Stereochemistry of Tervalent Aqua Ions: Low-temperature Neutron Diffraction Structures of $CsFe(SO_4)_2{\cdot}12H_2O$ and $CsFe(SeO_4)_2{\cdot}12H_2O$ †

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The structures of $CsFe(SO_4)_2{\cdot}12H_2O$ and $CsFe(SeO_4)_2{\cdot}12H_2O$ have been investigated by neutron diffraction at 15 K. Both alums crystallise in the cubic space group *Pa*3, *Z* = 4, with *a* = 12.354(6) Å for the sulphate and 12.593(10) Å for the selenate. The structures were refined using 802 [$CsFe(SO_4)_2{\cdot}12H_2O$] and 1 059 [$CsFe(SeO_4)_2{\cdot}12H_2O$] inequivalent reflections to give weighted *R* factors of 0.029 and 0.028 respectively. In agreement with prior *X*-ray crystallographic determinations, $CsFe(SO_4)_2{\cdot}12H_2O$ gives the β alum modification whereas $CsFe(SeO_4)_2{\cdot}12H_2O$ forms an α alum. The stereochemistry of water co-ordination to Fe^{III} differs in the two alums, with the angle between the metal(III)–water bond and the plane of the co-ordinated water molecule being 0.6(10)° for the sulphate and 18.6(10)° for the selenate. This tilting of the plane of the co-ordinated water molecule is shown to be related to the alum type. The iron(III)–water bond distance shows some sensitivity to the tilt of the co-ordinated water molecule, lengthening from 1.994(1) to 2.002(1) Å as the plane of the water molecule is tilted by 18.6°. The sensitivity of the alum type to the size of the constituent ions, and to the stereochemistry of water co-ordination to the tervalent cation, is discussed in light of the hydrogen bonding in the alum structures.

Owing to the predominance of water as a solvent in studies of transition-metal complexes, and given their thermodynamic and kinetic characteristics, metal–water bonding lies at the heart of co-ordination chemistry. On one level the bonding can be described using simple electrostatic models, with the variation of the hydration energies of the first-row bi- and ter-valent transition-metal cations providing one of the most clear demonstrations of the utility of crystal-field theory for the *d*-block elements.[1] A variety of other characteristics of the system are similarly well explained using simple crystal-field arguments, for example, metal–water bond lengths[2] and force constants[3] as well as the general features of the magnetism and *d–d* electronic spectra of the transition-metal aqua ions.[4] However it is increasingly clear that the deviations from the simple electrostatic bonding model do influence observable properties of these complex ions in many ways which are not easily rationalised. The mechanism of water self exchange as deduced from volumes of activation[5] and the intensities of the band arising from the $\nu_1(MO_6)$ vibrational mode[3] do not vary according to the charge/radius ratio of the metal ion as might be expected within the simple electrostatic picture. Further, the neutron diffraction structure of $[V(OH_2)_6][H_5O_2][CF_3SO_3]_4$ which has V^{III} on a low symmetry site (C_i) reveals that the overall symmetry of $[V(OH_2)_6]^{3+}$ is high and is approximately *all horizontal* D_{3d}.[6] In keeping with the Jahn–Teller prediction, this lowering of the symmetry of the complex from octahedral results in an orbital singlet ground term for the d^2 case (^3A_g). That a similar structure for the $[V(OH_2)_6]^{3+}$ ion is found in the caesium sulphate alum lattice[7] suggests that the metal ion may exercise a stereochemical preference for the orientation of the co-ordinated water molecule. In view of these observations it is important to characterise metal–water bonded species structurally, as well as spectroscopically, so that the influence of the electronic structure of the metal on the stereochemistry and stereochemical preference for water co-ordination can be identified. Owing to the poor *X*-ray scattering cross-section of hydrogen, these studies demand the application of neutron-scattering techniques. Surprisingly, neutron structural information for the tervalent hexa-aqua cations has been limited to Al,[8,9] V,[6,7] Cr,[10] and Rh,[7] with the structures for Al and Cr being of limited quality. There is a clear need to extend the range of structures for which high quality is available and further to have available structures of the same cation in a variety of different crystal environments.

