The Preparation of the $ReCl_6^-$ Ion

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Summary The ion $ReCl_6^-$ has been prepared in the compound $[PCl_4][ReCl_6]$ obtained by the reaction of PCl_5 and $ReCl_5$.

ALTHOUGH the ion ReF_6^- is known, as are the ions WCl_6^- and $MoCl_6^-$,[1] there has been no report of the $ReCl_6^-$ ion. Attempts to prepare the $ReCl_6^-$ ion by treating $ReCl_5$ with alkali-metal halide salts have been unsuccessful, yielding instead $ReCl_6^{2-}$.[1]

Machmer[2] has reported that the reaction of rhenium metal and phosphorus pentachloride in a sealed tube at 500° yielded $ReCl_5,PCl_3$. We have shown that if the reaction was carried out with an excess of chlorine present a different compound was obtained which we have shown by analysis to be $RePCl_{10}$. The same compound was synthesised by direct interaction of $ReCl_5$ and PCl_5 at 300° in a sealed tube. The compound was easily purified. Excess of phosphorus chlorides was removed by pumping at room temperature, and $RePCl_{10}$ was sublimed slowly *in vacuo* at 150°. Thus, $RePCl_{10}$ is much more stable than the $ReCl_5$–$SbCl_5$ reaction product which under similar conditions yielded $ReCl_4$.[3]

Despite the volatility of $RePCl_{10}$, spectroscopic studies suggest that the compound is ionised in the solid state as $[PCl_4^+][ReCl_6^-]$. The i.r. spectrum is summarised (Table), with data for Cs_2ReCl_6. The strong peak at 649 cm^{-1} is too high to be caused by an Re–Cl vibration[4] and too low for an Re=O vibration[5] arising from oxygen contamination of the product. PCl_5 vapour,[6] PCl_3[7] and $POCl_3$[7] do not absorb in this region but an absorption at about 649 cm^{-1} is characteristic of the PCl_4^+ ion[6] and similar bands have been observed at 650 and 640 cm^{-1} for $[PCl_4^+][VOCl_4^-]$ and $[PCl_4^+][VCl_5^-]$.[8] The peaks in the far-i.r. region have been assigned to $ReCl_6^-$ modes by comparison with the $ReCl_6^{2-}$ ion.[9] The increase in ν_3, and decrease in ν_4 on oxidation have been observed previously for WCl_6^{2-}/WCl_6^- [4,5] and $IrCl_6^{3-}/IrCl_6^{2-}$.[5]

The i.r. spectra of $RePCl_{10}$ *and* Cs_2ReCl_6

Assignment	Cs_2ReCl_6 (Ref. 9)	Cs_2ReCl_6 This work	$RePCl_{10}$
ν_3 (PCl_4^+) ..			649
$\nu_2 + \nu_3$ ..	584 m.w	584 w.	582 w.
$\nu_3 + \nu_5$ ..	473 w.	486 v.w.	490 v.w.
ν_3	313 v.s.	311 v.s.	318 v.s.
ν_4	172 s.	170s.	161 s.

Units: cm^{-1}.

0·0108 M- and 0·0048 M-Methyl cyanide solutions of $RePCl_{10}$ had molar conductivities of 104 and 121 ohm^{-1} cm^2 giving a value at infinite dilution of *ca.* 134 ohm^{-1} cm^2 which is very similar to that for $[PCl_4^+][SbCl_6^-]$ and consistent with a univalent electrolyte.[10] The conductivity decreased slowly with time, the stronger solution showing a 20% decrease in three days and this was accompanied by a decrease in the red colour of the solution. We postulate that this is caused by oxygen or water, since exposure to air causes the same reaction to occur in a few minutes.

Over the temperature range 92—290K the magnetic susceptibility of $[PCl_4^+][ReCl_6^-]$ obeys the Curie–Weiss Law within 1%, with a Curie constant of 0·904 and Curie–Weiss constant of 60°. μ_{eff} ranges from 2·11 B.M. at 92K to 2·47 B.M. at 290K. The results are reasonable for a d^2 ion in a close-to octahedral field with a medium antiferromagnetic interaction. The interaction is less than that observed for WCl_6^{2-} [11] salts but is to be expected because of the size of the PCl_4^+ cation.

Attempts to prepare other salts of $ReCl_6^-$ have so far been unsuccessful; alkali-metal halides reacted with $[PCl_4^+][ReCl_6^-]$ to give $ReCl_6^{2-}$ salts, and organic ammonium, phosphonium, or arsonium ions gave black tars.

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[1] J. H. Canterford and R. Colton, "Halides of the Second and Third row Transition Metals," Wiley-Interscience, New York, 1968, pp. 245 and 297.

[2] P. Machmer, *Inorg. and Nuclear Chem. Letters*, 1968, **4**, 91.

[3] P. W. Frais, A. Guest, and C. J. L. Lock, *Canad. J. Chem.*, 1969, **47**, 1069.

[4] R. J. H. Clark, *Spectrochim. Acta*, 1965, **21**, 955; D. M. Adams, H. A. Gebbie, and R. D. Peacock, *Nature*, 1963, **199**, 278; D. M. Adams and H. A. Gebbie, *Spectrochim. Acta*, 1963, **19**, 925.

[5] C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3552; N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *ibid.*, 1964, 1054.

[6] I. R. Beattie and M. Webster, *J. Chem. Soc.*, 1963, 38.

[7] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1963, pp. 86 and 112.

[8] I. M. Griffiths and D. Nichols, *Chem. Comm.*, 1970, 713.

[9] L. A. Woodward and M. J. Ware, *Spectrochim. Acta*, 1964, **20**, 71.

[10] L. Kolditz, *Z. anorg. Chem.*, 1957, **289**, 128.

[11] D. A. Edwards, R. D. Peacock, and A. Said, *J. Chem. Soc.*, 1962, 4643.