Influence of the Stereochemistry of Water Co-ordination to Metal(III) Cations on the M–O Bond Length and Electronic Structure of the Cation *

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The structures of $CsM(SO_4)_2 \cdot 12D_2O$ (M = Mo or Ru) have been determined at 15 K using neutron-diffraction techniques. The structures, which both conform to the β-alum modification, were refined using 607 (Mo) and 501 (Ru) unique reflections to give final *R* factors of 0.013 and 0.016 respectively. The Mo–O and Ru–O bond lengths of 2.094(1) and 2.010(1) Å respectively are in agreement with previous studies. The metal(III)–water bond lengths of second-row transition-metal aquaions are more sensitive to the stereochemistry of water co-ordination than are their first-row counterparts. For both molybdenum and ruthenium the stereochemisty of water co-ordination to M^{III} is trigonal planar with a small, but significant, difference of the angle between the plane of the water molecule and the MO_6 framework [−19.7(1)° for Mo^{III} and −22.0(2)° for Ru^{III}]. These results are shown to be in keeping with predictions based on the occupancy of the t_{2g} (O_h) orbitals. There are minimal structural differences between $CsRu(SO_4)_2 \cdot 12H_2O$ and its deuteriated analogue, an observation which supports the use of either set of structural data for the interpretation of physical measurements on alums.

High-quality neutron-diffraction results for a variety of tervalent hexaaqua cations[1–4] have revealed subtle differences in the stereochemistry of water co-ordination which can be ascribed to the metal–ligand interaction.[4] This may involve a tilt of the plane of the co-ordinated water relative to the M–O bond vector or, more subtly, a variation in the angle, φ, of the plane of the co-ordinated water molecule relative to the MO_6 framework (Fig. 1).[1,4–6] Since the metal–ligand interaction involves both σ and π contributions, with the latter being different in and out of the plane of the water molecule, the metal–ligand bond length ought to be sensitive to the stereochemistry of water co-ordination. To our knowledge no experimentally based examination of these effects has been conducted, presumably owing to the paucity of good-quality neutron-diffraction results from hydrates. We maintain that the available structural data of sufficient accuracy, in conjunction with the results for $CsMo(SO_4)_2 \cdot 12D_2O$ and $CsRu(SO_4)_2 \cdot 12D_2O$ presented herein, demonstrate that the M^{III}–O bond length depends on the stereochemistry of the M^{III}–O sub-unit for second-row but not first-row transition metals and that the interrelationship between electronic and molecular structure is well demonstrated by the structural chemistry of tervalent hexaaqua cations.

Experimental

Solutions of $[Mo(OH_2)_6]^{3+}$ are air sensitive and subject to oligomerisation leading to intensely coloured solutions. All manipulations of such solutions were conducted under an amtosphere of argon, and at as low a temperature as experimentally feasible. Caesium molybdenum sulfate alum was prepared by the hydrolysis of sodium hexakis(formato)molybdate(III) in [$^2H_1$]toluene-*p*-sulfonic acid (2 mol dm^{-3}) followed by the addition of a stoichiometric quantity of caesium sulfate.[7] Pale yellow crystals of $CsMo(SO_4)_2 \cdot 12D_2O$ were isolated in moderate yield (up to *ca.* 70%). We were unable to eliminate completely oligomerisation at this stage and the solutions were strongly coloured. Large single crystals of $CsMo(SO_4)_2 \cdot 12D_2O$ were grown from [$^2H_1$]toluene-*p*-sulfonic acid (1 mol dm^{-3}) using a thermal gradient technique in which the lower part of the apparatus, containing the polycrystalline solid, was held at 15 °C, while the upper part, in which a seed crystal was suspended, was maintained at 2 °C. A slow stream of argon was passed through a sintered-glass frit in the bottom of the apparatus so as to maintain a low partial pressure of oxygen. The compound $CsRu(SO_4)_2 \cdot 12H_2O$ was prepared according to the method outlined in the literature.[3] Crystals of $CsRu(SO_4)_2 \cdot 12D_2O$ were obtained from the hydrated salt by multiple recrystallisations from D_2SO_4 (1 mol dm^{-3}). The crystal used in the diffraction experiment was obtained from Professor J. K. Beattie, Sydney University.