The alums $M^IM^{III}(XO_4)_2{\cdot}12H_2O$ (X = S or Se) provide an excellent vehicle for the study of tervalent hexa-aqua cations, both because of the range of tervalent cations that can be accommodated in the lattice (M^{III} = Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Mo, Ru, Rh, and Ir when M^I = Cs and X = S) and for the ability of the structure to adapt to different stereochemistries of water co-ordination about M^{III}. The alums are known to exist in three different structural modifications, designated α, β, and γ, with the alum type being largely dependent on the relative sizes of the constituent ions. A description of the α- and β-alum structures is given in ref. 2. When the univalent cation is small, *e.g.* K or Rb, or the anion is large, *e.g.* SeO_4, α alums predominate, and alternatively β alums occur when the univalent cation is large, *e.g.* Cs, and the anion is sulphate. Dimorphism is known to occur for the methylammonium sulphate alums of aluminium[11] and chromium.[12] Moreover, for a given univalent cation and anion α or β alums may result depending on the identity of the tervalent cation. In such cases it is not the size of the tervalent cation which is responsible for the structure since examples of the expected structure occur with tervalent cations of both larger and smaller size. For the caesium sulphate alums, the α modification occurs where the water bonded to M^{III} adopts a trigonal pyramidal mode of water co-ordination[7,13] and the β modification occurs where the more usual trigonal planar mode of water co-ordination is found.

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† *Supplementary data available* (No. SUP 56768, 2 pp.): thermal parameters for $CsFe(SO_4)_2{\cdot}12H_2O$ and $CsFe(SeO_4)_2{\cdot}12H_2O$. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Data collection and analysis parameters *

	$CsFe(SO_4)_2{\cdot}12H_2O$	$CsFe(SeO_4)_2{\cdot}12H_2O$
M	597.0	690.7
a/Å	12.354(6)	12.593(10)
U/Å^3	1 885.5(10)	1 997.0(16)
Total no. reflections	2 194	4 700
No. unique reflections	940	1 122
No. used in refinement	802	1 059
Final R factor (F)	0.043	0.043
Weighted R factor (F)	0.029	0.028
Goodness of fit	2.08	1.89

* Data common to both determinations: space group = $Pa\bar{3}$; sample temperature = 15.0(1) K; λ = 0.847 5(3) Å; maximum (sin θ/λ) = 0.8 Å^{-1}; no. of variables = 73.

Indeed, a feature of all the available neutron structures is the adoption of trigonal planar water co-ordination to M^{III} for the β alums[7,9] and trigonal pyramidal water co-ordination to M^{III} for the α alums.[7,8,10]

We report the results of single-crystal neutron diffraction studies on $CsFe(SO_4)_2{\cdot}12H_2O$ and $CsFe(SeO_4)_2{\cdot}12H_2O$. This includes the first structural determination of the $[Fe(OH_2)_6]^{3+}$ cation by neutron diffraction. *X*-Ray structure determinations of caesium selenate alums have recently been performed[14] and these indicate that the general stuctural features of the sulphate α alums are preserved in the caesium selenate alums. Thus the differences in the environment about the tervalent aqua ions in the α and β sulphate alums are likely to apply in the two crystals under study. No other neutron studies of caesium selenate alums have been reported so it is of interest to establish the nature of water co-ordination to M^{III} and also to examine the hydrogen bonding of this type of alum. We have chosen to study the caesium iron alums in particular, since the electron density about the tervalent cation is spherical (high-spin d^5 electron configuration). Further, $[Fe(OH)_2)_6]^{3+}$ is of interest on account of its surprisingly low pK_a and the importance of the Fe^{3+}–Fe^{2+} self-exchange reaction in the development of electron-transfer theories.[15] Since $[Fe(OH_2)_6]^{3+}$ has an orbitally non-degenerate ground term ($^6A_{1g}$), these crystals are also well suited for subsequent study by polarised neutron diffraction, leading to a determination of the spin density and bonding within the complex ion. The interpretation of the polarised neutron spin-dependent Bragg intensities relies heavily on the availability of accurate structural parameters such as are provided by these experiments.

