Crystal Structures of the α Alums $CsM[SO_4]_2 \cdot 12H_2O$ (M = Rh or Ir) *

Robert S. Armstrong, James K. Beattie, and Stephen P. Best
School of Chemistry, University of Sydney, New South Wales 2006, Australia
Brian W. Skelton and Allan H. White
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009, Australia

Structure determinations of the alums $CsM[SO_4]_2 \cdot 12H_2O$ have been carried out for M = rhodium(III) and iridium(III), providing the first structurally characterized examples of the hexa-aqua-rhodium(III) and -iridium(III) species. Structures were determined at 295(1) K and refined to $R = 0.034$ and 0.028 for 546 and 696 independent 'observed' reflections for Rh and Ir respectively. Crystals are cubic, space group $Pa3$ with $a = 12.357(5)$ and 12.395(3) Å respectively; Rh–O is 2.016(3) and Ir–O 2.041(3) Å. Both alums are of the α type. Single-crystal Raman spectra of the S–O stretching vibrations are reported which distinguish between the α and β caesium alums.

In a recent study [1] we reported the determination of the crystal structures of the caesium sulphate alums $CsM[SO_4]_2 \cdot 12H_2O$ for the metals M = V, Cr, Mn, Fe, Co, Al, Ga, and In, good determinations for M = Al and Ti being already available; [2,3] the criteria for the classification of the alum types were discussed and revised and all of the above alums were assigned to the β category, excepting that of cobalt which was α. An unambiguous criterion for distinguishing between the α and β alums was found to be the geometry of the six water molecules about the monovalent cation. In the α alums they form a trigonal antiprism along the three-fold axis, which could be described as a puckered ring about the metal ion, perpendicular to the three-fold axis; in the β alums this ring is almost planar. As a sequel to this work we have determined the structures of the alums with M = Rh and Ir. These appear to be the first structure determinations of the hexa-aquarhodium(III) or hexa-aqua-iridium(III) species. The $[Rh(H_2O)_6]^{3+}$ ion has been known for some time [4] and the subject of several chemical and physical studies in solution.[5–7] Its caesium alum was readily prepared from hydrated rhodium trichloride by precipitation of the hydroxide,[8] followed by dissolution in H_2SO_4 (1 mol dm^{-3}), and addition of an approximately stoicheiometric quantity of caesium sulphate. The hexa-aquairidium(III) ion has only recently been described.[9] Its caesium alum was prepared similarly from the hydroxide obtained by the procedure of Gamsjäger and Beutler.[10] Thus the caesium alums serve as convenient hosts for isolating these hexa-aquametal(III) ions for further studies. Other alum salts were prepared using procedures summarized elsewhere.[1] Single crystals were grown from sulphuric acid solutions using a thermal difference technique.

Experimental

The crystallographic methodology follows closely that recently described in our report of caesium alum structure determinations; [1] details pertinent to the present example are given below.

Crystal Data for $CsRh[SO_4]_2 \cdot 12H_2O$.—$CsH_{24}O_{20}RhS_2$, $M = 644.1$, Cubic, space group $Pa3$ (T_h^6, no. 205), $a = 12.357(5)$ Å, $U = 1\,887(1)$ Å^3, $D_m = 2.23_8$ g cm^{-3},[11] $Z = 4$, $D_c = 2.27$ g cm^{-3}, $F(000) = 1\,264$, μ(Mo-K_α) = 29.4 cm^{-1}, λ(Mo-K_α) = 0.7107 Å. The specimen was a fragment *ca.* 0.30 mm in radius. $2\theta_{max.} = 80°$, 1 127 independent reflections, 546 with $I > 3\sigma(I)$ 'observed' for which $R = 0.034$, $R' = 0.051$.

Crystal Data for $CsIr[SO_4]_2 \cdot 12H_2O$.—$CsH_{24}IrO_{20}S_2$, $M = 733.4$, space group as above, $a = 12.395(3)$ Å, $U = 1\,904(1)$ Å^3, $D_m = 2.52(1)$ g cm^{-3}, $Z = 4$, $D_c = 2.56$ g cm^{-3}, $F(000) = 1\,392$, μ(Mo-K_α) = 89 cm^{-1}, λ as above. The specimen was a prismatic fragment of dimensions 0.30 × 0.44 × 0.22 mm. $2\theta_{max.} = 100°$, 1 832 independent reflections, 696 with $I > 3\sigma(I)$ 'observed' for which $R = 0.028$, $R' = 0.036$.

Final atomic co-ordinates are in Table 1 and bond distances and angles are in Table 2.

