

THE CRYSTAL STRUCTURE OF POTASSIUM HEXACHLORORUTHENATE(IV)*

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Potassium hexachlororuthenate(IV), in which ruthenium has a magnetic moment of 3.07 Bohr magnetons, is the most strongly paramagnetic compound of the platinum metals yet described (Mellor 1943). This, together with the fact that there has been some confusion about the identity of the complex chloro-salts of ruthenium and the fact that the octahedral covalent radius of Ru^{IV} has not hitherto been determined, is the reason for briefly recording the results of an X-ray examination of the compound. The substance was prepared by the method described by Charonnat (1931).

As would be expected, the crystal belongs to the cubic system and is isomorphous with K_2PtCl_6 (Ewings and Pauling 1928). The length of the edge of the unit cell of K_2RuCl_6 , determined by the Bradley-Jay extrapolation method from powder photographs taken with $\text{CoK}\alpha$ radiation, is $9.738 \pm 0.001 \text{ \AA}$. The first 30 lines of the powder photograph are listed in Table 1. The parameter

TABLE 1

<i>hkl</i>	$\text{Sin}^2 \theta$		\sqrt{I}		<i>hkl</i>	$\text{Sin}^2 \theta$		\sqrt{I}	
	Obs.	Calc.	Obs.	Calc.		Obs.	Calc.	Obs.	Calc.
111	0.0247	0.0252	<i>s</i> ⁺	40.3	711	0.4293	0.4285	<i>m</i> ⁻	17.8
200	0.0338	0.0336	<i>m</i> ⁺	22.6	551				
220	0.0677	0.0672	<i>s</i>	27.7	640	0.4375	0.4369	<i>w</i> ⁻	7.2
311	0.0932	0.0924	<i>m</i> ⁺	24.2	642	0.4710	0.4706	<i>w</i>	11.2
222	0.0997	0.1008	<i>s</i>	24.8	731	0.4966	0.4958	<i>w</i> ⁺	13.8
400	0.1353	0.1344	<i>s</i> ⁺	36.8	553				
331	0.1608	0.1597	<i>w</i>	15.6	800	0.5382	0.5378	<i>w</i> ⁻	9.9
420	0.1694	0.1681	<i>w</i> ⁺	14.1	733	—	—	<i>absent</i>	1.3
422	0.2032	0.2017	<i>w</i> ⁻	15.6	820	0.5729	0.5714	<i>w</i>	10.7
511	0.2280	0.2269	<i>m</i>	20.4	644				
333					822	0.6057	0.6050	<i>w</i>	12.2
440	0.2703	0.2689	<i>s</i>	28.7	660				
531	0.2950	0.2941	<i>m</i> ⁻	16.6	751	0.6312	0.6302	<i>w</i>	13.2
600	0.3049	0.3025	<i>w</i>	13.6	555				
442					662	0.6395	0.6386	<i>w</i> ⁻	10.9
620	0.3376	0.3361	<i>w</i>	11.3	840	0.6725	0.6722	<i>m</i>	19.2
533	0.3622	0.3613	<i>w</i> ⁻	1.7	911	0.6971	0.6974	<i>w</i>	14.0
622	0.3717	0.3697	<i>w</i>	13.4	753	0.7049	0.7058	<i>w</i> ⁻	5.6
444	0.4040	0.4033	<i>m</i> ⁻	16.6	842				

* Manuscript received April 9, 1952.

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u defining the Ru-Cl distance was determined by means of the method of inequalities and found to be 0.235 ± 0.005 , a value which leads to a reasonable agreement between observed and calculated intensities. The spots chosen for intensity comparisons were on rotation photographs taken with $\text{CuK}\alpha$ radiation. If one assumes a value of 0.99 \AA for the covalent radius of chlorine, the Ru-Cl distance of $2.29 \pm 0.04 \text{ \AA}$ leads to a value of $1.30 \pm 0.04 \text{ \AA}$ for the octahedral radius of Ru^{IV} . It is of interest to compare this value with the values obtained for covalent radii of the transition elements in different oxidation states, set out in Table 2 (Pauling 1939).

TABLE 2

Oxidation State	Fe	Co	Ni	Ru, Os	Rh, Ir	Pd, Pt	Ag, Au
II	1.23	1.32	1.39	1.33	1.43	1.50	
III		1.22	1.31	—	1.32	1.42	1.49
IV			(1.21)	1.30	1.29	1.31	1.41

The value shown in brackets is extrapolated. It will be noticed that as one goes diagonally across the table from left to right and down, as in the sequences Os^{II} , Ir^{III} , Pt^{IV} , and Ir^{II} , Pt^{III} , Au^{IV} , there is a regular decrease in radius. The uncertainty of the values of the radii quoted in Table 2, which is roughly the same throughout and about that of the uncertainty of the radius of Ru^{IV} , makes it debatable whether the regular decrease in the values for sequences of isoelectronic species is real.

The existence of such a decrease appears to be reasonable; if it is real, as it may be, Ru^{IV} fits into the sequence Co^{II} , Ni^{III} , Ru^{IV} .

On the assumption that the decrease is approximately 0.01 \AA in each step of the series, Ni^{II} appears to have an unusually large radius (1.39 \AA) in $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ (Wyckoff 1922) as compared with that of Rh^{IV} (1.29 \AA) (Dwyer, Nyholm, and Rogers 1947). Preliminary measurements indicate that the value for Ni^{II} is smaller and nearer to 1.33 \AA (Wunderlich, unpublished data). An attempt is also being made to determine the radius of Os^{III} in the compound $[\text{Os}(\text{NH}_3)_6]\text{ISO}_4$ which is isomorphous with the corresponding cobalt compound.

References

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