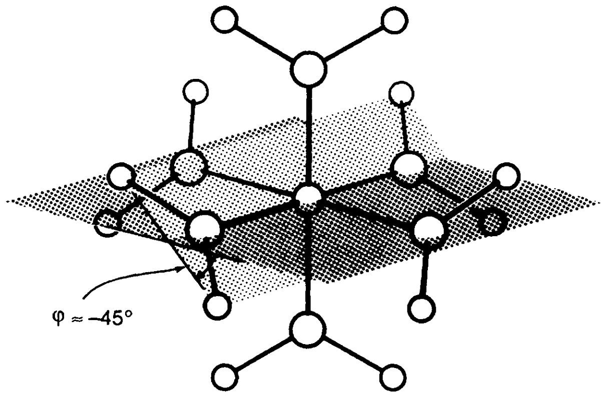

Fig. 1 Definition of the angle, φ, for a metal hexaaqua cation on a site of S_6 symmetry when viewed down the three-fold axis

The structures of $CsMo(SO_4)_2 \cdot 12D_2O$ and $CsRu(SO_4)_2 \cdot 12D_2O$ were determined using data collected on the D9 four-circle diffractometer at the Institut Laue Langevin, Grenoble. Its position at the hot source enabled us to use a relatively short wavelength of 0.8344(4) Å to reduce any extinction and we benefited from the presence of a small position-sensitive

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* *Non-SI unit employed:* f = 10^{-15} m.

Table 1 Data collection and analysis parameters[a]

	$CsMo(SO_4)_2\cdot 12D_2O$	$CsRu(SO_4)_2\cdot 12D_2O$
Formula weight	661.0	666.1
Sample weight/mg	41	35
Crystal size/mm	*ca* 2.5 × 3 × 3	*ca* 2 × 2.5 × 4.5
a/Å	12.436(3)	12.380(3)
U/Å^3	1923.3(10)	1897.9(10)
D_c/g cm^{-3}	2.28	2.33
Maximum (sin θ/λ)/Å^{-1}	0.85	0.80
Total no. reflections	1768	1260
No. unique reflections	609	514
No. used in refinement	607	501
Scattering length (H/D)/f	6.21(1)	6.53(2)
% Deuterium	95.5(2)	98.6(3)
φ^b/°	−19.7(1)	−22.0(2)
$R(F)$	0.013	0.016
$R'(F)$	0.012	0.016
Goodness of fit (χ^2)	1.67	1.30
$R(F^2)$, χ^2 on repeated measurements	1.5, 3.2	2.3, 5.1
$R(F^2)$, χ^2 on equivalent measurements	2.0, 5.3	1.8, 2.4
Maximum shift/e.s.d.	0.39 × 10^{-3}	0.32 × 10^{-3}
Average shift/e.s.d.	0.81 × 10^{-4}	0.83 × 10^{-4}

[a] Details in common: sample temperature 15.0(1) K; space group $Pa\bar{3}$; λ 0.8344(3) Å; number of variables 74; $R = \Sigma|F_o - |F_c||/\Sigma F_o$; $R' = \Sigma w|F_o - |F_c||/\Sigma w^{\frac{1}{2}}F_o$; $\chi^2 = [\Sigma w(F_o - |F_c|)^2/(M - N)]^{\frac{1}{2}}$, where N = number of reflections used in the refinement, M = number of parameters refined. [b] Defined in Fig. 1.

