Structural Studies on the Caesium Alums, $CsM^{III}[SO_4]_2{\cdot}12H_2O$ *

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Structure determinations of the caesium alums $CsM^{III}[SO_4]_2{\cdot}12H_2O$, M = V, Cr, Mn, Fe, Co, Al, Ga, or In, have been carried out at 295(1) K by *X*-ray diffraction methods. The data obtained include (*i*) M^{III}–O distances for the metals in the $[M(OH_2)_6]^{3+}$ species [V–O, 1.992(6); Cr–O, 1.959(3); Mn–O, 1.991(6); Fe–O, 1.995(4); Co–O, 1.873(5); Al–O, 1.877(3); Ga–O, 1.944(3); and In–O, 2.112(4) Å], (*ii*) an estimate of 1.3_4 Å for the effective co-ordinated radius for the water molecule in the cation, and (*iii*) the proposal of a new criterion for the classification of the different alum types, based on the disposition of the water molecules about the univalent cation.

In 1935, Lipson[1] reported that the structures of the alums $M^IM^{III}[SO_4]_2{\cdot}12H_2O$, all belonging to the same space group *Pa*3, could be disposed into three classes (at least), which he designated α, β, and γ. He noted that the alum type was related to the size of the univalent cation: whereas most alums had the α structure, those with large univalent cations such as caesium had the β structure, while the only example of the γ class, $NaAl[SO_4]_2{\cdot}12H_2O$, was found for the small sodium cation. These different structural types may be described and diffrentiated in terms of the disposition of the structural subunits along the three-fold crystallographic axis of the cubic unit cell. These subunits are the $[M^I(OH_2)_6]^+$ and $[M^{III}(OH_2)_6]^{3+}$ cations and the intervening SO_4^{2-} anion: the two metal ions, the sulphur, and one of the anion oxygen atoms lie on the three-fold axis. The trivalent metal-ion environment invariably comprises an octahedral array of six water molecules. In the unique γ alum, $NaAl[SO_4]_2{\cdot}12H_2O$, the sulphate ion is oriented with the single oxygen on the three-fold axis directed towards the univalent cation; in the α and β structures the sulphate ion is inverted, in some cases with disorder, along the three-fold axis, so that the three crystallographically equivalent oxygen atoms are directed toward the univalent cation. The distance of approach of these three oxygen atoms to the univalent cation varies between the two types: in the α alums the univalent metal ion is surrounded by 12 oxygen atoms, six from water molecules and six from two sulphate ions, defining an elongated icosahedron; whereas in the β alums the water molecules surrounding the univalent cation essentially lie in a plane normal to the three-fold axis and, together with the six sulphate oxygen atoms, define an approximately cuboctahedral array. Since the hole created by the 12 oxygens of a cuboctahedron is larger than the corresponding icosahedron, it is reasonable that the β-alum structure occurs with larger univalent ions than the α structure.

The co-ordination number of the univalent cation has been proposed as a criterion for distinguishing between α and β alums,[2] being six for the α alums (the six near water molecules) but expanded to 12 in the β alums where both water and sulphate oxygen atoms are quasi-equidistant from the central ion. This criterion suffers from the usual semantic difficulties of deciding when an atom is, or is not, co-ordinated. Since the absolute metal–oxygen distance will vary with the size of the univalent metal ion, the ratio of the metal–(sulphate)-oxygen to metal–(water)oxygen distance may perhaps be more appropriate. For the α alums hitherto studied, this ratio ranges from 1.2_0 to 1.2_9, for the β alums 1.0_3 to 1.0_5 (see below).

A number of observations, however, erode the general usefulness of such criteria. For example, the above ratio for the β methylammonium aluminium alum is 1.1_9; this alum, moreover, is found to be dimorphic,[3] as is its chromium analogue, suggesting that the size of the univalent cation is not the only determinant of the structure type. That this is not a peculiarity of the methylammonium cation is corroborated by the occurrence of sodium chromium alum in the α form,[4] in contrast with the sodium aluminium γ alum.

The question then arises whether perhaps there is a continuum of structures rather than distinct α and β types. The occurrence of dimorphism in the methylammonium alums of aluminium and chromium appears to refute this since it suggests two distinct energy minima, and attempts to distinguish between α and β types have been made by other physical measurements such as n.q.r.,[5] n.m.r.,[6] and e.s.r.[7] These attempts are not assisted by the relatively small number of β alums of proven structure which are known; the number of β alums assigned on the basis of early work using a limited number of reflections, some of which were considered as definitive of type,[8] has been greatly reduced by subsequent more definitive work.[9] In view of this, and because of the desirability of establishing a comprehensive array of $[M^{III}(OH_2)_6]^{3+}$ metal–oxygen distances, of which surprisingly few are available, it was decided to undertake a series of structure determinations on the caesium alums for as wide a range of trivalent ions as possible. The results are presented in this paper.

EXPERIMENTAL

Precise structure determinations are already available for the caesium aluminium[2] and titanium[10,†] alums, the

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* Discussion of alums in this paper is confined solely to sulphate anion systems.

† Note the atomic co-ordinate *x*/*a* of Ow(1) (ref. 10) should be negative.