Experimental

The caesium iron alums were prepared by methods described in the literature [$CsFe(SO_4)_2{\cdot}12H_2O$,[16] $CsFe(SeO_4)_2{\cdot}12H_2O$[3]]. Large single crystals were grown from solutions of sulphuric or selenic acid (1 mol dm^{-3}) by the controlled deposition onto a suspended seed. Both alums give rise to pale violet crystals of octahedral form, but with varying degrees of edge and corner truncation.

Alums crystallise in the space group $Pa\bar{3}$, which is retained to helium temperatures. The neutron diffraction data were collected using the D9 diffractometer on the hot source of the reactor at the Institut Laue–Langevin, Grenoble, France. The enhanced flux of higher-energy neutrons allowed us to work at a wavelength of 0.847 5(3) Å, which we were subsequently able to show gave little extinction in our crystals. All measurements were made at 15.0(1) K to reduce the effects of thermal vibration. Table 1 contains details of data collection for both the sulphate and selenate alums.

A crystal of $CsFe(SeO_4)_2{\cdot}12H_2O$ (33 mg) of octahedral form was wrapped in greased aluminium foil before mounting in the two-stage Displex refrigerator of the four-circle diffractometer. After cooling to 15 K, centring and determining the crystal orientation matrix, integrated intensity measurement was carried out in three stages. Following a preliminary check that good equivalence could be obtained from groups of five out of six of a number of axial reflections, rapid scans of 1.3 min duration were made on a set of reflections in one octant of reciprocal space, with a standard reflection being monitored every fifty reflections. These data were reduced using the minimum $\sigma I/I$ method[17] and those with $\sigma I/I > 0.06$ re-measured, increasing the monitor count used to determine the duration of each step in the scan by a factor of two for reflections with $0.06 < \sigma I/I < 0.33$ and by a factor of five for those with $\sigma I/I > 0.33$. A total of 4 700 measurements were made, out to a (sin θ)/λ limit of 0.8 Å^{-1} and absorption corrections were applied using routines from the Cambridge Crystallographic Subroutine Library (C.S.S.L.), which gave transmission factors differing by not more than 3%. 1 059 Inequivalent reflections of the 1 122 measured were positive by more than one standard deviation, derived from their differences from the mean, and these structure factors were used in a weighted ($1/\sigma^2$) least-squares refinement, also within C.S.S.L., to derive the 73 independent variables of the atomic positional and thermal parameters and a scale factor in the Becker–Coppens Lorentzian form of extinction correction.[18] The domain radius was fixed at a large value and the refined value for the mosaic spread of 0.19(3) × 10^{-4} rad showed that the extinction was very small. Isotropic thermal parameters were used for Cs and Fe. The final R factor (F) was 0.043 with a goodness of fit χ^2 of 1.89. The weighted R factor (sum of squares of weighted differences/sum of weighted observed structure factors) was 0.028. Table 2 contains the atomic co-ordinates of both the selenate and the sulphate alums, together with their standard deviations. Thermal parameters have been deposited as supplementary material (SUP 56768).

A similar procedure was used to obtain data from an approximately equi-axed crystal of $CsFe(SO_4)_2{\cdot}12H_2O$ (16.8 mg). A total of 2 194 measurements were reduced to 940 inequivalent reflections with 802 positive by at least σ, extending to the same limit of (sin θ)/λ of 0.8 Å^{-1}. The final R factor (F) was 0.043 with χ^2 of 2.08 and a weighted R factor of 0.029. The mosaic spread parameter was again very small [0.157(7) × 10^{-4} rad].

The improvement in R factor produced by modelling the extinction and allowing anisotropic thermal parameters on atoms other than hydrogen is significant. For example, without these parameters the selenate R factor is 0.056 with a χ^2 of 4.2.

