Relationship Between the Electronic and Molecular Structure of Tervalent Aqua Ions: Low-temperature Neutron Diffraction Structure of $CsCr(SO_4)_2 \cdot 12H_2O$†

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The alum $CsCr(SO_4)_2 \cdot 12H_2O$ has been investigated by single-crystal neutron diffraction at 15 K. The structure, which conforms to the β modification, was refined using a total of 651 unique reflections to give a weighted *R* value of 0.041. The stereochemistry of water co-ordination to chromium(III) is trigonal planar, with the Cr–O bond vector making an angle of 0.8(6)° with the plane of the co-ordinated water molecule. The angle between the plane of the co-ordinated water molecule and the CrO_6 framework, φ, is −19.0(4)°, similar to that found for the corresponding iron salt [−19.4(3)°], but smaller than found for the corresponding ruthenium [−22.0(3)°] and vanadium [−22(1)°] salts. The relationship between φ and the splitting of the t_{2g} (O_h) orbital energies is described using the angular overlap model. Accordingly, the preferred value of φ depends on the occupancy of the t_{2g} orbitals. Using this approach the φ values found for the caesium sulphate β alums are explained, and the electronic structures of the titanium and vanadium hexaaqua cations are discussed. The general features of the site of the tervalent cation in the alum lattice are described, these being important owing to the extensive use of the alum lattice for the spectroscopic study of tervalent aqua ions.

The absence of precise structural information on metal–water bonded systems leads to extreme difficulties with their study by *ab initio* techniques. This is because the electronic structure of the co-ordinating water molecule cannot be described accurately without a knowledge of the co-ordination sphere about the oxygen atom. This structural information may be obtained from neutron diffraction studies at low temperatures and its paucity has, until recently, precluded a well based account of metal–water bonding. However a number of low-temperature neutron diffractional structures of bi-[1–6] and ter-valent[7–9] hexaaqua cations have now been determined of which our own contribution has concentrated on the tervalent ions in the caesium sulphate alum lattice.[8,9] The importance of these structural data is made all the more pointed by the extent to which the alum lattice has already been used as a vehicle for the study of tervalent hexaaqua cations by a range of physical techniques (UV/VIS,[10] IR,[11,12] Raman,[13,14] NMR,[15,16] NQR,[16] EPR,[17–19] and Mössbauer[17] spectroscopy and magnetochemistry[20,21]). The correct interpretation of these results relies on a knowledge of the full stereochemistry of the tervalent cation and several misinterpretations of its structure, and even of its symmetry,[22–25] demonstrate that there is a clear need for an accurate structural description of the tervalent hexaaqua cation in the alum lattice. Such a description is possible for the caesium sulphate β alums within the range of structures currently available, which includes the structure of $CsCr(SO_4)_2 \cdot 12H_2O$ reported herein.

The alums crystallise in the cubic space group $Pa\bar{3}$ and give rise to three distinct structural modifications, α, β and γ.[26] Whereas the site symmetries of the constituent atoms are the same in the different modifications there are differences, for example, in the stereochemistry of water co-ordination to the tervalent cation. This is manifest not by a distortion of the $M^{III}O_6$ group from octahedral but by the relationship between the plane of the co-ordinated water molecule and the MO_6 axes. For the α alums the plane of the co-ordinated water molecule is aligned with the MO_6 framework but tilted away from the M–O bond vector,[8] whereas for the β alums the water molecules are co-ordinated in a trigonal-planar arrangement but the plane of the water molecule is twisted with respect to the MO_6 framework (by −19 to −22°‡).[8,9,27] The salt $NaAl(SO_4)_2 \cdot 12H_2O$ is the only example of the γ modification[25] and it has not been subject to study by neutron techniques.