TABLE 1

Crystallographic parameters for caesium alums $CsM[SO_4]_2\cdot 12H_2O$, (1)—(8) [a]

Compound	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
M	V	Cr	Mn	Fe	Co	Al	Ga	In
M	592.2	593.2	596.2	597.1	600.2	568.2	611.0	656.0
a/Å	12.452(10)	12.413(5)	12.432(8)	12.449(3)	12.292(8)	12.357(6)	12.419(3)	12.540(7)
U/Å^3	1 931(3)	1 912(1)	1 921(2)	1 930(1)	1 857(4)	1 887(3)	1 915(1)	1 972(2)
D_m/g cm^{-3}	2.03 [b]	2.06 [b]	2.05(1)	2.06 [b]	2.18(1)	1.97 [b]	2.12(1)	2.20(1)
D_c/g cm^{-3}	2.04	2.06	2.06	2.06	2.15	2.00	2.12	2.21
F(000)	1 176	1 180	1 184	1 188	1 192	1 136	1 208	1 280
μ_{Mo}/cm^{-1}	25.4	26.5	27.3	28.1	30.4	22.1	34.7	31.3
$2\theta_{max.}$/°	60	65	45	100	75	70	70	70
N	940	1 158	651	3 354	988	1 396	1 420	1 468
$N_o(3\sigma)$	385	536	341	818	302	622	596	517
R	0.041	0.033	0.045	0.050	0.047	0.043	0.030	0.034
R'	0.057	0.043	0.054	0.072	0.037	0.055	0.044	0.046

[a] For M = Ti, $M = 589.1$, $a = 12.45$ Å (23 °C, ref. 10). [b] 'Handbook of Chemistry and Physics,' 47th edn., Chemical Rubber Co., Cleveland, Ohio, 1967.

former being augmented by a neutron-diffraction study as well. Crystals of the vanadium, chromium, manganese, iron, and cobalt alums were prepared as described elsewhere.[11] Gallium and indium alums were prepared from (aqueous) equimolar solutions of the appropriate sulphates in 1 mol dm^{-3} H_2SO_4 and recrystallised from 1 mol dm^{-3} H_2SO_4.

Crystallography.—The following features are common to all structures; details specific to each compound are given in Table 1. In each case an approximately equidimensional (0.3—0.4 mm) (cub)octahedrally faceted single crystal was used for the analysis [exception: the vanadium compound, (1), in which a fragment from a larger crystal was used]. Data were obtained at 295 K within a preset $2\theta_{max.}$ limit (assessed from consideration of its probable extent and the anticipated longevity of the crystal) using Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers fitted with monochromatic Mo-K_α radiation sources ($\lambda = 0.7106_9$ Å) in conventional θ—2θ scan mode. (For the initial samples, full spheres of data to the specified limit were measured; in a number of cases, however, serious discrepancies were observed in 'equivalent' reflections, the deviations lying outside the range which could reasonably be compensated for by subsequent absorption correction. Previous work on the caesium titanium alum has demonstrated the occurrence of close twinning in that complex; although photographic examination of the diffractometer linewidths of the present specimens showed no macroscopic evidence for the presence of twinning, this may be the most likely explanation for the above inequivalences. In consequence unique data sets were used throughout, and it is likely that the thermal parameter standard deviations, at least, are unrealistically low. By contrast, the general consistency of the thermal parameters themselves throughout the whole range of compounds is good, suggesting that no serious errors in the series of structures generally result from the above anomaly.) N Independent reflections were obtained for each structure; N_o with $I > 3\sigma(I)$ were considered observed and used in the full-matrix least-squares refinement of the structure after absorption correction. All non-hydrogen atoms in all structures were refined with anisotropic thermal parameters. For the hydrogen atoms, (x,y,z) were refined, U_H being constrained at a value consistent with the thermal motion of the neighbouring oxygen atoms [exception: the manganese compound (3), in which (x,y,z) were constrained also at positions based on 'improved' difference map estimates]. Conventional residuals R,R' are quoted, reflection weights being set at $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral-atom scattering factors were employed (exception: Cs^+), corrected for anomalous dispersion (f',f'').[12] Computation was carried out using the 'X-RAY '76' program system.[13] Material deposited in Supplementary Publication No. SUP 23100 (57 pp.) * comprises structure factor amplitudes and thermal parameters.

No abnormal features were noted in the structures themselves: unlike some alums, there appears to be no disorder throughout the present series. In no case was any evidence found to suggest the space group to be other than the normal $Pa3(T_h^6$, no. 205). The crystal of (3) decomposed by some 15% during data collection, this being compensated for by appropriate scaling. Results are presented as atomic co-ordinates (Table 2) and interatomic geometries (Table 3). Atomic co-ordinates are derivative of those previously established for the $KAl[SO_4]_2\cdot 12H_2O$ α alum and the $CsTi[SO_4]_2\cdot 12H_2O$ β alum, being intended to bring both α and β types into as close a conformity as possible for the purposes of this paper.

RESULTS AND DISCUSSION

The structures of the caesium sulphate alums of V, Cr, Mn, Fe, Co, Al, Ga, and In^{III} have been determined by single-crystal X-ray diffraction studies; the structures of the titanium and aluminium derivatives have been previously determined, and the present redetermination of the latter is in substantial agreement with the earlier work. The structures are of interest from a number of aspects.