Discussion

Selected bond lengths and angles for the caesium iron sulphate and selenate alums are given in Table 3. The atom connectivities are the same for both salts and are independent of the alum type. In general there is good agreement between the room-temperature structures and those obtained in this work; however, for the selenate there are unexpectedly large discrepancies in the Se–O and Fe–O bond distances. On cooling $CsFe(SO_4)_2{\cdot}12H_2O$ from room temperature to 15 K a decreases from 12.499(3)[2] to 12.354(6) Å. For the selenate the corresponding reduction of a is negligible [12.615(5)[14] to 12.593(10) Å]. The difference in temperature dependence of a is likely to arise from differences in the α and β alum structures, with the volume of the α structure (which is more dense for a given set of constituent ions[2]) being much less temperature dependent than that of the β structure. It is important to note that the volume reduction of the sulphate on lowering the temperature is largely

Table 2. Atomic fractional cell co-ordinates for $CsFe(XO_4)_2 \cdot 12H_2O$

	X = Se			X = S		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cs	0.500 00	0.500 00	0.500 00	0.500 00	0.500 00	0.500 00
Fe	0.000 00	0.000 00	0.000 00	0.000 00	0.000 00	0.000 00
X	0.316 33(4)	0.316 33	0.316 33	0.327 90(15)	0.327 90	0.327 90
O(1)	0.241 02(5)	0.241 02	0.241 02	0.259 00(7)	0.259 00	0.259 00
O(2)	0.319 48(5)	0.269 22(5)	0.438 11(5)	0.280 87(7)	0.335 80(8)	0.437 55(7)
O(a)	0.048 68(6)	0.142 61(5)	0.294 48(6)	0.053 12(8)	0.208 80(8)	0.341 29(8)
H(1a)	0.004 12(12)	0.204 04(11)	0.278 20(12)	0.009 98(15)	0.229 51(17)	0.278 49(15)
H(2a)	0.120 63(11)	0.169 94(12)	0.287 27(13)	0.127 26(14)	0.220 56(17)	0.318 52(16)
O(b)	0.158 43(5)	0.008 97(6)	−0.009 86(5)	0.161 37(7)	−0.002 18(8)	−0.000 33(9)
H(1b)	0.207 71(11)	0.024 34(11)	0.051 29(11)	0.209 28(15)	−0.064 11(15)	0.022 47(16)
H(2b)	0.195 70(11)	0.028 67(12)	−0.076 78(10)	0.205 41(15)	0.060 20(15)	−0.022 76(16)

Table 3. Bond lengths (Å) and angles (°) which characterise the co-ordination environments of $CsFe(XO_4)_2 \cdot 12H_2O$ *

	$CsFe(SO_4)_2 \cdot 12H_2O$		$CsFe(SeO_4)_2 \cdot 12H_2O$	
(*i*) XO_4^{2-}				
X–O(1)	1.474(3)	[1.468(2)]	1.643(1)	[1.628(3)]
X–O(2)	1.477(3)	[1.477(4)]	1.645(1)	[1.632(5)]
O(1)–X–O(2)	109.9(2)	[110.2(2)]	110.1(1)	[110.5(2)]
O(2)–X–O(2)	109.0(2)	[108.8(2)]	108.8(1)	[108.4(2)]
(*ii*) $[Fe(OH_2)_6]^{3+}$				
Fe–O(b)	1.994(1)	[1.995(4)]	2.002(1)	[1.989(4)]
O(b)–Fe–O(b)	90.9(1)	[91.2(2)]	90.5(1)	[90.8(2)]
(*iii*) Cs^+				
Cs–O(2)	3.470(1)	[3.486(4)]	3.771(1)	[3.795(5)]
Cs–O(a)	3.306(1)	[3.359(5)]	3.209(1)	[3.227(5)]
O(2)–Cs–O(2′)	40.6(1)	[40.3(1)]	41.5(1)	[40.8(1)]
O(a)–Cs–O(a)	60.0(1)	[60.0(1)]	66.2(1)	[66.2(1)]
O(2)–Cs–O(a)	66.1(1)	[66.8(1)]	58.8(1)	[59.7(1)]
O(2)–Cs–O(a′)	77.4(1)	[76.7(1)]	71.1(1)	[81.6(1)]
O(2)–Cs–O(a″)	80.2(1)	[80.1(1)]	81.4(1)	[82.6(1)]
(*iv*) Water molecules				
O(a)–H(1a)	0.975(3)	[1.06(7)]	0.974(2)	[0.80(–)]
O(a)–H(2a)	0.969(3)	[0.80(7)]	0.977(2)	[0.66(–)]
O(b)–H(1b)	1.007(3)	[1.03(8)]	1.008(2)	[1.05(–)]
O(b)–H(2b)	0.983(3)	[0.79(8)]	0.996(2)	[0.97(–)]
H(1a)–O(a)–H(2a)	104.3(2)	[101(6)]	103.6(2)	[112(–)]
H(1b)–O(b)–H(2b)	110.4(2)	[102(8)]	108.0(2)	[99(–)]
(*v*) Hydrogen bonds				
H(1a) ··· O(2)	1.788(3)	[1.72(7)]	1.778(2)	
H(2a) ··· O(1)	1.848(3)		1.854(2)	
H(1b) ··· O(a)	1.592(3)	[1.58(8)]	1.616(2)	
H(2b) ··· O(2)	1.667(3)	[1.88(8)]	1.655(2)	
O(a)–H(1a) ··· O(2)	174.1(2)	[178(6)]	170.4(2)	
O(a)–H(2a) ··· O(1)	170.5(2)		163.9(2)	
O(b)–H(1b) ··· O(a)	176.1(2)	[170(7)]	175.4(2)	
O(b)–H(2b) ··· O(2)	178.9(2)	[166(8)]	174.0(2)	

