  $\mu$ . X-Ray diffraction powder photographs were obtained with Debye–Scherrer and Guinier focusing cameras with filtered Cu  $K_\alpha$  radiation ( $\lambda = 1.54051 \text{ \AA}$ ).

We are indebted to Professor J. Lewis (Manchester University) for discussion of the infrared data, and Mr. P. J. Jones for nitrogen analyses.

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<sup>20</sup> Colton, Peacock, and Wilkinson, *Nature*, 1958, **182**, 393; *J.*, 1960, 1374.

<sup>21</sup> Meloche, Martin, and Webb, *Analyt. Chem.*, 1957, **29**, 527.

<sup>22</sup> Vogel, "A Text-book of Quantitative Inorganic Analysis," Longmans, London, 2nd edn., 1951, (a) p. 248; (b) p. 401.

<sup>23</sup> Colton, AERE Report R-4186 (1962).