The caesium sulphate alums, $CsM^{III}(SO_4)_2 \cdot 12H_2O$, form a particularly attractive series for the study of metal(III)–water interactions owing to the extremely diverse range of tervalent cations able to be accommodated within the lattice (Al,[28] Ga,[29] In,[29] Ti,[30] V,[29] Cr,[29] Mn,[29] Fe,[29] Co,[29] Mo,[31] Ru,[32] Rh[33] and Ir[33]). Whereas the stereochemistry of the tervalent cation is in most cases determined by the hydrogen bonding within the lattice, there is evidence which suggests that the tervalent cation can exert an overriding influence over the stereochemistry of the ion, for example when M^{III} = Co, Rh or Ir the α rather than the expected β alum modification is found.[29,33] For ions subject to Jahn–Teller distortions which arise from partial occupancy of the t_{2g} orbitals there is the suggestion that there is a preferred twist angle of the water molecule about the metal(III)–water bond and that this may be responsible for the failure of vanadium(III) to form α alums with K, Rb or NH_4 univalent cations.[34] Further there is the suggestion that these electronic factors may lead to differences in the structures of the caesium sulphate β alums.[9] Thus, the comparative study of tervalent cations in a well defined lattice affords considerable advantages in the identification of the relationship between the stereochemistry of the aqua cation and its electronic structure. This is of key importance for the elucidation of metal–water bonding.

Experimental

Caesium chromium sulphate alum was prepared by using the methods described in the literature[35] and large single crystals were obtained by recrystallisation from sulphuric acid (1 mol

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

‡ The angle between the plane of the water molecule and the MO_6 framework is given in terms of φ, which is defined in Fig. 2. Previous reports of this angle correspond to its absolute value.

dm^{-3}). The structure of $CsCr(SO_4)_2 \cdot 12H_2O$ was determined using data collected on the D9 (15 K) and D10 (10 K) four-circle diffractometers at the Institut Laue Langevin, Grenoble. We benefitted from the presence on D9 of a small position-sensitive gas-filled multidetector which gave us better precision in the integrated intensities of weak peaks.[36] The 788 D10 reflections were carefully scrutinised and the integrated intensities determined using the minimum $\sigma I/I$ technique of Lehmann and Larson.[37] The intensities of the 779 reflections measured on D9 in the range $0.562 < (\sin\theta)/\lambda < 0.8$ Å^{-1} were extracted using the program RETREAT.[38] The standard deviations in the observed moduli of the structure factors were estimated from the agreement amongst equivalents, generally two or three in number, or the counting statistics whichever was highest. The mean transmission factors for the D9 and D10 samples were calculated to be 0.774 and 0.663 respectively with maximum deviations about these values of 3.4 and 1.8%. Since even smaller deviations were associated with equivalent reflections, no corrections were made for absorption. After averaging over equivalent reflections, the final data for the least-squares refinement contained 243 reflections from D10 and 408 reflections from D9. The weighted $(1/\sigma^2)$ least-squares refinement (Cambridge Crystallographic Subroutine Library, CSSL[39]) gave a final R factor of 0.053, weighted R factor = 0.041, and $\chi^2 = 1.19$ for the 651 observables with a total of 74 variables comprising 23 positional parameters, two isotropic thermal parameters for Cs and Cr, 46 anisotropic thermal parameters for the remaining atoms, two scaling parameters, and a single parameter to describe the crystalline mosaic spread in the Becker–Coppens model for extinction.[40] The domain radius parameter was fixed at a large value of 50 μm, since this had little effect on the correction for the small degree of extinction present in the samples. The scattering lengths used in the structure-factor calculations were 5.42(Cs), 3.635(Cr), 2.847(S), 5.805(O) and −3.741(H) fermi.[41] Refinement of the D9 and D10 data separately led to no significant differences in the structural parameters, though the estimated standard deviations for the D9 parameters were smaller since these data extend to a higher limit in $(\sin\theta)/\lambda$. The unit-cell dimension was determined from a least-squares refinement of the D9 diffractometer angles for 10 Friedel pairs of centred reflections of the form $\{hk0\}$. The values so obtained were consistent with, but more precise than, the values obtained from the orientation matrix derived from 136 strong reflections with general indices. The final refinement gave a value of 12.334(6) Å, which includes the uncertainty in the incident wavelength. The data collection and analysis parameters are summarised in Table 1, the fractional cell coordinates and thermal parameters in Table 2.