(1) *Structural Classification of Alums*.—The distinguishing feature of the γ alum, namely the orientation of the sulphate group, so that the oxygen which lies along the three-fold axis is directed toward the univalent cation is relatively unequivocal. None of the present series conforms to this category. A variety of other criteria have been suggested for distinguishing between α and β types and these are now examined in the light of the present work; the relevant data are given in Table 4. These data are based on information derived from the atomic parameters obtained from precise single-crystal studies and do not include criteria of other types which have been previously suggested, such as relative reflection intensity obtained in the powder pattern.

(*a*) A possibly general reliable criterion has seemed to us to be the sulphur atom fractional co-ordinate. For the

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

available precise structures of α alums, this is found to lie in the range 0.307_5—0.312_7, while for the β alums it is 0.327_6—0.332_9, the two structural types being characterized by two discrete narrow ranges. The present determinations extend the range for the β alums to 0.326_8—0.332_9, but the data point for the cobalt(III) alum is quite anomalous, lying midway between those for the α and β series, being 0.317_8.

TABLE 2

Atomic fractional cell co-ordinates for the caesium alums with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) Caesium vanadium alum (1)			
Cs	0.500 0(—) *	0.500 0(—) *	0.500 0(—) *
V	0.000 0(—) *	0.000 0(—) *	0.000 0(—) *
S	0.326 8(2)	0.326 8(2) *	0.326 8(2) *
O(1)	0.258 4(4)	0.258 4(4) *	0.258 4(4) *
O(2)	0.279 0(5)	0.337 0(5)	0.435 4(4)
O(a)	0.052 1(6)	0.210 9(6)	0.342 6(6)
H(a1)	0.018(9)	0.226(9)	0.297(11)
H(a2)	0.117(9)	0.222(8)	0.326(9)
O(b)	0.160 0(4)	−0.000 6(5)	−0.002 1(5)
H(b1)	0.208(9)	−0.056(8)	0.015(8)
H(b2)	0.215(8)	0.062(9)	−0.026(8)
(*b*) Caesium chromium alum (2)			
Cs	0.500 0(—) *	0.500 0(—) *	0.500 0(—) *
Cr	0.000 0(—) *	0.000 0(—) *	0.000 0(—) *
S	0.328 13(8)	0.328 13(8) *	0.328 13(8) *
O(1)	0.260 1(2)	0.260 1(2) *	0.260 1(2) *
O(2)	0.279 9(3)	0.338 5(3)	0.435 9(3)
O(a)	0.051 3(3)	0.213 0(3)	0.341 8(3)
H(a1)	0.019(5)	0.228(5)	0.289(6)
H(a2)	0.109(5)	0.217(4)	0.317(5)
O(b)	0.158 1(3)	−0.002 1(3)	0.000 0(3)
H(b1)	0.194(5)	−0.060(5)	0.007(4)
H(b2)	0.197(5)	0.050(5)	−0.015(4)
(*c*) Caesium manganese alum (3)			
Cs	0.500 0(—) *	0.500 0(—) *	0.500 0(—) *
Mn	0.000 0(—) *	0.000 0(—) *	0.000 0(—) *
S	0.327 9(2)	0.327 9(2) *	0.327 9(2) *
O(1)	0.260 0(4)	0.260 0(4) *	0.260 0(4) *
O(2)	0.280 7(5)	0.337 9(5)	0.435 1(4)
O(a)	0.051 5(5)	0.212 6(5)	0.341 6(5)
H(a1)	0.018(—)	0.226(—)	0.297(—)
H(a2)	0.117(—)	0.222(—)	0.326(—)
O(b)	0.160 1(4)	−0.002 3(4)	−0.000 4(5)
H(b1)	0.208(—)	−0.056(—)	0.015(—)
H(b2)	0.215(—)	0.062(—)	−0.026(—)
(*d*) Caesium iron alum (4)			
Cs	0.500 0(—) *	0.500 0(—) *	0.500 0(—) *
Fe	0.000 0(—) *	0.000 0(—) *	0.000 0(—) *
S	0.328 04(9)	0.328 04(9) *	0.328 04(9) *
O(1)	0.260 0(3)	0.260 0(3) *	0.260 0(3) *
O(2)	0.280 7(3)	0.337 9(3)	0.436 3(3)
O(a)	0.051 2(4)	0.211 8(4)	0.340 9(4)
H(a1)	0.009(5)	0.239(5)	0.272(6)
H(a2)	0.111(6)	0.211(6)	0.318(6)
O(b)	0.160 2(3)	−0.002 2(3)	−0.001 1(4)
H(b1)	0.209(6)	−0.068(7)	0.012(5)
H(b2)	0.202(7)	0.044(7)	−0.011(6)
(*e*) Caesium cobalt alum (5)			
Cs	0.500 0(—) *	0.500 0(—) *	0.500 0(—) *
Co	0.000 0(—) *	0.000 0(—) *	0.000 0(—) *
S	0.317 8(2)	0.317 8(2) *	0.317 8(2) *
O(1)	0.249 2(4)	0.249 2(4) *	0.249 2(4) *
O(2)	0.329 6(4)	0.269 0(4)	0.425 5(4)
O(a)	0.048 0(5)	0.150 8(6)	0.287 5(5)
H(a1)	0.111(7)	0.173(6)	0.287(7)
H(a2)	0.003(7)	0.196(8)	0.287(8)
O(b)	0.152 3(4)	0.000 6(4)	−0.005 7(4)
H(b1)	0.185(6)	0.026(6)	−0.066(6)
H(b2)	0.199(7)	0.013(6)	0.046(6)
(*f*) Caesium aluminium alum (6)			
Cs	0.500 0(—) *	0.500 0(—) *	0.500 0(—) *
Al	0.000 0(—) *	0.000 0(—) *	0.000 0(—) *
S	0.328 41(9)	0.328 41(9) *	0.328 41(9) *
O(1)	0.259 3(3)	0.259 3(3) *	0.259 3(3) *
O(2)	0.279 0(3)	0.340 3(3)	0.436 2(3)
O(a)	0.050 3(4)	0.215 2(3)	0.342 6(4)
H(a1)	0.010(6)	0.232(6)	0.277(7)
H(a2)	0.109(6)	0.225(6)	0.323(6)
O(b)	0.151 8(3)	−0.002 2(3)	−0.000 2(3)
H(b1)	0.198(6)	−0.051(6)	0.017(5)
H(b2)	0.187(6)	0.045(6)	−0.018(5)
(*g*) Caesium gallium alum (7)			
Cs	0.500 0(—) *	0.500 0(—) *	0.500 0(—) *
Ga	0.000 0(—) *	0.000 0(—) *	0.000 0(—) *
S	0.328 01(8)	0.328 01(8) *	0.328 01(8) *
O(1)	0.259 6(2)	0.259 6(2) *	0.259 6(2) *
O(2)	0.279 5(2)	0.338 8(2)	0.435 7(2)
O(a)	0.050 2(3)	0.213 3(3)	0.342 1(3)
H(a1)	0.013(4)	0.227(5)	0.272(5)
H(a2)	0.094(5)	0.215(5)	0.327(5)
O(b)	0.156 6(2)	−0.001 4(2)	−0.000 3(3)
H(b1)	0.202(4)	−0.054(4)	0.008(4)
H(b2)	0.202(4)	0.050(4)	−0.014(4)
(*h*) Caesium indium alum (8)			
Cs	0.500 0(—) *	0.500 0(—) *	0.500 0(—) *
In	0.000 0(—) *	0.000 0(—) *	0.000 0(—) *
S	0.327 1(1)	0.327 1(1) *	0.327 1(1) *
O(1)	0.259 4(3)	0.259 4(3) *	0.259 4(3) *
O(2)	0.280 9(4)	0.336 0(4)	0.434 6(3)
O(a)	0.052 4(4)	0.207 6(5)	0.340 1(5)
H(a1)	0.023(7)	0.226(7)	0.296 (8)
H(a2)	0.108(7)	0.212(7)	0.327(7)
O(b)	0.168 4(3)	−0.001 6(4)	−0.002 4(5)
H(b1)	0.197(6)	−0.043(6)	0.022(7)
H(b2)	0.216(6)	0.050(7)	−0.017(6)