Table 2 Atomic fractional cell coordinates, isotropic (B_{iso}) and anisotropic thermal parameters*

Atom	x	y	z	B_{iso}	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
(*a*) $CsMo(SO_4)_2\cdot 12D_2O$										
Cs	0.500 00	0.500 00	0.500 00	0.27(1)						
Mo	0.000 00	0.000 00	0.000 00	0.26(1)						
S	0.327 37(7)	0.327 37	0.327 37		0.23(2)			0.01(2)		
O(1)	0.258 58(4)	0.258 58	0.258 58		0.51(1)			−0.08(1)		
O(2)	0.281 58(4)	0.333 37(4)	0.436 94(4)		0.58(1)	0.50(1)	0.35(1)	0.03(1)	0.16(1)	0.06(1)
O(a)	0.054 25(4)	0.205 60(4)	0.340 22(4)		0.56(2)	0.64(2)	0.45(1)	−0.04(1)	0.00(1)	0.01(1)
D(a1)	0.010 58(5)	0.227 63(5)	0.279 15(5)		1.17(2)	1.72(2)	1.01(2)	0.06(1)	−0.30(1)	0.13(2)
D(a2)	0.127 59(5)	0.218 74(5)	0.317 03(5)		0.82(2)	1.78(2)	1.40(2)	−0.01(2)	0.10(1)	−0.05(1)
O(b)	0.168 40(3)	−0.001 97(4)	−0.001 15(4)		0.30(1)	0.49(1)	0.85(1)	0.19(1)	0.01(1)	0.01(1)
D(b1)	0.215 25(5)	−0.062 82(4)	0.022 38(5)		0.90(2)	0.96(2)	1.41(2)	0.20(1)	−0.04(1)	0.19(1)
D(b2)	0.211 84(5)	0.060 60(4)	−0.023 37(5)		0.92(2)	0.94(2)	1.49(2)	0.21(1)	0.09(1)	−0.19(1)
(*b*) $CsRu(SO_4)_2\cdot 12D_2O$										
Cs	0.500 00	0.500 00	0.500 00	0.25(2)						
Ru	0.000 00	0.000 00	0.000 00	0.32(2)						
S	0.326 48(12)	0.326 48	0.326 48		0.22(3)			0.02(3)		
O(1)	0.257 32(6)	0.257 32	0.257 32		0.50(2)			−0.09(2)		
O(2)	0.278 98(6)	0.334 05(6)	0.435 50(6)		0.64(3)	0.52(2)	0.34(2)	0.02(2)	0.11(2)	0.11(2)
O(a)	0.053 24(6)	0.209 01(6)	0.343 20(6)		0.61(3)	0.67(2)	0.45(2)	−0.02(2)	−0.01(2)	−0.03(2)
D(a1)	0.009 10(7)	0.229 00(7)	0.281 32(7)		1.25(3)	1.81(3)	1.07(3)	0.08(2)	−0.36(2)	0.08(3)
D(a2)	0.126 81(7)	0.220 26(8)	0.318 33(7)		0.87(3)	1.82(3)	1.49(3)	0.02(2)	0.08(2)	−0.03(2)
O(b)	0.162 33(6)	−0.000 44(7)	−0.002 36(8)		0.37(2)	0.76(2)	1.67(3)	0.72(3)	0.00(2)	0.01(2)
D(b1)	0.208 53(7)	−0.061 35(7)	0.022 90(7)		0.97(3)	1.14(3)	1.45(3)	0.26(2)	−0.05(2)	0.16(2)
D(b2)	0.204 91(7)	0.061 77(7)	−0.027 13(7)		0.97(3)	1.02(3)	1.60(3)	0.30(2)	0.09(2)	−0.22(2)

* Thermal parameters are in units of Å^2.

