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Crystal structure and magnetic properties of the $(\text{Ru}_2\text{Cl}_9)^{3-}$ ion in $\text{Cs}_3\text{Ru}_2\text{Cl}_9$

by

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ABSTRACT. — The crystal structure of $\text{Cs}_3\text{Ru}_2\text{Cl}_9$ has been determined from three-dimensional X-ray data and found to be similar to that of $\text{Cs}_3\text{B}_2\text{Cl}_9$ ($\text{B}=\text{Mo}, \text{Fe}, \text{Cr}$). Two-thirds of the octahedral sites of the 6H perovskite-related structure are filled by ruthenium atoms. Ordering between occupied and empty octahedra leads to isolated $(\text{Ru}_2\text{Cl}_9)^{3-}$ clusters. Magnetic studies indicate that metal-metal interactions occur in $\text{Cs}_3\text{Ru}_2\text{Cl}_9$, so that only temperature-independent paramagnetism is observed. This interpretation is supported by the metal-metal distances observed by the structural determination.

RÉSUMÉ. — La structure cristalline de $\text{Cs}_3\text{Ru}_2\text{Cl}_9$, déterminée sur monocristal, a été trouvée similaire à celle de $\text{Cs}_3\text{B}_2\text{Cl}_9$ ($\text{B} = \text{Mo}, \text{Fe}, \text{Cr}$). Les deux tiers des sites octaédriques de la structure du type pérovskite 6H sont occupés par des atomes de ruthénium. L'établissement d'un ordre entre sites octaédriques vacants et occupés mène à des clusters $(\text{Ru}_2\text{Cl}_9)^{3-}$ isolés. L'étude magnétique montre que des interactions métal-métal se produisent dans $\text{Cs}_3\text{Ru}_2\text{Cl}_9$, de sorte qu'on observe seulement un paramagnétisme indépendant de la température. Cette interprétation est confortée par les distances métal-métal qui ressortent de la détermination structurale.

INTRODUCTION

Many ternary halides and oxides of general composition ABX_3 , where A is a large cation and B a transition element cation have perovskite or perovskite related structures. They may be described on the basis of close-packed AX_3 layers [1] with the smaller B cations in octahedral interstices. Different packings of the AX_3 layers result in a variety of structures. Many $\text{A}_3\text{B}_2\text{X}_9$ halides and recently a $\text{Ba}_3\text{W}_2\text{O}_9$ oxide can be described in terms

of close-packed AX_3 layers in which some octahedral sites are empty [2-6]. One structure commonly adopted by halides such as $Cs_3Cr_2Cl_9$ is the six-layer hexagonal $BaTiO_3$ structure, but where B cations occupy only two-thirds of the octahedral sites [4]. The distribution of the B ions is such that only the face sharing octahedra are filled. The structure can be described in terms of isolated binuclear $(B_2X_9)^{3-}$ groups.

We report here the new phase in the $CsCl-RuCl_3$ system with formula $Cs_3Ru_2Cl_9$ as the first example of a ruthenium halide having the $Cs_3Cr_2Cl_9$ structure.

EXPERIMENTAL PROCEDURES AND RESULTS

Sample preparation

$Cs_3Ru_2Cl_9$ was prepared by solid state reaction at 700° C using stoichiometric proportions of $CsCl$ and $RuCl_3$. The reaction was performed in sealed vycor tubes which were evacuated under vacuum. Repeated grindings of the mixture were necessary in order to promote a complete reaction and thus ensure a single phase product. By heating at 850° C for three days, small red crystals appeared in the upper part of the tube. These crystals of $Cs_3Ru_2Cl_9$ appeared to be stable in open air.

X-ray data and structural determination

The similarity of the X-ray powder patterns of $Cs_3Ru_2Cl_9$ and $Cs_3B_2Cl_9$ ($B = Cr, Fe$ and Mo) suggests that the compounds are isostructural. The hexagonal unit-cell dimensions were obtained from a least square fit of 20 lines. Table I summarizes the X-ray powder diffraction pattern and the lattice parameters for $Cs_3Ru_2Cl_9$.