Raman spectra were recorded using a Delor XY spectrometer in conjunction with an intensified diode array. The spectrometer was configured as a subtractive double monochromator plus spectrograph. Samples were irradiated with between 0.5 and 5 mW of 514.5 nm radiation according to their sensitivity to decomposition. An Olympus microscope, which was integrated into the optics of the spectrometer, was used to collect spectra.

Table 1 Data collection and analysis parameters for $CsCr(SO_4)_2 \cdot 12H_2O$

M	593.0
D_c/g cm^{-3}	2.10
Sample temperature, (K)	10.0(3) (D10), 15.0(1) (D9)
Sample volume (mm^3)	14.6 (D10), 11.2 (D9)
Sample weight (mg)	31.5 (D10), 23.5 (D9)
a/Å	12.334(6)
U/Å^3	1876.3(9)
Space group	$Pa\bar{3}$
λ/Å	1.240(3) (D10), 0.8444(3) (D9)
Maximum $[(\sin\theta)/\lambda]$/Å^{-1}	0.561 (D10), 0.8 (D9)
Total no. reflections	788 (D10), 779 (D9)
No. unique reflections	243 (D10), 408 (D9)
No. used in refinement	243 (D10), 408 (D9)
No. variables	74
Final R factor (F)	0.053
Weighted R factor (F)	0.041
Goodness of fit (χ^2)	1.19

Results and Discussion

In general terms the neutron diffraction structure of $CsCr(SO_4)_2 \cdot 12H_2O$ is in close agreement with the previous room-temperature X-ray determination[29] and in qualitative agreement with an early (1958) neutron study of $KCr(SO_4)_2 \cdot 12H_2O$.[42] Selected bond lengths and angles are included in Table 3. The Cs–O(a) distances exhibit the greatest temperature dependence, being 0.041(5) Å shorter in the low-temperature structure; similar behaviour is observed for the corresponding iron(III) and ruthenium(III) alums. The sulphate group has very similar dimensions in all of the low-temperature structures of caesium sulphate alums so far determined, this being reflected by their low-temperature Raman spectra where the band due to the $\nu_1(SO_4^{2-})$ mode is remarkably constant for a wide range of M^{III}.[14] It is therefore very surprising that the S–O(1)and S–O(2) distances are 0.023(4) and 0.008(4) Å shorter in the room-temperature structure. Further to investigate this anomaly, room-temperature Raman spectra were recorded on the caesium sulphate alums of Al, Cr, Fe and Ru in the region appropriate for the $\nu_1(SO_4^{2-})$ mode. No difference in the wavenumber of $\nu_1(SO_4^{2-})$ was detected (987 ± 1 cm^{-1}). Under the experimental conditions used the wavenumber of the spectrograph was not adjusted between running the spectra and so the reproducibility of the position of the band due to $\nu_1(SO_4^{2-})$ in each case was better than the wavenumber accuracy of the measurement. Since significant variations of the S–O bond distances are bound to be reflected by the wavenumber of $\nu_1(SO_4^{2-})$ the short S–O(1) distance in the room-temperature structure of $CsCr(SO_4)_2 \cdot 12H_2O$ must be questioned. A possible explanation would be sulphate disorder,

Table 2 Atomic fractional cell coordinates, isotropic (B_{iso}) and anisotropic thermal parameters for $CsCr(SO_4)_2 \cdot 12H_2O$*