Discussion

Although the previous study [1] of the caesium sulphate alums, $CsM[SO_4]_2 \cdot 12H_2O$, demanded reconsideration of the criteria defining the α and β types, it was apparent that the cobalt alum was uniquely of the α type compared with the β structures observed for the remainder (Ti, V, Cr, Mn, Fe, Al, Ga, and In). The M^{III}–OH_2 distance in the cobalt alum is the shortest observed [1.873(5) Å], similar to that for aluminium [1.877(3) Å], and considerably shorter than found in the others, which range from 1.944(3) Å for gallium to 2.112(4) Å for indium.

It was therefore anticipated that the rhodium and iridium derivatives, having metal radii appreciably greater than cobalt(III), would lie in the β alum category. According to the criteria enumerated in ref. 1, this is not so. The sulphur atom fractional co-ordinates of the present two alums [0.3182(1) for Rh and 0.3174(1) for Ir (Table 1)] lie astride the value found in the cobalt alum [0.3178(2)], well below the range observed for the β alums (0.3268—0.3329), and well above the those other known α alums which do not contain caesium [criterion (a)]. The angles between the transition metal–water molecule bond and the crystallographic axis are 2.2 (Rh), and 2.9° (Ir) in the present cases (*cf.* 2.2° for cobalt), higher than the range established for the β alums (0.2—1.4°), but much lower than the range for the other α alums [criterion (b)]. The ratio of the two independent metal–oxygen distances of the univalent cation lies in the range 1.02—1.06 for the β alums and 1.20—1.29 for the α alums [criterion (c)]. The cobalt alum is anomalous, with this ratio being 1.09; the present examples are also anomalous, with ratios

* *Supplementary data available* (No. SUP 23640, 12 pp.): thermal parameters, observed and calculated structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Fractional atomic co-ordinates for $CsM[SO_4]_2 \cdot 12H_2O$

Atom [a]	M = Rh			M = Ir		
	x	*y*	*z*	*x*	*y*	*z*
Cs	0.5000 [b]	0.5000 [b]	0.5000 [b]	0.5000 [b]	0.5000 [b]	0.5000 [b]
M	0.0000 [b]	0.0000 [b]	0.0000 [b]	0.0000 [b]	0.0000 [b]	0.0000 [b]
S	0.318 2(1)	0.318 2(1) [b]	0.318 2(1) [b]	0.317 4(1)	0.317 4(1) [b]	0.317 4(1) [b]
O(1)	0.250 5(3)	0.250 5(3) [b]	0.250 5(3) [b]	0.249 6(3)	0.249 6(3) [b]	0.249 6(3) [b]
O(2)	0.326 8(4)	0.270 3(3)	0.426 0(3)	0.325 3(4)	0.271 6(4)	0.426 0(4)
O(a)	0.048 5(4)	0.151 1(3)	0.290 9(3)	0.048 8(4)	0.151 7(4)	0.290 9(4)
H(a1)	0.101(6)	0.176(6)	0.300(6)	0.104(5)	0.164(6)	0.300(6)
H(a2)	0.025(7)	0.192(8)	0.260(5)	0.004(6)	0.195(7)	0.317(7)
O(b)	0.163(2)	−0.001 6(3)	−0.005 9(3)	0.164 5(3)	−0.001 8(4)	−0.008 1(3)
H(b1)	0.200(5)	0.024(5)	−0.047(6)	0.183(6)	0.028(5)	−0.057(6)
H(b2)	0.212(5)	0.019(5)	0.040(6)	0.204(7)	0.008(5)	0.038(6)

[a] Atom numbering follows that defined in ref. 1. [b] Parameter constrained by symmetry.

Table 2. Interatomic distances and angles *

	Distances (Å)		Angles (°)
(*i*) The sulphate group			
S–O(1)	1.450(2), 1.455(2)	O(1)–S–O(2)	109.6(2), 110.2(2)
S–O(2)	1.461(4), 1.465(5)	O(2)–S–O(2^{i})	109.4(3), 108.7(3)
(*ii*) The metal, M			
M–O(b)	2.016(3), 2.041(3)	O(b)–M–O(b^{i})	92.6(2), 93.4(2)
(*iii*) The caesium atom			
Cs–O(a^{ii})	3.244(4), 3.259(5)	O(a^{ii})–Cs–O(a^{iii})	114.7(1), 114.7(1)
Cs–O(2)	3.670(4), 3.681(5)		

Transformations of the asymmetric unit: I *z*, *y*, *x* (*etc.*); II $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; III $1 - z, \frac{1}{2} + x, \frac{1}{2} - y$.