*Parameters constrained by symmetry.

(*b*) A second possible criterion is the orientation of the regular octahedron of the water molecules co-ordinated to the trivalent metal ion relative to the crystal axes; the angles between the cubic axes of the octahedron and those of the crystal are given in Table 4. For the β alums, this angle was very small for previous examples (0.2—1.4°), while for the α alums, it lay between 7.5 and 10.5°. For the present examples, we find that all except the cobalt conform to the criterion for a β alum, within the range 0.2—1.0°; for the cobalt alum, the value of 2.2° indicates that, in terms of this criterion, it lies nearer the β-alum limit than that of the α type.

(*c*) The co-ordination environment of the univalent cation, and the elimination of its usefulness as a criterion by the methylammonium alum examples, has been described above; the data given in Table 4 for previously studied and present examples show that, for the present series (the cobalt alum excluded), the metal–oxygen distance ratio classifies the present series as β also, the range being extended to 1.0_3—1.0_6. Once again the cobalt alum is anomalous, the ratio of 1.0_9 observed lying well outside this range, and well below the range of the α alums (1.2_0—1.2_9).

(*d*) A further new criterion suggests itself which at least has the merit of succeeding in classifying the cobalt example, without disturbing the otherwise relatively well defined α and β categories suggested by the above criteria. If we consider the geometry of the six water molecules about the univalent cation, we find that 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. Hence in the β alums H_2O–M–OH_2 is almost exactly 60°, while in the α alums it is some 4—6° larger. For the β alums studied *in toto*, the angle lies in the 60.0—60.2° range; for the α alums it is 64.6—66.5° and this range includes the cobalt derivative (Table 4). On this basis, we thus classify the caesium cobalt sulphate alum as being of the α type.