gas-filled multidetector which gives better precision in the integrated intensities of weak peaks. The reflections were measured using an omega scan and their intensities were extracted using the program RETREAT.[8] The standard deviations in the observed moduli of the structure factors were estimated from the agreement among equivalents, generally two or three in number, or the counting statistics whichever was highest. The merging R factors (on F^2) for equivalent reflections were 2.0 (Mo) and 1.8 (Ru) with corresponding values of 1.5 (Mo) and 2.3 (Ru) for repeated measurements, including a standard reflection measured every 30 reflections. This indicates a general level of precision achievable and was taken as the limit of accuracy in cases where no equivalents were measured. The weighted ($1/\sigma^2$) least-squares refinement (Cambridge Crystallographic Subroutine Library[9]) converged to give excellent final R and weighted R factors. However the values of χ^2 for both refinements remained at 3.0 (Mo) and 4.1 (Ru). Examination of the observed and calculated structure factors showed that for weak reflections the values of the observed structure factors were systematically greater than calculated such as would be expected if multiple scattering were significant. An estimate of the average contribution due to this effect was made from some 20–30 weak reflections in both cases and subtracted from all observed reflections and their estimated standard deviations (e.s.d.s) were also modified to take account of the standard deviation of the estimated average multiple scattering correction. Reflections with a resultant negative intensity were rejected. Final refinements gave χ^2 values of 1.67

Table 3 Bond lengths (Å) and angles (°) which define the co-ordination environments

	$CsMo(SO_4)_2 \cdot 12X_2O$		$CsRu(SO_4)_2 \cdot 12X_2O$	
	X = D	H[a]	X = D	H[b]
(*i*) $SO_4{}^{2-}$				
S–O(1)	1.482(2)	1.478(1)	1.483(2)	1.482(2)
S–O(2)	1.479(2)	1.478(1)	1.475(2)	1.475(2)
O(1)–S–O(2)	109.8(1)	109.83(5)	109.6(2)	109.7(1)
O(2)–S–O(2)	109.1(1)	109.11(8)	109.4(2)	109.2(1)
(*ii*) $[M(OX_2)_6]^{3+}$				
M–O(b)	2.094(1)	2.089(1)	2.010(1)	2.0143(7)
O(b)–M–O(b)	91.1(1)	91.00(6)	91.0(1)	90.85(3)
(*iii*) Cs^+				
Cs–O(2)	3.505(1)	3.509(1)	3.514(1)	3.5127(6)
Cs–O(a)	3.308(1)	3.311(1)	3.301(1)	3.2982(6)
O(2)–Cs–O(2′)	40.2(1)		40.1(1)	40.0(1)
O(a)–Cs–O(a′)	60.0(1)	60.02(4)	60.0(1)	60.0(1)
O(2)–Cs–O(a)	65.6(1)		66.6(1)	66.6(1)
O(2)–Cs–O(a′)	78.6(1)		77.2(1)	77.3(1)
O(2)–Cs–O(a″)	80.5(1)	80.49(3)	80.3(1)	80.3(1)
(*iv*) Water molecules				
O(a)–X(a1)	0.973(1)	0.68(4)	0.973(2)	0.972(2)
O(a)–X(a2)	0.970(1)	0.75(4)	0.971(2)	0.972(2)
O(b)–X(b1)	0.999(1)	0.75(3)	0.997(2)	1.002(2)
O(b)–X(b2)	0.987(1)	0.80(3)	0.982(2)	0.983(2)
X(a1)–O(a)–X(a2)	104.2(1)	101(5)	103.9(2)	104.0(2)
X(b1)–O(b)–X(b2)	111.1(1)	110(4)	112.5(2)	112.6(2)
(*v*) Hydrogen bonds				
X(a1) ··· O(2)	1.802(1)		1.804(2)	1.800(2)
X(a2) ··· O(1)	1.851(1)		1.842(2)	1.837(2)
X(b1) ··· O(a)	1.606(1)		1.606(2)	1.597(2)
X(b2) ··· O(2)	1.654(1)		1.646(2)	1.646(2)
O(a)–X(a1) ··· O(2)	174.1(1)	170(4)	174.0(1)	173.9(3)
O(a)–X(a2) ··· O(1)	171.4(1)	173(3)	171.2(1)	171.1(3)
O(b)–X(b1) ··· O(a)	176.8(1)	176(3)	174.1(1)	174.5(3)
O(b)–X(b2) ··· O(2)	178.2(1)	175(3)	177.9(2)	177.5(3)