* The two values in each entry are for the rhodium and iridium alums respectively.

1.13 (both). The six water molecule oxygens which describe a trigonal antiprism about the univalent cation and its three-fold axis coalesce to coplanarity normal to that axis in the β alums, with O–Cs–O being 60°, while in the α alums the range is 64.9—66.5° (containing the cobalt derivative, 65.5°) [criterion (d)]. In the present examples, this angle is 65.3° (both).

Clearly, the good agreement of the parameters of the present structures with those of the caesium cobalt sulphate alum require that they be classified as the same type, in spite of the considerable change in transition metal–oxygen distance. Moreover, it shows that, with this latter parameter as the only geometrical variable in the atoms concerned, the two series α and β are capable of side-by-side existence. The determinant of the alum type therefore appears to be some particularly subtle parameter of the trivalent metal atom. The common feature of the cobalt, rhodium, and iridium alums is the presence of the low-spin $(t_{2g})^6$ *d*-electron configuration. In all the other caesium sulphate alums the t_{2g} orbitals are only partially occupied. Given the almost identical trivalent metal atom sizes of aluminium and cobalt it would appear that the origin of the difference may lie in the relative susceptibility of the trivalent metal ion to polarization by the nearby hydrogen atoms, but it is not obvious how this can be. We are presently undertaking neutron diffraction studies to examine this question further.

The differences found by *X*-ray crystallography between the α-CsRh and α-CsIr alums and the other β caesium alums should be manifest in other physical properties.[12] Previous workers [13–15] have observed differences between the alum classes by vibrational spectroscopy. Their studies have been ambiguous, however, because the change in alum class was effected by a change in the univalent ion. This change in the size of the univalent cation is accompanied by a change in the degree of disorder found for the sulphate ion in the α alums.[15] The degree of disorder is related to the size of the univalent ion and not to the structural class of the alum. There is no disorder in the caesium alums.[1] Hence differences in the spectra can be related to the structural class.

Single-crystal Raman spectra at liquid nitrogen temperature have been obtained for a number of caesium alums; [16,17] those recorded in the present study were obtained as previously described.[16] Differences in the spectra of the α and β alums are observed. These are most evident in the spectra of the internal modes of the sulphate ion, particularly $\nu_1(SO_4^{2-})$ and $\nu_3(SO_4^{2-})$, which are the symmetric (A_1) and antisymmetric (F_2) S–O stretching vibrations.

Within the crystal lattice, coupling among the equivalent sulphate sites within the unit cell can result in A_g, E_g, and F_g components.[15,16] The spectra containing the F_g component between 950 and 1 200 cm^{-1} are illustrated in the Figure.

The $\nu_1(SO_4^{2-})$ mode for all six of the β caesium alums occurs at 988 ± 1 cm^{-1}. In contrast, for the α caesium rhodium and iridium alums this mode occurs at 995 cm^{-1}, 7 cm^{-1} to higher energy. For the $\nu_3(SO_4^{2-})$ mode a similar shift of 10—15 cm^{-1} to higher energy occurs between the β and α alums, accompanied by a change in band profile. The bandshape of all six β alums is similar. These differ from the bandshape of the α alums CsRh and CsIr, which is similar to that reported for the α-RbAl alum.[15] While a detailed explanation of the factor group coupling which accounts for these differences would be complex, these qualitative observations confirm the