TABLE 3

Co-ordination environments of $CsM[SO_4]_2\cdot12H_2O$.* Also included for comparison are the previously published data on the titanium(III) analogue, appropriately transformed

Compound M	Ti	(1) V	(2) Cr	(3) Mn	(4) Fe	(5) Co	(6) Al	(7) Ga	(8) In
(*i*) The sulphate group									
(*a*) Distances/Å									
S–O(1)	1.475(5)	1.476(3)	1.460(2)	1.461(3)	1.468(2)	1.460(4)	1.480(2)	1.472(2)	1.469(3)
S–O(2)	1.484(5)	1.482(6)	1.469(3)	1.462(6)	1.477(4)	1.460(5)	1.472(4)	1.473(3)	1.472(4)
(*b*) Angles/°									
O(1)–S–O(2)	109.6(3)	110.1(3)	109.9(2)	110.1(4)	110.2(2)	110.1(2)	109.9(2)	109.9(1)	110.2(2)
O(2)–S–O(2^{I})	109.3(3)	108.8(3)	109.0(2)	108.8(3)	108.8(2)	108.8(3)	109.0(2)	109.0(2)	108.7(3)
(*ii*) The metal, M									
(*a*) Distances/Å									
M–O(b)	2.028(5)	1.992(6)	1.959(3)	1.991(6)	1.995(4)	1.873(5)	1.877(3)	1.944(3)	2.112(4)
(*b*) Angles/°									
O(b)–M–O(b^{I})	90.3(2)	91.0(2)	90.7(2)	91.0(2)	91.2(2)	91.9(2)	90.9(2)	90.6(1)	91.3(2)
(*iii*) The caesium ion									
(*a*) Distances/Å									
Cs–O(2)	3.493(5)	3.513(6)	3.476(4)	3.485(6)	3.486(4)	3.646(5)	3.460(4)	3.485(3)	3.529(5)
Cs–O(a^{II})	3.314(5)	3.340(8)	3.349(4)	3.358(7)	3.359(5)	3.257(6)	3.352(5)	3.355(4)	3.351(6)
(*b*) Angles/°									
O(2)–Cs–O(2^{I})	40.5(1)	40.1(1)	40.27(8)	39.9(1)	40.3(1)	38.0(1)	40.54(9)	40.25(7)	39.6(1)
O(a^{II})–Cs–O(a^{III})		60.0(2)	60.01(10)	60.0(1)	60.0(1)	65.5(2)	60.03(11)	60.01(9)	60.0(1)
O(2)–Cs–O(a^{II})	64.4(1)	66.9(2)	67.13(9)	67.2(1)	66.8(1)	62.7(1)	67.49(9)	67.36(9)	66.4(1)
O(2)–Cs–O(a^{III})	79.3(1)	80.3(2)	80.15(9)	80.2(1)	80.1(1)	82.1(1)	79.99(10)	79.99(8)	80.7(1)
O(2)–Cs–O(a^{IV})		76.6(2)	76.22(9)	76.6(2)	76.7(1)	110.1(1)	75.37(11)	75.99(9)	77.9(1)
(*iv*) Water molecule a									
(*a*) Distances/Å									
O(a)–H(a1)		0.7(1)	0.79(7)	0.7(—)	1.06(7)	0.82(8)	0.98(8)	1.00(6)	0.71(10)
O(a)–H(a2)		0.8(1)	0.79(6)	0.8(—)	0.80(7)	0.79(9)	0.77(8)	0.58(6)	0.72(8)
(*b*) Angles/°									
H(a1)–O(a)–H(a2)		109(12)	97(6)	111(—)	101(6)	115(9)	101(7)	98(7)	108(10)
(*v*) Water molecule b									
(*a*) Distance/Å									
O(b)–H(b1)	1.0(1)	0.9(1)	0.85(6)	0.9(—)	1.03(8)	0.90(7)	0.86(7)	0.87(5)	0.70(8)
O(b)–H(b2)	1.0(1)	1.1(1)	0.83(6)	1.1(—)	0.79(8)	0.87(8)	0.76(7)	0.87(5)	0.90(8)
(*b*) Angles/°									
H(b1)–O(b)–H(b2)	118(9)	101(9)	113(6)	101(—)	102(8)	104(7)	104(7)	98(5)	106(8)
(*vi*) Hydrogen atoms (O · · · H, <2.0 Å)									
(*a*) Distances/Å									
H(a1) · · · O(2^{V})		[2.1(1)]	1.99(7)	[2.1(—)]	1.72(7)		1.80(8)	1.80(6)	[2.1(1)]
H(b1) · · O(a^{VI})	1.9(1)	1.7(1)	1.76(6)	1.7(—)	1.58(8)		1.74(7)	1.75(5)	1.93(8)
H(b2) · · · O(2^{VII})	1.6(1)	1.6(1)	1.83(6)	1.6(—)	1.88(8)		1.90(7)	1.80(5)	1.76(8)
(*b*) Angles/°									
O(a)–H(a1) · · · O(2^{V})					178(6)		173(7)	167(5)	
O(b)–H(b1) · · · O(a^{VI})	169(10)	177(9)	163(6)	175(—)	170(7)		177(7)	169(5)	165(9)
O(b)–H(b2) · · · O(2^{VII})	152(8)	171(9)	174(5)	173(—)	166(8)		177(8)	168(5)	165(7)

* Only independent values are given. Transformations of the asymmetric unit are: I z, x, y; II $z, \frac{1}{2} - x, \frac{1}{2} + y$; III $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; IV $\frac{1}{2} - y, 1 - z, \frac{1}{2} + x$; V $z - \frac{1}{2}, x, \frac{1}{2} - y$; VI $\frac{1}{2} - y, z - \frac{1}{2}, x$; VII $x, \frac{1}{2} - y, z - \frac{1}{2}$.