[a] Obtained from an X-ray diffraction study of $CsMo(SO_4)_2 \cdot 12H_2O$ at 110 K.[6] [b] Obtained from a neutron diffraction study of $CsRu(SO_4)_2 \cdot 12H_2O$ at 15 K.[3]

(Mo) and 1.30 (Ru). In neither case was the resultant structure affected by the application of the multiple scattering correction, although for the ruthenium salt the *R* factors and e.s.d.s were significantly improved by application of the correction. A single scattering length for the deuterium sites was allowed to vary in the refinement; the extent of deuterium substitution was then obtained using the known scattering lengths of hydrogen (−3.741 fermi) and deuterium (6.674 fermi).[10]

For both salts the unit-cell dimensions were derived from the UB matrix generated from the program RETREAT. The UB matrix was calculated using the centroids of approximately 60 strong reflections covering the full range of sin θ/λ. The quoted uncertainty in the unit-cell dimension takes into account the uncertainty in the incident wavelength. A summary of the data collection and analysis parameters is given in Table 1 and the atomic fractional cell coordinates and thermal parameters are assembled in Table 2.

Results and Discussion

The salts $CsM(SO_4)_2 \cdot 12D_2O$ (M = Mo or Ru) have structures typical of the β-alum modification which has previously been described.[2,11] The general features of the structures of the two salts are in close agreement with previous structural investigations[3,6] as is apparent by comparison of the bond lengths and angles which define the co-ordination environments (Table 3). Moreover, perusal of Table 3 shows that no significant structural changes are evident as a consequence of the exchange of hydrogen by deuterium in the alum lattice, at least for the ruthenium salt for which a low-temperature neutron-diffraction structure of the hydrate is available. This observation is in keeping with inferences drawn from the effects of deuteriation on the Raman spectra of the alums[12] and supports the use of either set of structural data (hydrate or deuteriate) for the analysis of physical measurements on alums.

Whereas the variation of the metal(III)–water bond lengths with electron configuration has been discussed previously,[11] the stereochemistry of water co-ordination has not been taken into account. The values of the metal–oxygen bond length, $r(M^{III}\text{–}O)$, of tervalent hexaaqua cations in the alum lattice are given in Fig. 2, with the data limited to the most precise structural determinations available (Al,[11] Ti,[13] V,[14] Cr,[4] Mn,[11] Fe,[2] Co,[11] Ga,[11] Mo, Ru,[3] Rh,[15] In,[11] Ir[15]). For the first-row transition metals, increasing occupancy of the t_{2g} orbitals leads

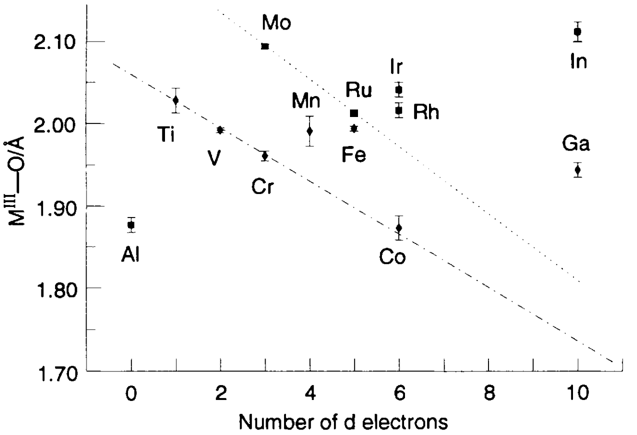

Fig. 2 The dependence of the metal(III)–oxygen bond length on the number of d electrons in the valence shell for $[M(OH_2)_6]^{3+}$ in the alum lattice. Error bars are drawn at the 3 e.s.d. limit