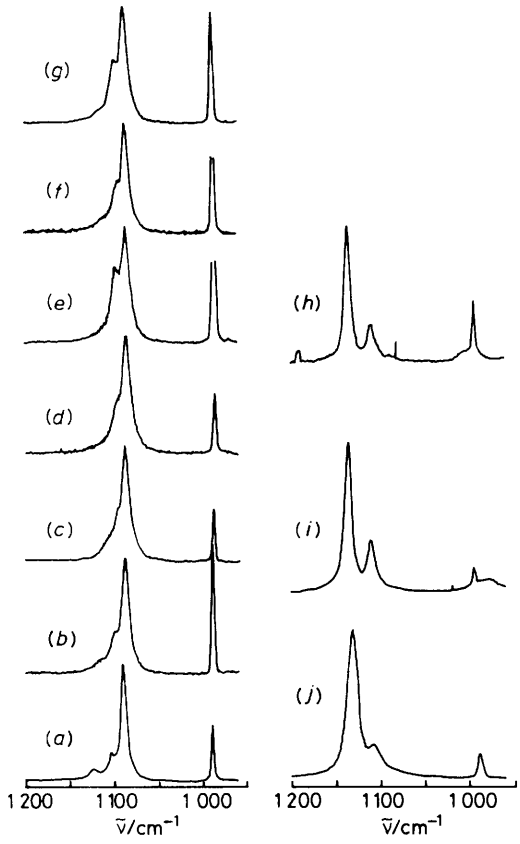

Figure. The F_g component of the Raman spectrum (950—1 200 cm^{-1}) of caesium alums, $CsM[SO_4]_2 \cdot 12H_2O$, M = (*a*) Al, (*b*) Ga, (*c*) In, (*d*) Ti, (*e*) V, (*f*) Cr, (*g*) Fe, (*h*) Ir, and (*i*) Rh recorded at close to 77 K and of $RbAl[SO_4]_2 \cdot 12H_2O$ (*j*) recorded at room temperature (reproduced from ref. 15)

structural results which indicate that the CsRh and CsIr alums belong to a different structural class from the six other caesium alums. The similarity of their spectra to that of the RbAl alum is consistent with their classification as α alums.

The present study establishes for the first time precise distances for the metal–oxygen bonds in the hexa-aqua-rhodium(III) and -iridium(III) species, the values being 2.016(3) and 2.041(3) Å, respectively. The effect of the lanthanide contraction is immediately apparent. The addition of 18 electrons from cobalt to rhodium increases the bond length 0.14 Å, while the addition of 32 electrons from rhodium to iridium increases the bond length by only 0.03 Å. Hence many of the properties of rhodium and iridium complexes are similar, and different from those of the cobalt analogue. These include, for example, the partial molar volumes and the volumes of reaction of the $[M(NH_3)_5(OH_2)]^{3+}$ complexes.[18]

The effective co-ordinated radius of the water molecule can be calculated to be 1.35 Å, using the metal ion radius of 0.665 Å for six-co-ordinate rhodium(III) given by Shannon [19] from oxide structures. This value is in good agreement with the average value of 1.34 Å obtained previously.[1] Conversely, the radius of six-co-ordinated iridium(III), which was only estimated by Shannon [19] to be 0.68 Å, can be calculated to be 0.69 Å from the difference between the rhodium and iridium bond distances.

Acknowledgements

We gratefully acknowledge a grant from the Australian Research Grants Committee in support of this work.

References

1 J. K. Beattie, S. P. Best, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 2105.
2 D. T. Cromer, M. I. Kay, and A. C. Larson, *Acta Crystallogr.*, 1966, **21**, 383.
3 J. Sygusch, *Acta Crystallogr., Sect. B*, 1974, **30**, 662.
4 G. H. Ayres and J. S. Forrester, *J. Inorg. Nucl. Chem.*, 1957, **3**, 365.
5 R. J. Buchacek and G. M. Harris, *Inorg. Chem.*, 1976, **15**, 926.
6 P. K. Mehrotra and P. T. Manoharan, *Chem. Phys. Lett.*, 1976, **39**, 194.
7 I. P. Alimarin, V. I. Shlenskaya, and O. A. Efremenko, *Russ. J. Inorg. Chem.*, 1970, **15**, 530.
8 S. K. Shukla, *Ann. Chim. (Paris)*, 1961, **6**, 1383.
9 P. Beutler and H. Gamsjåger, *J. Chem. Soc., Chem. Commun.*, 1976, 554.
10 H. Gamsjåger and P. Beutler, *J. Chem. Soc., Dalton Trans.*, 1979, 1415.
11 'Handbook of Chemistry and Physics,' 47th edn., ed. R. C. Weast, Chemical Rubber Co., Cleveland, Ohio, 1967.
12 S. Haussühl, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1961, **116**, 371.
13 N. Strupler, J. Cuillermet, J. Hoffelt, and F. Froment, *Bull. Soc. Chim. Fr.*, 1974, 1830.
14 J. A. Campbell, D. P. Ryan, and L. M. Simpson, *Spectrochim. Acta, Part A*, 1970, **26**, 2351.
15 H. H. Eysel and J. Eckert, *Z. Anorg. Allg. Chem.*, 1976, **424**, 68.
16 S. P. Best, R. S. Armstrong, and J. K. Beattie, *J. Chem. Soc., Dalton Trans.*, 1982, 1655.
17 S. P. Best, R. S. Armstrong, and J. K. Beattie, unpublished work.
18 T. W. Swaddle, *J. Chem. Soc., Chem. Commun.*, 1982, 832.
19 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

Received 13*th December* 1982; *Paper* 2/2082