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The Crystal Structure of Potassium Hydroxy-Chlororuthenate, $K_4Ru_2Cl_{10}O.H_2O$

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For many years there was confusion regarding the identity of some of the chloro-complexes of ruthenium. Through the work of Howe (1927*a*, *b*) and Charonnat (1931), the existence of at least three compounds has been established: (1) $K_2RuCl_5.H_2O$, (2) K_2RuCl_5OH, (3) K_2RuCl_6. Magnetic studies (Mellor, 1943) revealed that (1) and (3) were paramagnetic with moments corresponding to one and two unpaired electrons respectively, in agreement with the moments predicted for complexes of Ru^{III} and Ru^{IV} by Pauling (1931). However (2) was diamagnetic although, like (3), it contained Ru^{IV}. At the time no explanation could be given. Analysis of this compound has been carried out to determine if the detailed structure would aid in elucidating the anomalous behaviour.

Potassium hydroxy-pentachloro-ruthenate was prepared by the method of Antony & Lucchesi (1899). Suitable crystals were obtained by slowly evaporating a 50% hydrochloric acid solution on a water bath.

Cell dimensions were measured on rotation films, the values being refined by powder diffraction data taken on a 19 cm. camera using filtered Cu $K\alpha_{1,2}$ radiation. The unit cell is tetragonal with

$$a = 7{\cdot}10 \quad \text{and} \quad c = 16{\cdot}95\ \text{Å}\,.$$

The density, measured by benzene displacement, was 2·88 g.cm.$^{-3}$ and the density calculated for four units of K_2RuCl_5OH, 2·98 g.cm.$^{-3}$. Systematic absences were observed for hkl when $h+k+l = 2n+1$ and for $0kl$ when $k+l = 2n+1$. Since the Laue symmetry is $4/mmm$, the space group is $I\bar{4}2m$, $I\bar{4}m2$, $I4mm$ or $I4/mmm$. A piezo-electric test for a centre of symmetry was indeterminate. Intensity data for [010] zonal reflexions were recorded with filtered Mo $K\alpha$ radiation on a Weissenberg goniometer, using multiple-film packs interleaved with tin foil. The intensities were estimated visually against a standard scale.

A Patterson vector map of the projection on (010) was computed from the measured $F_2(h0l)$ values. Because of the special position of the ruthenium atoms on the fourfold axis, the Ru–Ru vector was readily detected. The close approach of the two ruthenium atoms (3·60 Å) indicated that they must be associated in one large anion. The most reasonable explanation was that the two metal atoms were linked to an oxygen atom placed at the origin. Five chlorine atoms could

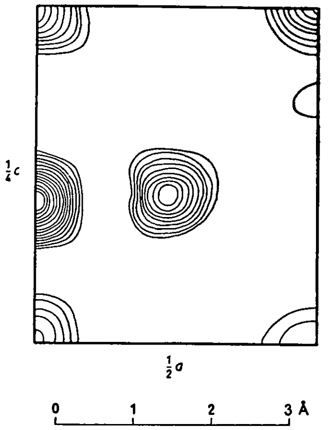

Fig. 1. Electron-density projection along the *b* axis.

Table 1. *Comparison of calculated and observed structure amplitudes for* $K_4Ru_2Cl_{10}O\,.\,H_2O$

$h0l$	$\lvert F_o/10\rvert$	$\lvert F_c/10\rvert$
002	< 4	10
004	22	23
006	28	32
008	47	49
0,0,10	24	27
0,0,12	< 10	4
0,0,14	24	29
200	18	22
400	46	54
101	27	26
103	13	13
105	20	23
107	< 7	2
109	22	19
1,0,11	< 9	6
1,0,13	< 10	9
1,0,15	11	11
202	< 6	4
204	38	30
206	< 8	4
208	< 9	12
2,0,10	< 10	4
2,0,12	21	21
301	13	10
303	< 7	7
305	23	9
307	< 9	2
309	17	10
402	< 9	4
404	16	14
406	21	22
408	30	35
4,0,10	19	19
4,0,12	< 11	5
4,0,14	20	22
501	22	17
503	< 9	9
505	21	19
507	< 11	3
509	18	18