It is of interest to consider the relationship of the more obvious crystallographic parameters to the nature of the metal atoms involved and the type. In Table 5 we list the alums hitherto studied in terms of cell dimension and (*a*) univalent cation and (*b*) trivalent cation. If, within the series $M^{I}M^{III}[SO_4]_2\cdot12H_2O$, M^{III} is held constant we see that crystallographic *a* is strongly dependent on the univalent cation for a given alum type; there is also a considerable variation with M^{III} when M^{I} is held constant.

Figure 1 is a plot of *a* against M^{III}-OH_2 for the latter case and shows within the β alums a good linear dependence for the caesium alums. The point for the α-cobalt alum lies well off the line, indicating a more dense structure for this alum.

It is apparent from a comparison of the cobalt and aluminium alums, which differ only in the identity of the trivalent cation, that the factors which determine whether an alum has the α or β structure can be very subtle, since both display the same metal–oxygen bond lengths. The polymorphism arises from different hydrogen-bonding orientations required by the different atomic arrangements around the univalent cation. The cobalt-ion octahedron adopts the orientation typical of β alums. It accommodates the hydrogen-bonding pattern of the α-alum structure by a tilt in the plane of the water molecule co-ordinated to the trivalent metal ion. This produces an orientation of hydrogen bonds similar to that obtained by the reorientation of the complete $[M(OH_2)_6]^{3+}$ octahedra in other α alums. The reasons for these differences from the usual structures in the cobalt alum are not apparent, but they may be related to the $(t_{2g})^6$ electron density of the d^6 cobalt(III) ion, which could affect the orientation of the co-ordinated water molecule.

Finally, it should be noted that crystal morphology remains the most reliable simple guide to the classification of alum structures. In 1961, Haussühl [14] reported that the occurrence of a (210) face is typical of β alums and thereby classified the caesium cobalt alum as α, alone among the caesium sulphate alums. None of his classifications has yet proved incorrect. It will be interesting to test his predictions that both the potassium and rubidium vanadium alums and the rubidium titanium alum have the β structure, unlike the other alums with these univalent ions.

(2) M^{III}–O *Distances*.—Some of the M^{III}–O bond lengths given in Table 6 can be compared with those previously determined in other salts. They are in good agreement, indicating that the co-ordinate bond is not

TABLE 4

Criteria for the classification of α and β alums

Alum	Type	Fractional S co-ordinate	Ratio M^I–O(S) / M^I–O(W)	Angle/° To crystal axes	Angle/° O(W)–M^I–O(W)	Ref.
NaCr	α	0.310	1.26	8.21	65.8	*a*
KAl	α	0.3075	1.271	10.29	66.5	*b*
KCr	α	0.309	1.292	7.50	65.7	*c*
RbAl	α	0.3127	1.201	8.33	65.9	*b*
RbCr	α	0.312	1.22	7.95	64.6	*d*
NH_4Al	α	0.3092	1.254	9.10	66.3	*b*
$NMeH_3Al$	α	0.308	1.257	10.45	66.2	*e*
$NMeH_3Al$	β	0.3329	1.19	1.43	60.2	*f*
$NMeH_3Cr$	α	0.310	1.25	9.75	66.4	*g*
CsAl	β	0.3284	1.026	0.75	60.0	*h*
CsTi	β	0.3276	1.054	0.19	60.0	*i*
CsV	β	0.3268	1.052	0.78	60.0	*h*
CsCr	β	0.3281	1.037	0.76	60.0	*h*
CsMn	β	0.3279	1.038	0.83	60.0	*h*
CsFe	β	0.3280	1.032	0.88	60.0	*h*
CsCo	α	0.3178	1.092	2.16	65.5	*h*
CsGa	β	0.3280	1.039	0.52	60.0	*h*
CsIn	β	0.3271	1.063	0.98	60.0	*h*

[a] Ref. 4. [b] A. C. Larson and D. T. Cromer, *Acta Crystallogr.*, 1967, **22**, 793. [c] G. E. Bacon and W. E. Gardner, *Proc. R. Soc. London, Ser. A*, 1958, **246**, 78. [d] Ref. 9. [e] R. O. W. Fletcher and H. Steeple, *Acta Crystallogr.*, 1962, **15**, 960. [f] Y. Okaya, M. S. Ahmed, R. Pepinsky, and V. Vand, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1957, **109**, 367. [g] Ref. 3. [h] This work. [i] Ref. 10.

TABLE 5

Values of crystallographic *a* (Å) for those univalent–trivalent metal combinations for which full structure determinations of the alums $M^IM^{III}[SO_4]_2 \cdot 12H_2O$ are available [a]

	Na^+	K^+	Rb^+	Cs^+	$NMeH_3^+$	Other
Al^{3+}	12.21$_3$ [b]	**12.15$_7$** [c,d]	**12.24** [c,d]	*12.35$_7$* [c,e]	**12.17**, [f] *12.50* [f]	**12.24$_0$** [f] (NH_4^+)
Ga^{3+}				*12.41$_9$* [e]		
In^{3+}				*12.54$_0$* [e]		
Ti^{3+}				*12.39$_3$**, [g] *12.45* [g]		
V^{3+}				*12.45$_2$* [e]		
Cr^{3+}	**12.40** [h]	**12.17*** [i]	**12.30** [j]	*12.41$_3$* [c]	**12.44** [g] *12.52* [j,k]	*12.24* [j] (Tl^+)
Mn^{3+}				*12.43$_2$* [e]		
Fe^{3+}				*12.44$_9$* [e]		
Co^{3+}				**12.29** [e]		