* The values in square brackets were obtained from room-temperature *X*-ray studies of $CsFe(SO_4)_2 \cdot 12H_2O$ [2] and $CsFe(SeO_4)_2 \cdot 12H_2O$.[14]

accommodated by a reduction of the Cs–O(a) distance [3.359(5) to 3.306(1) Å].

The co-ordination sphere about caesium is markedly different in the two structures and reflects the α and β alum types. The twelve oxygens about the caesium cation define a cubo-octahedron in the case of $CsFe(SO_4)_2 \cdot 12H_2O$ and an icosahedron in the structure of $CsFe(SeO_4)_2 \cdot 12H_2O$ (Figure 1). Thus for the sulphate the O(a)–Cs–O(a) angle is 60.0(1)°, indicative of

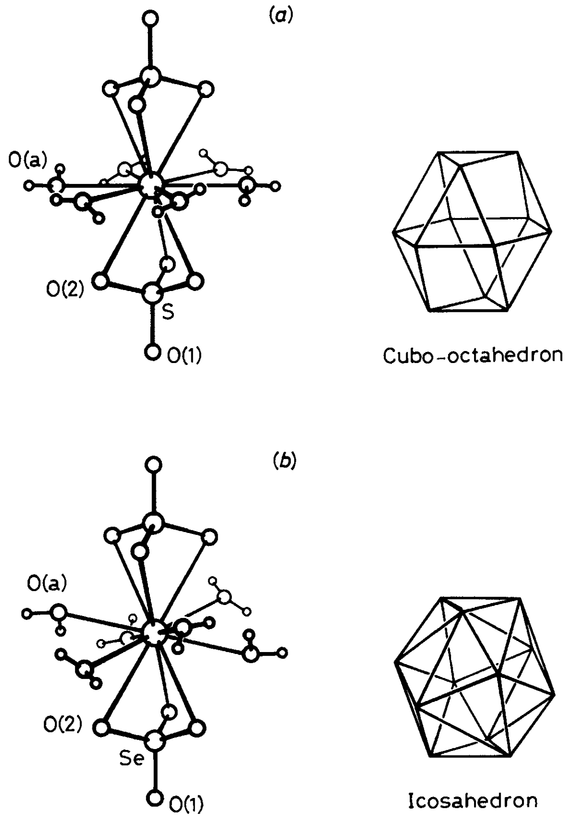
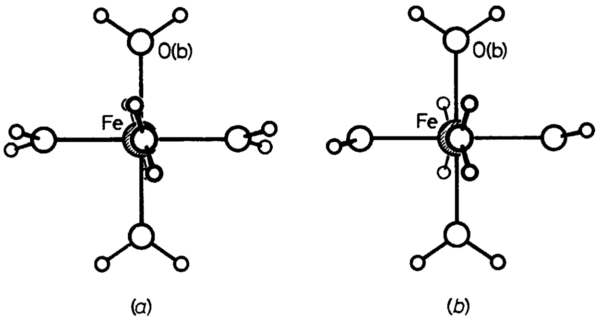