To confirm this hypothesis for the structure of $Cs_3Ru_2Cl_9$ a single-crystal X-ray study was carried out. Preliminary Weissenberg photographs showed that the crystal has $6/mmm$ Laüe symmetry with the only condition: $l = 2n$ for $h h \bar{2}h l$ (possible space groups: $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$). Intensities were collected using an Enraf Nonius C. A. D. 3 diffractometer with $MoK\alpha$ radiation and a graphite monochromator. A total of 309 independent reflections were used. Structure factors were derived by applying only Lorentz-polarisation corrections. Both space group $P6_3/mmc$ and coordinates of the appropriate atoms from the final refinement of $Cs_3Cr_2Cl_9$ [4] were assumed for the initial refinement of the $Cs_3Ru_2Cl_9$ structure. After three cycles of least-squares refinement on all variable coordinates and isotropic thermal parameters, the residue was $R = 0.040$. Anisotropic thermal parameters were then introduced and two further cycles yielded

the final value of $R = 0.035$. The final atomic and thermal parameters are given in Table II, while some significant distances and angles are given in Table III.

TABLE I

*X-ray powder diffraction data for $\text{Cs}_3\text{Ru}_2\text{Cl}_9$
Space group : $\text{P6}_3/\text{mmc}$.*

Lattice Parameters : $a = 7.221(4) \text{ \AA}$, $c = 17.556(8) \text{ \AA}$, $Z = 2$ (S = strong, vS = very strong, m = medium, w = weak, vw = very weak).

$h k l$	$d_{\text{obs.}} (\text{\AA})$	$d_{\text{calc.}} (\text{\AA})$	I obs.	$h k l$	$d_{\text{obs.}} (\text{\AA})$	$d_{\text{calc.}}$	I obs.
0 0 2	8.81	8.78	S	2 2 0	1.804	1.805	m
1 0 0	6.27	6.25	m	1 2 7	1.720	1.720	vw
0 1 1	5.90	5.89	m	1 3 2	1.700	1.702	vw
0 1 2	5.10	5.09	w	0 3 6		1.698	
0 0 4	4.39	4.39	w	1 3 3	1.664	1.663	vw
0 1 3	4.27	4.27	m	0 2 9	1.656	1.655	vw
1 1 0	3.62	3.61	vS	1 2 8	1.608	1.608	w
1 1 2	3.35	3.34	w	1 3 5	1.555	1.555	w
0 1 5	3.06	3.06	m	0 4 2	1.538	1.539	
0 2 2	2.950	2.954	m	2 2 6		1.536	w
0 0 6	2.928	2.926	vS	0 2 10	1.532	1.531	w
0 2 3	2.760	2.757	S	0 3 8		1.511	
0 1 6	2.651	2.650	vw	0 4 3	1.511	1.510	w
0 2 4	2.547	2.547	m	0 4 4	1.472	1.473	vw
0 2 5	2.336	2.335	w	0 0 12	1.464	1.463	m
0 0 8	2.193	2.195		1 3 7	1.427	1.427	
2 1 3		2.192	w	0 1 12		1.425	vw
0 2 6	2.137	2.136	vw	1 4 0		1.365	
3 0 0	2.085	2.085	m	2 3 4	1.364	1.364	w
0 1 8		2.071		2 3 5		1.328	
0 3 1	2.072	2.070	m	0 4 7	1.327	1.327	vw
1 2 5		1.961		1 2 11		1.323	
0 2 7	1.959	1.956	m	0 1 13	1.321	1.320	vw
1 1 8	1.876	1.875	vw				
1 2 6	1.840	1.839	vw				

TABLE II

Atomic and thermal parameters for $\text{Cs}_3\text{Ru}_2\text{Cl}_9$. ^a The Wyckoff notation is given in parentheses. The point symmetries of the special positions impose the following restriction on the β_{ij} : position (k), $\beta_{12} = 1/2\beta_{22}$, $\beta_{13} = 1/2\beta_{23}$; position (h), $\beta_{12} = 1/2\beta_{22}$, $\beta_{13} = \beta_{23} = 0$; positions (b), $\beta_{11} = \beta_{22} = 2\beta_{12}$, $\beta_{13} = \beta_{23} = 0$; position (f); $\beta_{11} = \beta_{22} = 2\beta_{12}$, $\beta_{13} = \beta_{23} = 0$.