[a] Values for α alums are in bold type, β alums in italics; the remainder are γ alums. An asterisk denotes a low-temperature (liquid nitrogen) value. [b] D. T. Cromer, M. I. Kay, and A. C. Larson, *Acta Crystallogr.*, 1967, **22**, 182. [c] Ref. 14. [d] See footnote *b*, Table 4. [e] This work. [f] See footnote *e*, Table 4. [g] Ref. 10. [h] Ref. 4. [i] A. H. C. Ledsham, H. Steeple, and W. Hughes, *Acta Crystallogr., Sect. B*, 1970, **26**, 1240. [j] Ref. 9. [k] Ref. 3.

TABLE 6

Calculation of radius of water co-ordinated in $M(OH_2)_6$ (high-spin *d* electron configurations of Mn^{3+}, Fe^{3+}, Mn^{2+}, Fe^{2+}, and Co^{2+}, low-spin of Co^{3+})

Metal ion	Effective ion radius/Å [a]	M–OH$_2$ distance/ Å	Effective OH$_2$ radius/Å	Ref.
Al^{3+}	0.535	1.877(3)	1.342	*b*
Ti^{3+}	0.670	2.028(5)	1.358	*c*
V^{3+}	0.640	1.992(6)	1.352	*b*
Cr^{3+}	0.615	1.959(3)	1.344	*b*
Mn^{3+}	0.645	1.991(6)	1.346	*b*
Fe^{3+}	0.645	1.995(4)	1.350	*b*
Co^{3+}	0.545	1.873(3)	1.328	*b*
Ga^{3+}	0.620	1.944(3)	1.324	*b*
In^{3+}	0.800	2.112(4)	1.312	*b*
Mn^{2+}	0.830	2.173(2) (av.)	1.343	*d*
Fc^{2+}	0.780	2.123(6) (av.)	1.343	*e*
Co^{2+}	0.745	2.081(1)	1.336	*f*
Ni^{2+}	0.690	2.047(1)	1.357	*f*
Zn^{2+}	0.740	2.078(1)	1.338	*f*

[a] Ref. 19. [b] This work. [c] Ref. 10. [d] H. L. Carrell and J. P. Glucker, *Acta Crystallogr., Sect. B*, 1973, **29**, 638. [e] J. Strouse, S. W. Layten, and C. E. Strouse, *J. Am. Chem. Soc.*, 1977, **99**, 562. [f] S. Ray, A. Zalkin, and D. H. Templeton, *Acta Crystallogr., Sect. B*, 1973, **29**, 2741.

strongly affected by the structure of the lattice. The Al–O distance of 1.877(3) Å is identical with that of 1.880(4) Å found in $[Al(OH_2)_6][RuCl_6]\cdot4H_2O$.[15] The Cr–O distance of 1.959(3) Å is nearly identical with that of 1.965(2) Å found in $[NH_4]_2[Cr(OH_2)_6]F_5$.[16] The Fe–O distance of 1.995(4) Å is identical with that of 1.986(7) Å found in $[Fe(OH_2)_6][NO_3]_3\cdot3H_2O$.[11] We are unaware of precisely determined structures containing the hexa-aquametal(III) ions of V, Co, Ga, or In with which to make similar comparisons. There is an estimate of the In–O distance from *X*-ray scattering by a 3 mol dm^{-3} indium perchlorate solution; the value of 2.15(3) Å[17] is in reasonable agreement with the distance of 2.112(4) Å found in the caesium alum.

The variation of M^{III}–O distance with *d*-electron configuration follows the expected pattern (Figure 2). A decrease in distance occurs from Ti^{III} (d^1) through V^{III} (d^2) to Cr^{III} (d^3) as the σ-non-bonding t_{2g} orbitals are occupied. An increase occurs from Cr^{III} through Mn^{III} (d^4) to Fe^{III} (d^5) as the σ-antibonding e_g* orbitals are filled. Note that the high-spin d^4 $[Mn(OH_2)_6]^{3+}$ occurs in a $\bar{3}$ symmetry environment presumably consistent with dynamic Jahn–Teller distortion at the 295 K temperature of the crystal-structure determination, although there is no evidence of exceptionally large thermal parameters. Finally, there is a sharp decrease between high-spin d^5 Fe^{III} and low-spin d^6 Co^{III}. In fact, the Co^{III}–O distance could almost be predicted by extrapolation from the $(t_{2g})^1$—$(t_{2g})^3$ distances. In addition, the Sc^{III}–O distance is predicted to be 2.07 Å by extrapolation back to the d^0 configuration. Combined with the unit-cell dimension (12.51 Å) this implies that the caesium scandium alum[18] has the β structure (Figure 1).

