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The Configuration of the Anion in CsReCl_4

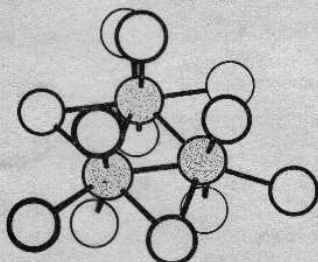
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LIGAND field theory has been used to predict that the anion $[\text{ReCl}_4]^-$ is regular tetrahedral¹ with a d^4 electron configuration for Re(III) . The magnetic moment² of RbReCl_4 does not contradict this prediction. With a view to confirming the stereochemistry of rhenium in this anion we have carried out an X-ray analysis of the compound of empirical composition CsReCl_4 .

The crystals are orthorhombic with the non-centrosymmetric space group $Ama2$. There are 12 CsReCl_4 units in a unit cell of dimensions $a = 10.66$, $b = 14.08$, and $c = 14.02$ Å. All atoms have been located with the aid of three-dimensional electron-density maps and, for the incompletely refined structure, the R factor for all observed (hkl) reflections is 0.21.

The $[\text{ReCl}_4]^-$ anion is not tetrahedral but is trimetric with a triangle of bonded rhenium atoms. Each of these is bonded to two bridging chlorine atoms



and one terminal chlorine atom in the plane of the triangle and also to two chlorine atoms on opposite sides of this plane (see Figure). Rhenium atoms are

therefore seven-co-ordinate and each is at the centre of a distorted pentagonal bipyramid which has as its apices two chlorine atoms. If there are to be sufficient bonding orbitals it is clear that a seven-co-ordinate rhenium(III) atom requires a spin-paired d^4 electron configuration.³

The space group requires of the ion only a plane of symmetry. This passes through one rhenium and its three attached terminal chlorines, and also the bridging chlorine to which it is not bonded. However, the ion possesses symmetry D_{3h} ($= D_{3d}$) within experimental error, the three-fold axis being normal to the triangle of rhenium atoms.

Mean values for bond lengths are: $\text{Re-Re} = 2.50$ Å, Re-Cl (bridging) = 2.43 Å, Re-Cl (terminal in plane of rhenium atoms) = 2.60 Å, and Re-Cl (terminal off plane of rhenium atoms) = 2.35 Å.

A detailed account of the crystal structure analysis will be presented later together with a full discussion of this most interesting, and previously unreported stereochemical arrangement.

All calculations were carried out on the University of Canterbury IBM 1620 computer using programmes written by us and by Dr. D. van der Helm of the Institute for Cancer Research, Philadelphia 11, Pa., U.S.A. The work was supported by the New Zealand Universities Research Committee by grants for equipment and a Research Fellowship (to W.T.R.).

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¹ Orgel, "Quelques Prob. de Chemie Minerale," 10th Solvay Conf., 1956, 289.

² Klemm and Frischmuth, *Z. anorg. Chem.*, 1943, 13, 253.

³ Nyholm, *Proc. Chem. Soc.*, 1961, 273.