Figure 1. Co-ordination environment about Cs^I in the caesium iron sulphate (*a*) and selenate (*b*) alums



(*a*) (*b*)

Figure 2. The $[Fe(OH_2)_6]^{3+}$ species in the caesium iron sulphate (*a*) and selenate (*b*) alums

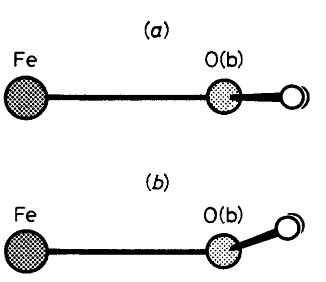


Figure 3. The stereochemistry of the metal–water bond in the caesium iron sulphate (*a*) and selenate (*b*) alums

the water molecules lying in a plane while for the selenate the corresponding angle is 66.2(1)°, *i.e.* in the range expected for the α alums.[2] While this feature of the structure provides the most clear distinction between the α and β alum structures, it is by no means clear how the stereochemistry of water co-ordination to M^{III} leads to one of the structures being favoured over the other. We consider this point later. The Cs–O(2) and Cs–O(a) bond lengths depend on the alum, with the ratio $[r_{Cs-O(2)}/r_{Cs-O(a)}]$ increasing on selenate (1.18) for sulphate (1.05) substitution. This variation is partly due to the differences in the alum type and partly due to the different sizes of the two anions. It is clear from the large temperature dependencies of the caesium to oxygen bond lengths that they are more sensitive to hydrogen bonding than to Cs–O interactions. On examination of the structural parameters which characterise the α and β alum type, it is clear that the classification of caesium iron selenate to the α alum type is appropriate. Indeed, in terms of the relationship between the constituent ions in the lattice, the structures of the sulphate α alums and the caesium iron selenate alum are remarkably similar, an observation in keeping with the single-crystal Raman spectra of caesium sulphate α alums and caesium selenate alums.[19]

The $[Fe(OH_2)_6]^{3+}$ cations occur on sites of S_6 symmetry in both the sulphate and selenate alums with the FeO_6 octahedron closely aligned with the crystallographic axes in the sulphate alum (as is expected for the β alums) but inclined by 4.8(1)° in the selenate alum (which is less than that generally observed for α alums,[2] 7.5—10.5°). The unique O–Fe–O angle is close to 90° in both structures. The main difference between the two ions is the positions of the hydrogen atoms with respect to the FeO_6 octahedron (Figure 2). For the sulphate the Fe–O bond vector is contained within the HOH plane whereas an 18.6° angle is obtained for the selenate (Figure 3). Further, for the sulphate there is a twist of the plane of the co-ordinated water molecule about the Fe–O bond which takes the symmetry of the cation from T_h towards D_{3d}. The Fe–O bond lengths differ by 0.008(2) Å, being 1.994(1) Å in the sulphate and 2.002(1) Å in the selenate. Although this difference may reflect the dependence of the Fe–O bond length on the stereochemistry of water co-ordination, we note that at room temperature the Fe–O bond lengths are within experimental uncertainty for the sulphate and selenate alum (Table 3) and also that $\nu_1(FeO_6)$ occurs at the same wavenumber in both $CsFe(SO_4)_2{\cdot}12H_2O$ and $CsFe(SeO_4)_2{\cdot}12H_2O$ (80 K).[3] In both structures the hydrogen bonds involving the hydrogens of the water molecule co-ordinated to the tervalent cation are the strongest in the lattice, *i.e.* they have the longest O–H bond lengths and the shortest O···O distances. These hydrogen bonds are approximately linear and give rise to OH stretching vibrations at *ca.* 2 750 and *ca.* 3 100 cm^{-1}.[20] The strength of these hydrogen bonds are dependent on the metal, but not on the metal–water bond length, *i.e.* for the aluminium alums the $Al-OH_2$ bond is shorter than the $Fe-OH_2$ bond yet the OH bond lengths are also shorter when M^{III} = Al.