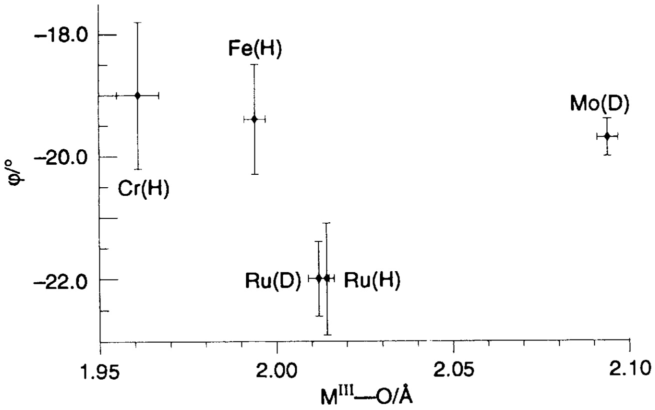

Fig. 3 Relationship between the twist angle of the plane of the co-ordinated water molecule to the MO_6 axes (φ) and the metal(III)–oxygen bond length. Error bars are drawn at the 3 e.s.d. limit

to a regular decrease in the metal–water bond length, *viz.* the $r(M^{III}–O)$ values for titanium (t_{2g}^1), vanadium (t_{2g}^2), chromium (t_{2g}^3) and cobalt (t_{2g}^6) define a straight line (Fig. 1). Further, the deviation from this relation is related to the occupancy of the e_g orbitals, *viz.* the deviation for iron ($t_{2g}^3e_g^2$) is half that of Ga ($t_{2g}^6e_g^4$). Whereas these observations are in close agreement with predictions based on crystal-field theory, the adherence of cobalt to this relationship is surprising since the hexaaqua ion has a different structure, with the plane of the co-ordinated water molecule inclined by approximately 35° to the Co–O bond vector.[16] For the remainder of the first-row transition metals and Group 13 cations the structural data have been obtained from β-alums where the corresponding angle is 0 ± 2°. For these cations the metal(III)–water bond length is insensitive to the tilt of the co-ordinated water molecule, a conclusion supported by the observation that the imposition of a tilt angle of 18.6° for water co-ordinated to iron (as is induced by exchanging sulfate for selenate in the caesium alum lattice) is associated with a small change in the r(Fe–O) value [0.008(2) Å].[2] Recent neutron-scattering experiments conducted on electrolyte solutions containing chromium(III)[17] are also consistent with the strength of the chromium–water interaction being insensitive to the stereochemistry of water co-ordination. Neutron diffraction experiments on aqueous solutions of chromium(III) perchlorate (2.2 mol dm^{-3}) give the tilt of the plane of the co-ordinated water molecule as 34 ± 6° and a Cr–O bond distance of 1.98(2) Å.[17] Whereas the uncertainty of the r(Cr–O) value is too high to permit useful comparison, the frequency of the totally symmetric stretching mode of $[Cr(OH_2)_6]^{3+}$, $\nu_1(CrO_6)$, obtained from Raman spectra of a range of crystals and of solutions of chromium(III) salts has values which are closely related.[12] Since the frequency of $\nu_1(MO_6)$ is simply related to the M–O force constant, the similarity of $\nu_1(MO_6)$ for the range of different tilt angles for water co-ordinated to chromium(III) also implies an insensitivity of the metal–ligand force constant to the stereochemistry of water co-ordination.