Atom	x	y	z	B_{iso}	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Cs	0.5000	0.5000	0.5000	0.40(4)						
Cr	0.0000	0.0000	0.0000	0.34(7)						
S	0.3283(2)	0.3283	0.3283		0.31(5)			0.00(5)		
O(1)	0.2588(1)	0.2588	0.2588		0.67(4)			−0.03(3)		
O(2)	0.2807(1)	0.3364(1)	0.4379(1)		0.78(5)	0.60(5)	0.54(4)	−0.02(3)	0.17(3)	0.07(4)
O(a)	0.0528(1)	0.2102(1)	0.3421(1)		0.71(5)	0.82(5)	0.65(5)	−0.01(4)	0.09(4)	0.00(4)
H(a1)	0.0097(2)	0.2306(2)	0.2791(2)		1.77(11)	2.50(12)	1.24(9)	0.26(8)	−0.18(8)	0.21(8)
H(a2)	0.1270(2)	0.2215(2)	0.3180(2)		1.03(9)	2.49(11)	1.96(11)	0.08(9)	0.23(7)	−0.14(7)
O(b)	0.1590(1)	−0.0017(1)	−0.0006(1)		0.43(4)	0.65(4)	0.84(4)	0.09(4)	−0.03(4)	−0.04(4)
H(b1)	0.2066(2)	−0.0637(2)	0.0218(2)		1.45(9)	1.26(9)	2.04(11)	0.21(8)	−0.19(8)	0.20(7)
H(b2)	0.2029(2)	0.0611(2)	−0.0227(2)		1.19(8)	1.54(9)	2.17(11)	0.27(9)	−0.09(8)	−0.21(7)

* Thermal parameters are in units of Å^2

Table 3 Bond lengths (Å) and angles (°) which define the co-ordination environments within $CsCr(SO_4)_2{\cdot}12H_2O$*

(*i*) SO_4^{2-}		
S–O(1)	1.483(3)	[1.460(2)]
S–O(2)	1.477(3)	[1.469(3)]
O(1)–S–O(2)	109.8(2)	[109.9(2)]
O(2)–S–O(2)	109.2(2)	[109.0(2)]
(*ii*) $[Cr(OH_2)_6]^{3+}$		
Cr–O(b)	1.961(2)	[1.959(3)]
O(b)–Cr–O(b)	90.8(1)	[90.7(2)]
(*iii*) Cs^+		
Cs–O(2)	3.461(2)	[3.476(4)]
Cs–O(a)	3.308(2)	[3.349(4)]
O(2)–Cs–O(2′)	40.4(1)	[40.27(8)]
O(a)–Cs–O(a)	60.0(1)	[60.01(10)]
O(2)–Cs–O(a)	66.3(1)	[67.13(9)]
O(2)–Cs–O(a′)	77.0(1)	[76.22(9)]
O(2)–Cs–O(a″)	80.0(1)	[80.15(9)]
(*iv*) Water molecules		
O(a)–H(a1)	0.974(4)	[0.79(7)]
O(a)–H(a2)	0.972(4)	[0.79(6)]
O(b)–H(b1)	1.003(4)	[0.85(6)]
O(b)–H(b2)	0.984(4)	[0.83(6)]
H(a1)–O(a)–H(a2)	103.5(3)	[97(6)]
H(b1)–O(b)–H(b2)	110.7(3)	[113(6)]
(*v*) Hydrogen bonds		
H(a1)···O(2)	1.788(4)	[1.99(7)]
H(a2)···O(1)	1.841(4)	[1.76(6)]
H(b1)···O(a)	1.597(4)	
H(b2)···O(2)	1.661(4)	[1.83(6)]
O(a)–H(a1)···O(2)	174.2(3)	
O(a)–H(a2)···O(1)	171.2(3)	
O(b)–Hb1)···O(a)	175.7(3)	[163(6)]
O(b)–H(b2)···O(2)	177.7(3)	[174(5)]

* The values in square brackets were obtained from a room-temperature X-ray study of $CsCr(SO_4)_2{\cdot}12H_2O$.[29]

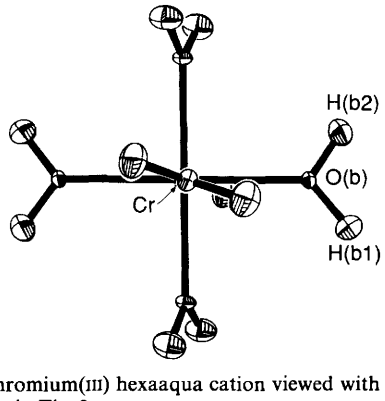

Fig. 1 The chromium(III) hexaaqua cation viewed with the three-fold axis oriented as in Fig. 2

this being prevalent in the alums with smaller monovalent cations,[43] however such an explanation is unlikely since the thermal parameters of the atoms of the sulphate group obtained in the X-ray study of $CsCr(SO_4)_2{\cdot}12H_2O$ are similar to those of the other caesium sulphate alums which have S–O(1) distances in agreement with those obtained at low temperature.