It is clear from Table 3 that the positions of the hydrogen atoms obtained in the *X*-ray studies are so subject to error as to be of very limited use in defining the hydrogen bonding in the crystal or the orientation of the water molecules with respect to either the uni- or ter-valent cations. The relationship between the four hydrogen bonds in the asymmetric unit of the unit cell is shown in Figure 4. The influence of the highly polarising tervalent cation on its co-ordinated water molecule is to make the hydrogens more acidic and the hydrogen bonds thus formed comparatively strong. These strong hydrogen bonds are intimately involved with the atoms which comprise the co-ordination sphere of the univalent cation (Figure 4) and provide the link between the orientation of water molecules co-ordinated to the tervalent cation and the alum type. It is important to note that, on cooling the crystal, it is the Cs–O bond distances which show the greatest temperature dependence and not the hydrogen bonds involving O(b): thus the directional properties of the hydrogen bonds determine the co-ordination environment about the caesium cation. Since both the Cs and Fe atoms lie along the unit-cell axes, the tilt of the tervalent hexa-aqua cation or of the co-ordinated water molecules with respect to the unit-

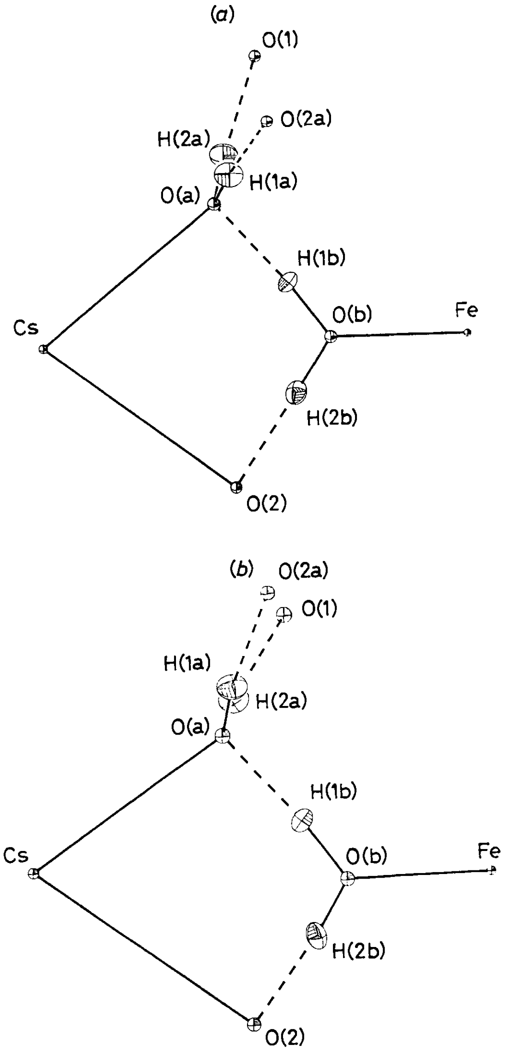


Figure 4. The relationship between the four hydrogen bonds in the asymmetric unit of the caesium iron sulphate (*a*) and selenate (*b*) alums

cell axes alters the co-ordination environment about caesium. The link between the tilt of the $M^{III}O_6$ octahedron with respect to the unit-cell axes, the co-ordination geometry of water about M^{III}, and the alum type is well demonstrated by the structures of the caesium sulphate α alums where the required co-ordination about Cs is achieved by the combination of a large tilt (*ca.* 35°) of the water molecule co-ordinated to the tervalent cation and a small (*ca.* 2°) inclination of the $M^{III}O_6$ cation to the unit-cell axes.[7] For the α alums of K, Rb, or NH_3 the corresponding co-ordination about M^I is obtained by a smaller tilt of the plane of the co-ordinated water molecule (*ca.* 18°) and larger tilt of the tervalent hexa-aqua cation relative to the unit-cell axes (*ca.* 9°).[8] Thus the observation of α/β dimorphism among the alums for a given univalent cation is due to the tervalent cation exerting some preference for the geometry of water co-ordination. Therefore the minimum in the potential-energy surface for tilting the plane of the water molecule against the metal–water bond or the twisting of the water molecule about the metal–water bond occurs at an angle which is metal dependent, and the slope of this surface is sufficient to influence or even determine the lowest-energy hydrogen-bonding arrangement in the crystal. This observation is contrary to expectations based on an electrostatic model of the bonding where the ligand (water) is treated as a point charge.