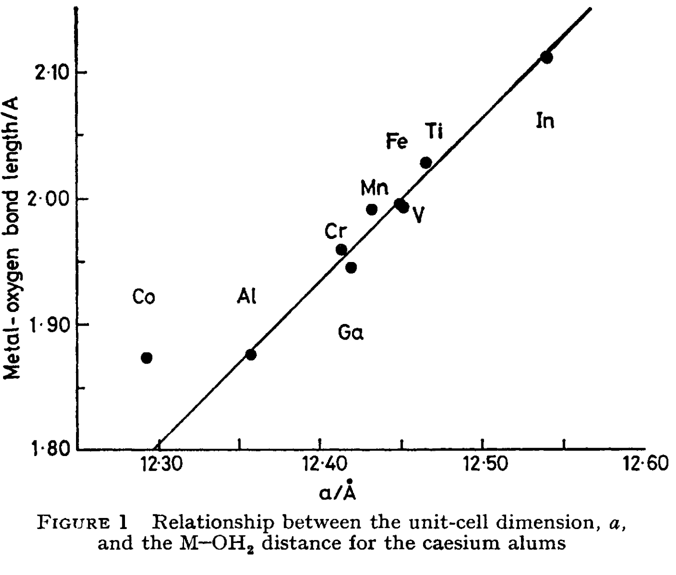

FIGURE 1 Relationship between the unit-cell dimension, *a*, and the M–OH$_2$ distance for the caesium alums

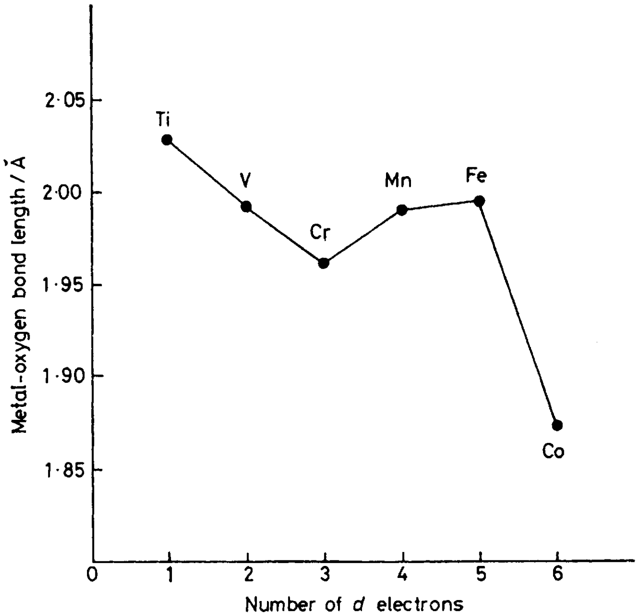

FIGURE 2 Variation in M–OH$_2$ distance with the number of *d* electrons for the caesium–transition-metal alums

(3) *Estimate of the Water Molecule Radius.*—An estimate of the effective co-ordinated radius of the water molecule can be made using the metal-ion radii of Shannon and Prewitt,[19] revised by Shannon.[20] These radii were determined by assuming a radius of 1.40 Å for oxygen in oxide structures. From the data assembled in Table 6 for hexa-aquametal-ion structures it can be seen that the radius of the water ligand is almost constant at 1.34 Å, 0.06 Å smaller than the oxide ion. Furthermore, the same radius is observed in $[M(OH_2)_6]^{3+}$ and $[M(OH_2)_6]^{2+}$ species, indicating that the effect of oxidation state is the same for the water molecule as for the oxide ions used to derive the metal-ion radii.

The original purpose of this work was to examine the effect of a change in oxidation state on metal–water bond lengths.[21] Between Co^{II} $(t_{2g})^5(e_g{}^*)^2$ and Co^{III} $(t_{2g})^6$ this difference is 21 pm. This reflects a change in the occupation of the σ-antibonding e_g* orbitals by two electrons. Between Mn^{II} $(t_{2g})^3(e_g{}^*)^2$ and Mn^{III} $(t_{2g})^3(e_g{}^*)^1$ the difference is 18 pm, reflecting a change in only one $e_g{}^*$ electron. Between Fe^{II} $(t_{2g})^4(e_g{}^*)^2$ and Fe^{III} $(t_{2g})^3(e_g{}^*)^2$ the difference is 13 pm, reflecting a change in only one t_{2g}, σ-non-bonding, electron. Hence the major part of the difference in metal–water bond lengths is due to the change in oxidation state, independent of the nominal occupancy of the $e_g{}^*$ orbitals.

This point can also be illustrated by a comparison of the bond lengths for metal ions with the same number of *d* electrons in the two oxidation states. For the high-spin d^5 ions, $(t_{2g})^3(e_g{}^*)^2$, the manganese(II)–water bond is 18 pm larger than the iron(II)–water bond. For the d^6 ions Fe^{II} and Co^{III} the difference is 25 pm, which includes a spin-state change between $(t_{2g})^4(e_g{}^*)^2$ and $(t_{2g})^6$.

Hence the spin-state change of two $e_g{}^*$ electrons is estimated to produce a bond-length change of only 7 pm for $M(OH_2)_6$ complexes. This is less than observed in spin-equilibrium complexes containing the FeN_6 co-ordination sphere, which reflects the fact that, for weak-field ligands such as H_2O, the one-electron distinction between t_{2g} and $e_g{}^*$ orbitals is less valid. For the same reason there is a substantial change in both lengths between oxidation states in all $M(OH_2)_6$ complexes, regardless of the nominal change in occupancy of the $e_g{}^*$ orbitals, since all of the *d* electrons in these weak-field complexes have some antibonding character.

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

[1/388 *Received, 9th March,* 1981]

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