In this report we focus on the tervalent aqua ion since the overall structure of the salt is typical of the β alum modification

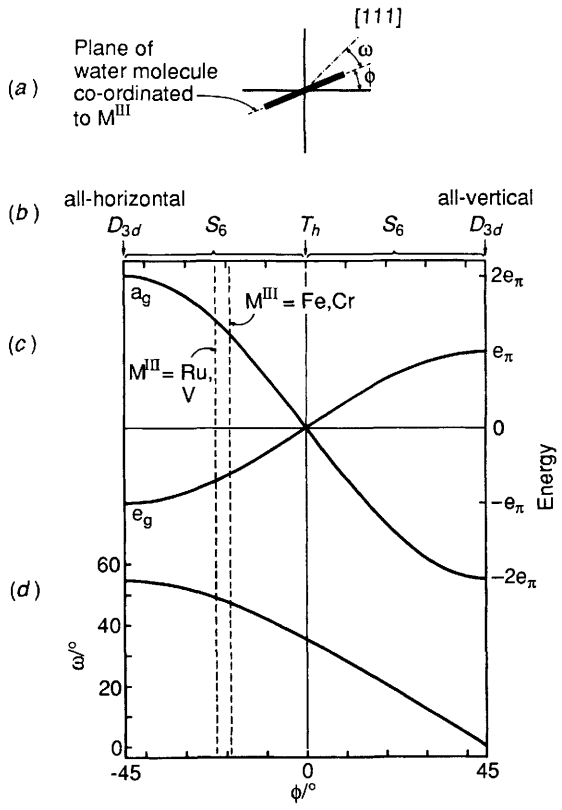

Fig. 2 Relationship between the molecular structure and the energies of the t_{2g} (O_h) orbitals for an hexaaqua cation occupying Wycoff site *a* ($\bar{3}$) in space group $Pa\bar{3}$ for a trigonal-planar co-ordinated water molecule with oxygen at *x*, 0, 0,. (*a*) Definition of the angles φ and ω, (*b*) the symmetry of the hexaaqua cation as a function of φ, (*c*) relative energies of the a_g and e_g components of the t_{2g} (O_h) orbitals calculated using the a.o.m. model, and (*d*) the relationship between the angle made by the plane of the water molecule and the MO_6 axes (φ) and the three-fold axis (ω)

and is analogous to the structure of $CsFe(SO_4)_2{\cdot}12H_2O$ which we have already described in full.[8] The chromium(III) hexaaqua cation lies on a site of S_6 symmetry with its co-ordinated water molecule occupying a site of C_1 symmetry. The O–Cr–O bond angle is 90.8(1)° and the hexaaqua cation is closely aligned with the unit-cell axes [0.6(1)°]. The water molecule's co-ordination is trigonal planar, with the angle between the Cr–O bond vector and the plane of the water molecule being 0.8(6)° (Fig. 1). The plane of the water molecule is rotated by an angle φ of −19.0(4)° with respect to the CrO_6 framework [Fig. 2(*a*)]; alternatively, the plane of the water molecule makes an angle of 47.2(4)° with the three-fold axis of the hexaaqua cation. Thus, the stereochemistry of the cation is approximately midway between T_h (plane of the water molecules aligned with the O_h axes, φ = 0°) and *all-horizontal* D_{3d} (plane of the water molecules normal to the σ_v planes in D_{3d}, φ = −45°). The relationship between the angle that the plane of the water molecule makes to the O_h axes, the S_6 axis (parallel to [111]), and the energy difference between the a_g and e_g (S_6) components of the t_{2g} (O_h) orbitals are shown in Fig. 2. Orbital energies were calculated using equation (1) which is derived from the angular overlap model

$$\delta = |\, 3e_\pi \sin(2\varphi) \,| \qquad (1)$$

(a.o.m.)[22,44] assuming; (*i*) trigonal planar co-ordination of the water molecule, (*ii*) the ion has S_6 symmetry, (*iii*) no metal–ligand π interaction in the plane of the water molecule, and (*iv*) configuration interaction can be neglected. Here δ is the absolute magnitude of the trigonal-field splitting and e_π is an a.o.m. parameter related to the metal–ligand π interaction

