Structure of a Nitrido-bridged Ruthenium Complex

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Summary In the crystal structure of $K_3[Ru_2NCl_8(H_2O)_2]$ the complex ion is nitrido-bridged with very short Ru–N distances.

TRANSITION-METAL μ-nitrido complexes are rare,[1,2] and no structural information exists about them. Cleare and Griffith[3] have recently shown, on the basis of spectroscopic data that the compounds $K_3[Ru_2NX_8(H_2O)_2]$ (X = Cl or Br) belong to this category. We have determined the crystal structure of $K_3[Ru_2NCl_8(H_2O)_2]$ and find that the complex ion is indeed nitrido-bridged with very short Ru–N distances of 1·718 Å.

Potassium μ-nitrido-bis[tetrachloroaquoruthenate(IV)] crystallises from dilute hydrochloric acid as deep red plates which are monoclinic. The unit-cell dimensions are $a = 15·89$, $b = 7·34$, $c = 8·16$ Å, $\beta = 120·4°$, $U = 820·8$ Å^3, $D_m = 2·64$, $D_c = 2·64$ g.cm.$^{-3}$ for $Z = 2$, space group $C2/m$.

The structure was solved by Patterson and Fourier methods on the basis of 702 independent reflections, recorded with Cu-K_α radiation and estimated visually. Least-squares refinement, using isotropic temperature factors for all atoms, has now reached $R = 0·094$.

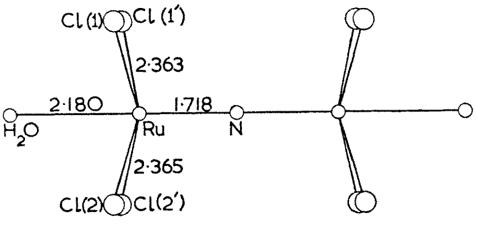

FIGURE. *The* $[Ru_2NCl_8(H_2O)_2]^{3-}$ *ion. The mirror plane is in the plane of the paper. Standard deviations are*: Ru–N, 0·003; Ru–Cl, 0·006; Ru–O (*water*), 0·026 Å.

The structure contains the $[Ru_2NCl_8(H_2O)_2]^{3-}$ ion which has $2/m$ crystallographic symmetry, with the bridging nitrogen atom lying on a centre of symmetry. The Figure shows that the ruthenium atoms, which lie on mirror planes, have a distorted octahedral co-ordination with water molecules *trans* to the nitrogen. The Ru–N–Ru bridge is very short with Ru–N distances of 1·718 Å. There is therefore multiple bonding present with a considerable amount of π-character.[1,4] The distance may be compared with Ru–O distances of 1·80 Å found in $[Ru_2OCl_{10}]^{4-}$ (ref. 5) and Re–O of 1·86 Å in $[Re_2OCl_{10}]^{4-}$ (ref. 6).

The chlorine atom configuration is *eclipsed*—this unusual feature is a consequence of the rigidity of the multiple Ru–N–Ru bond, and is similar to that found in the $Re_2Cl_8^{2-}$ ion.[7] The chlorine atoms are moved away from the nitrogen such that the N–Ru–Cl angles are ≈ 95° (see Table) and the distances between the eclipsed chlorines are >3·8 Å. This is much longer than is found in $Re_2Cl_8^{2-}$ (3·32 Å) and suggests that this bending is because of the π-bonding rather than simply because of packing considerations (the Ru–Ru distance of 3·44 Å would allow sufficient clearance for an N–Ru–Cl angle of 90°). The Ru–Cl distances are of usual length. The Ru–O (water) distance of 2·18 Å is rather long. This may be because of the bending of the chlorines towards the water molecule, although a *trans*-influence is another possibility.

TABLE

Angle		σ
N–Ru–Cl(1)	94·1	0·2
N–Ru–Cl(2)	95·1	0·2
O–Ru–Cl(1)	85·4	0·4
O–Ru–Cl(2)	85·1	0·4
Cl(1)–Ru–Cl(1′)	89·5	0·2
Cl(1)–Ru–Cl(2)	90·0	0·2
Cl(2)–Ru–Cl(2′)	89·0	0·2
N–Ru–O	179·7	0·5

There are two crystallographically independent potassium ions in the structure. Both are co-ordinated to eight chlorines at the corners of a distorted cube, with K–Cl distances of 3·19—3·37 Å. In both cases there are two more distant neighbours sticking out of opposite faces of the cube; an oxygen at 3·42 and a nitrogen at 3·76 Å in one case, and two nitrogens at 3·67 Å in the other.

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