Atom α^a	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Cs(b)	0	0	1/4	96(4)	96	14(1)	48	0	0
Cs(f)	1/3	2/3	0.0746(1)	130(4)	130	12(1)	65	0	0
Ru(f)	1/3	2/3	0.8276(2)	84(3)	84	10(1)	42	0	0
Cl(h)	0.5096(5)	1.0192	1/4	65(11)	146(25)	10(2)	73	0	0
Cl(k)	0.8193(3)	1.6386	0.0961(3)	89(9)	168(19)	12(2)	84	-11(3)	-22

TABLE III

Bond distances and angles within the $(\text{Ru}_2\text{Cl}_9)^{3-}$ anion ^a.

^a See Fig. 2 for the notation of the atoms.

metal-metal = 2.725(3) Å	metal-Cl(<i>h</i>) = 2.391(4) Å	metal-Cl(<i>k</i>) = 2.332(4) Å
Cl(<i>h</i>)-Cl'(<i>h</i>) = 3.403(5) Å	Cl(<i>h</i>)-Cl'(<i>h</i>) = 3.306(5) Å	Cl'(<i>h</i>)-Cl'(<i>k</i>) = 3.325(5) Å
Cl(<i>h</i>)-metal-Cl(<i>h</i>) = 90.7(2)°	Cl(<i>k</i>)-metal-Cl'(<i>k</i>) = 90.3(2)°	Cl(<i>k</i>)-metal-Cl(<i>k</i>) = 89.5(2)°
metal-Cl(<i>h</i>)-metal = 69.5(2)°		

Magnetic properties

The magnetic susceptibility of $\text{Cs}_3\text{Ru}_2\text{Cl}_9$ was measured for powder samples. The used temperature range was 4.2 to 300 K. The measurements were carried out on a Faraday balance. The independence of the magnetic susceptibility from the magnetic field strength was checked over the whole temperature range. The diamagnetism was estimated to be -373×10^{-6} CGS using Pascal's Tables. Fig. 1 shows the temperature dependence of the

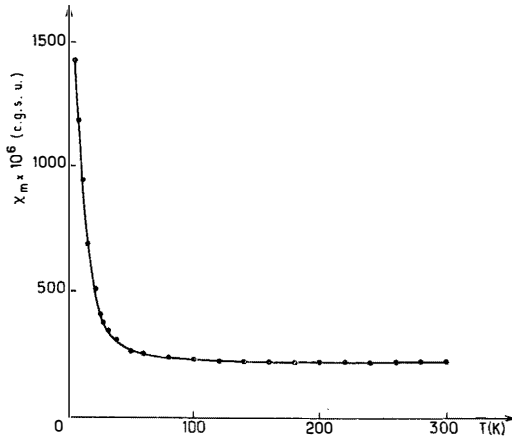


Fig. 1. — Variation of the susceptibility of $\text{Cs}_3\text{Ru}_2\text{Cl}_9$ with temperature.

average molar magnetic susceptibility χ . Above 50 K, the magnetic susceptibility of $\text{Cs}_3\text{Ru}_2\text{Cl}_9$ becomes small and constant, the value being 220×10^{-6} CGS. The effective magnetic moment calculated using the formula $\mu_{\text{eff}} = 2.828\sqrt{\chi T}$ B. M. is small (T = 300 K, $\mu_{\text{eff}} = 0,51$ BM per Ru).

DISCUSSION

$\text{Cs}_3\text{Ru}_2\text{Cl}_9$ has the same structure as $\text{Cs}_3\text{B}_2\text{Cl}_9$ ($\text{B} = \text{Cr}, \text{Fe}$ and Mo) [4, 7, 8]. The structure is characterized by the existence of binuclear ions $(\text{Ru}_2\text{Cl}_9)^{3-}$ as isolated units. The structure of $(\text{Ru}_2\text{Cl}_9)^{3-}$ results from the sharing of a trigonal face between two RuCl_6 octahedra (fig. 2). The site symmetry of each Ru^{III} ion is C_{3v} and the symmetry of the cluster is D_{3h} .