We are not prepared, at this stage, to discuss the role played by covalency in the stereochemistry and bonding of tervalent hexa-aqua cations. However, studies of a series of transition-metal bivalent hexa-aqua cations in ammonium Tutton salts, $(NH_4)_2M^{II}(SO_4)_2{\cdot}6H_2O$, have shown that their covalency is weak but that it can be determined from the spatial distribution of their aligned paramagnetism at low temperatures and in an applied magnetic field. The polarised neutron diffraction measurements of V^{2+}, Mn^{2+}, and Ni^{2+} are modelled with 3*d*, 4*s*, and 4*p* orbitals on the transition metal, (sp^2) hybrid orbitals on the oxygen, a 1*s* orbital on hydrogen, and a Gaussian function to represent metal–oxygen overlap density.[21–23] A consistent qualitative picture emerges which is in accord with the varying t_{2g} and e_g configurations: V^{2+} and Mn^{2+} have t_{2g} populations and substantial in-plane π spin delocalisation in diffuse metal and O–H bond orbitals, Ni^{2+} and Mn^{2+} have e_g populations but σ transfer of spin in an antibonding orbital and the density in diffuse metal orbitals and oxygen lone pairs is less. Similar measurements have already been made on the iron(II) Tutton salt by Figgis *et al.*[24] and we are engaged in a parallel determination of the magnetisation density in one of our iron(III) alums. These latter experiments should allow us to quantify the variation in covalency which accompanies a change in the cation valency and to estimate its significance.

Conclusions

The acquisition of high-quality neutron data on $CsFe(SO_4)_2{\cdot}12H_2O$ and $CsFe(SeO_4)_2{\cdot}12H_2O$ has enabled us to characterise fully the $[Fe(OH_2)_6]^{3+}$ cation in environments which are similar in terms of the identity and basicity of their hydrogen-bonding partners, but different in terms of the spatial arrangement of these partners. It is found that some distortion of the co-ordination geometry occurs as a result of the different spatial arrangement of the hydrogen bonds and that this takes the form of tilting the plane of the co-ordinated water molecule by 18.6° from the trigonal planar arrangement and a slight lengthening of the Fe–O bond [0.008(2) Å]. The co-ordinated water molecules are themselves perturbed with long O–H bonds and involvement in comparatively strong hydrogen bonds. The average O–H bond length for the waters co-ordinated to Fe^{III} is 0.995(3) Å (sulphate) and 1.002(2) Å (selenate), this being longer than that found for Al^{III} [0.988(7) Å][8] or V^{III} [0.985(4) Å],[6] and differs from the expected order based on the $M–OH_2$ bond lengths (where $r_{Al–O} < r_{V–O} < r_{Fe–O}$).

The structure of the caesium selenate alum lattice has been determined for the first time using neutron techniques. This lattice exhibits the same general features as the sulphate α alum lattice of K, Rb, and NH_4. In particular, the directional character of the hydrogen bonding is accommodated by a tilt of the tervalent hexa-aqua cation by *ca.* 5° with respect to the unit-cell axes and a tilt of the plane of the water co-ordinated to M^{III} by *ca.* 18° from the trigonal planar arrangement.

Acknowledgements

We thank the Institut Laue–Langevin for the time made available on the D9 diffractometer, Professors B. N. Figgis and J. K. Beattie for helpful discussions and for access to preprints of papers relevant to this work, and the referees for several helpful suggestions.

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Received 23*rd January* 1989; *Paper* 9/00377K