then be grouped in pyramidal formation around each ruthenium atom. The potassium ions and the remaining water molecule were disposed in special positions providing rational ionic bonding and coordination. Comparison of a synthetic vector map derived from this model gave close agreement with the calculated map. The satisfactory fit confirmed that the space group is $I4/mmm$. A Fourier synthesis (Fig. 1) was carried out for this projection to obtain more accurate atomic parameters, the phase angles being calculated from the postulated model. The discrepancy factor between calculated and observed structure amplitudes, Table 1, was reduced to 0·15.

The atomic parameters, in terms of the cell coordinates tabulated in *Internationale Tabellen* (1935) for space group $I4/mmm$, are

2 O in (*a*)
2 H_2O in (*b*)
4 K_1 in (*c*)
4 K_2 in (*d*)
4 Ru in (*e*) with $z = 0{\cdot}106$
4 Cl_1 in (*e*) with $z = 0{\cdot}245$
16 Cl_2 in (*m*) with $x = y = 0{\cdot}235$, $z = 0{\cdot}111$

The unit cell contains eight potassium ions, two water molecules and two complex anions, $(Cl_5RuORuCl_5)^{4-}$. The main feature of interest is the anion (Fig. 2). Two ruthenium atoms are linked to an oxygen atom which thus occupies one corner, common to the two octahedra, while the remaining corners are filled by chlorine atoms. This disposition results in a linear arrangement of the two O–Ru bonds which, although somewhat unusual for oxygen, has been observed in anions $(Si_2O_7)^{6-}$, where tetrahedral corners are shared (Wells, 1950, p. 577). The Ru–O distance, 1·80 Å, although different from the sum of single-bond radii, 1·98 Å, is close to the larger of the two values, 1·74 Å, observed in the electron-diffraction study of RuO_4 (Braune & Stute, 1938). The Ru–Cl distance of 2·34 Å is in reasonable agreement with the sum of single-bond radii, 2·32 Å. The Cl–Cl separation distance between each half of the anion is 3·76 Å, which allows for a slight repulsion of the chlorine atoms, the van der Waals radius being 1·80 Å. The separation between chlorine atoms of different anions is 3·62 Å. Each anion is in contact with eight other anions, the potassium ions and water molecules being accommodated in holes left by anion contacts. The measured K–Cl distance is 3·14 Å, the sum of ionic radii being 3·13 Å.

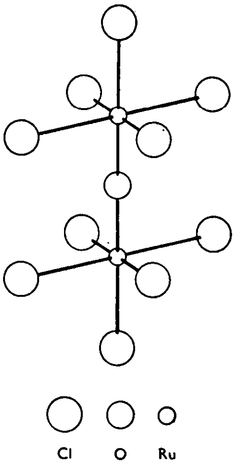

Fig. 2. Diagram of the complex anion $(Ru_2Cl_{10}O)^{4-}$.

The existence of the complex anion is supported by the observation of Charonnat (1931) that one molecule of water was expelled on heating the compound to 300° C.

A possible explanation for the diamagnetism of the ion $(Cl_5RuORuCl_5)$ is that the spins of the unpaired electrons on each Ru^{IV} atom are antiparallel but uncoupled. Alternatively some type of electron pairing may take place. A similar observation on anomalous magnetic behaviour has been made on $Fe_2(CO)_9$ (Berkman & Zocher, 1926) the structure of which shows that the two iron atoms are linked by covalent bonds to shared carbon atoms (Powell & Ewans, 1939). The covalent bonding brings the iron atoms sufficiently close to modify the non-bonding orbitals as suggested above, and the compound is diamagnetic instead of paramagnetic as expected.*

The correct formula for the compound is $K_4Ru_2Cl_{10}O.H_2O$.

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* In a private communication to D. P. Mellor, L. Pauling has suggested that if each ruthenium atom has seven orbitals of which two are required for bond formation with the oxygen atom, the diamagnetism would be explained. However, the structure involving oxygen associated with two double bonds appears improbable.