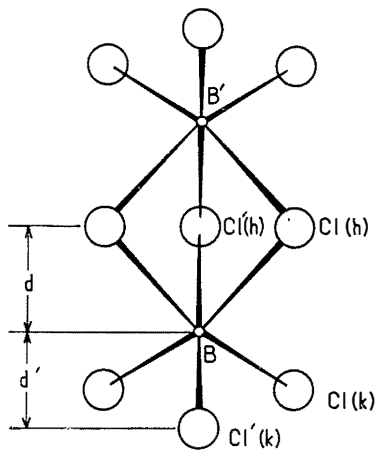


Fig. 2. — The $(\text{B}_2\text{Cl}_9)^{3-}$ ion ($\text{B} = \text{Cr}, \text{Fe}, \text{Mo}, \text{Ru}$).

In Table IV we compare some significant distances in enneachlorodimetallates whose structure has been determined. The Ru atoms are close to the center of their octahedra, so that the metal-metal internuclear distance is 2.725 \AA . The distance between the center of the triangle made by the bridging Cl atoms and the Ru atom is $d = 1.362 \text{ \AA}$. The corresponding distance to the center of the terminal Cl atom triangle is $d' = 1.339 \text{ \AA}$ (fig. 2, Table IV). In $\text{Cs}_3\text{Mo}_2\text{Cl}_9$ the metallic atoms are also close to the center of their octahedra, but there is a slight shift towards the plane of the bridging chlorine atoms (Table IV). On the contrary in $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ and $\text{Cs}_3\text{Fe}_2\text{Cl}_9$,

TABLE IV

Some significant distances in cesium enneachlorodimetallates.

	$\text{B}-\text{B}'$	d	d'
$\text{Cs}_3\text{Ru}_2\text{Cl}_9$	2.725 \AA	1.362 \AA	1.339 \AA
$\text{Cs}_3\text{Mo}_2\text{Cl}_9$	2.655 \AA	1.328 \AA	1.351 \AA
$\text{Cs}_3\text{Cr}_2\text{Cl}_9$	3.12 \AA	1.56 \AA	1.27 \AA
$\text{Cs}_3\text{Fe}_2\text{Cl}_9$	3.421 \AA	1.710 \AA	1.145 \AA

the metallic atoms are strongly displaced from each other along the trigonal axis towards the plane of the terminal chlorine atoms (Table IV).

As for $\text{Cs}_3\text{Mo}_2\text{Cl}_9$ [9, 10] one observes in $\text{Cs}_3\text{Ru}_2\text{Cl}_9$ a temperature independent paramagnetism between 50 and 300 K which is characteristic of a strongly interacting system. Below 50 K (fig. 1) the magnetic susceptibility increases despite these Ru-Ru couplings. A similar behaviour has been observed for compounds of same type [10, 11, 12]. The low temperature behaviour arises probably from small amount of paramagnetic monomers which may not necessarily be chemical impurities, but which could result from breaking of some Ru^{III} pairs in the sample.

Conversely, the magnetic moments of $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ and $\text{Cs}_3\text{Fe}_2\text{Cl}_9$ at 300 K are close to those expected for usual octahedra. The magnetic properties have been interpreted on the basis of the existence of a weakly-coupled spin system [11, 13, 15]. The magnetic interaction is described by a Heisenberg-Dirac-Van Vleck hamiltonian.

In conclusion, the magnetic behaviour of such isolated groups depends heavily upon metal-metal distances. In $(\text{Mo}_2\text{Cl}_9)^{3-}$ and $(\text{Ru}_2\text{Cl}_9)^{3-}$ ions it seems that attraction forces exist between the metallic atoms, as indicated by the magnetic data. The magnetic susceptibilities are small and temperature independent. Conversely, in $(\text{Cr}_2\text{Cl}_9)^{3-}$ and $(\text{Fe}_2\text{Cl}_9)^{3-}$ ions the structure illustrate the existence of a net repulsion between metallic atoms and the magnetic behaviour can be interpreted on the basis of a Heisenberg-Dirac-Van Vleck model.

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