Of the second-row transition metals only molybdenum, ruthenium and rhodium are known to give well defined tervalent hexaaqua cations. For the purpose of estimating the relationship between the occupancy of the t_{2g} orbitals and r(M–O) we limit consideration to molybdenum and ruthenium since in these cases trigonal-planar water co-ordination pertains and accurate structural data are available. The gradient of this relation is greater than that found for the first-row transition metals, an observation in keeping with the greater radial extent of the 4 d than 3 d orbitals. For rhodium the Rh–O bond vector is inclined by 35° to the plane of the co-ordinated water molecule and the r(Rh–O) value deviates from that predicted by in excess of 15 e.s.d.s.[18] Indeed, the r(Rh–O) value is not significantly different from that of ruthenium, contrary to expectations based on the variation of the size of the cation as the period is traversed. Since it is clearly the case that the caesium sulfate alum lattice can accommodate cations both larger and smaller than rhodium the r(Rh–O) value reflects the metal–ligand interaction. Both the observed stereochemistry of water co-ordination and the r(Rh–O) value are likely to be related to the fact that the t_{2g} orbitals are completely filled for rhodium(III) with concomitant loss of stabilisation of the trigonal-planar co-ordination geometry by d_π–p_π bonding. Hence the failure of the first-row transition-metal cations to exhibit sensitivity of r(M–O) to the tilt of the plane of the co-ordinated water molecule and/or the complete occupancy of the t_{2g} orbitals suggests that, in those cases, d_π–p_π bonding is comparatively unimportant. The variation of the sensitivity of r(M–O) to the tilt angle of the co-ordinated water molecule represents a striking difference between the properties of the first-row transition metals and their heavier congeners. It is perhaps significant that no examples of α-alums of molybdenum or ruthenium have yet been isolated (including our own recent attempts), since in these cases a tilting of the plane of the water molecule co-ordinated to M^{III} leads to a disruption of the d_π–p_π interaction and this has a significant effect on the bonding. This barrier to a change in the stereochemistry of water co-ordination is not significant for first-row or Group 13 metals.

For $CsMo(SO_4)_2·12D_2O$ the close agreement between the neutron and X-ray coordinates for the hydrate[6] indicate that the positions of the heavy atoms are little changed on cooling the crystal from 110 to 15 K. Further, it is clear that the analysis of high-quality X-ray diffraction data sets, even when these are measured at low temperatures, fails to locate the hydrogen atoms with sufficient accuracy for structural evaluation [*cf.* φ = −22(3)° for the high-quality X-ray study at 110 K [6]]. The MoO_6 fragment of the $[Mo(OD_2)_6]^{3+}$ cation has approximate O_h symmetry although the molybdenum site symmetry is only $S_6(\bar{3})$. For the purpose of this report the key structural parameter is φ, which is −19.7(1)° for $[Mo(OD_2)_6]^{3+}$ and −22.0(2)° for $[Ru(OD_2)_6]^{3+}$. These values must be compared with those available from other low-temperature neutron-diffraction structures of caesium sulfate β-alums, *viz.* −19.0(4) for Cr,[4] −19.4(3) for Fe[2] and −22.0(3)° for Ru.[3] The new and more reliable values obtained for the deuteriated salts confirm that the observed φ values fall into two groups, the first in the range −19 to −20°, the other at −22° (Fig. 3). The cations which give φ between −19 and −20° have equal occupancy of the d orbitals which comprise the t_{2g} (O_h) set. The variation of the structural parameters is in accord with predictions based on ligand-field theory.[4,7] Given the range of sizes of tervalent cations now considered it is therefore reasonable to exclude size effects as the driving force for the structural differences.

Conclusion

Metal–water d_π–p_π interactions make an important contribution to the stereochemistry of water co-ordination which may, in some cases, compete successfully with the hydrogen bonding. Significant differences in the sensitivity of the metal(III)–water bond length to the tilt of the co-ordinated water molecule are evident for first- and second-row transition metals, this difference being related to the relative importance of metal–ligand d_π–p_π bonding. For first-row transition metals the insensitivity of the metal–water bond length to the tilt of the plane of the co-ordinated water molecule is apparent both in structural data from single crystals (which are limited in extent) and from neutron diffraction and spectroscopic studies of electrolyte solutions.

The low-temperature neutron diffraction structures of $CsM(SO_4)_2 \cdot 12D_2O$ (M = Mo or Ru) provide the strongest evidence to date for the proposition that metal–ligand π interactions perturb the twist angle of trigonal-planar co-ordinated water. This follows from the greater precision of the determination of the angle between the plane of the co-ordinated water molecule and the MO_6 framework and the exclusion of size effects as the source of the structural differences. It is clear that high-quality structural data are required for the examination of these effects and that X-ray data, even when collected at low temperatures, are insufficient for this purpose.

Acknowledgements

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