normal to the plane of the water molecule. The assumption that the metal–ligand π interaction in the plane of the water molecule be zero is not essential for a.o.m. predictions of the type shown in Fig. 2. It is necessary, however, that the in- and out-of-plane metal–ligand π interaction be anisotropic. This anisotropy is represented by the parameter $e_{g\pi}$. The relative magnitudes of the in- and out-of-plane metal–ligand π interactions influence the sign of e_π, and accordingly whether the a_g or e_g orbital lies lower in energy. The single-crystal electronic spectra of (NH_4)-$V(SO_4)_2 \cdot 12H_2O$ provide clear evidence of the anisotropy of the metal–ligand π interaction[45] and together with the magnetochemistry[20] suggest that the metal–ligand π interaction normal to the plane of the water molecule is dominant, an interpretation supported by arguments based on orbital overlap and energy matching. This underlies our setting the in-plane metal–ligand π interaction to zero.

Consideration of Fig. 2 shows that for chromium(III) there is no electronic stabilisation energy to be gained by adopting a particular value of φ since each of the t_{2g}-derived orbitals is singly occupied. The observed twist angle of $-19.0(4)°$ is, within experimental error, also that found for the corresponding iron alum [$-19.4(3)°$] where similar considerations apply. For the ruthenium(III) cation the $(t_{2g})^5$ configuration achieves its maximum electronic stabilisation energy when $\varphi = -45°$. In this case the observed twist angle of $-22.5(3)°$ is a compromise between the hydrogen-bonding and electronic requirements.

These arguments are most usefully tested by consideration of the d^2 and d^1 hexaaqua cations of vanadium(III) and titanium(III) where the preferred values of φ are -45 and 45° respectively. In the case of vanadium(III), good quality neutron data have been collected for $[V(OH_2)_6]^{3+}$ in the triflate salt, $[V(OH_2)_6][H_5O_2][CF_3SO_3]_4$.[7] Although the site symmetry of V is only C_1 the overall stereochemistry of the $[V(OH_2)_6]^{3+}$ cation is approximately *all horizontal* D_{3d}, $\varphi = -45°$. This is in keeping with the electronic preference for the vanadium(III) cation. Furthermore, a preliminary room-temperature neutron differention study of $CsV(SO_4)_2 \cdot 12H_2O$ indicates that φ is $-22(1)°$,[27] in close agreement with that found for the ruthenium alum for which similar electronic considerations apply. Electronic Raman spectra of $CsV(SO_4)_2 \cdot 12H_2O$[46] gives the splitting of the energy of the t_{2g} orbitals as 1950 cm^{-1} (*i.e.* e_π = 935 cm^{-1}) and accordingly the electronic stabilisation gained by changing φ from 0 to $-22°$ is 1300 cm^{-1} (15.6 kJ mol^{-1}). The magnitude of this effect is sufficient to influence the structure in strongly hydrogen-bonded crystals, rather than to be the determining factor. Accordingly, the value of φ found in $CsV(SO_4)_2 \cdot 12H_2O$ shows some deviation from that favoured by the lattice [defined by the twist angle observed for tervalent cations with either a full or half-full t_{2g} (O_h) orbital set] towards that which maximises the electronic stabilisation.

For titanium(III) the results of a recent EPR and electron spin-echo study of $[Ti(OH_2)_6]^{3+}$ in an amorphous propan-2-ol–D_2O glass suggests that it adopts the *all-vertical* D_{3d} conformation as predicted based on the foregoing interpretation of the structures of the alums, Fig. 2.[23] Although no neutron diffraction structure of $CsTi(SO_4)_2 \cdot 12H_2O$ is available, it is known to adopt the β modification[30] and therefore φ is expected to lie in the range -17 to $-23°$. This in turn suggests that the trigonal field of the alum lattice acts to remove the degeneracy of the $^2T_{2g}$ (O_h) ground term of titanium(III) to give an orbital doublet (Fig. 2), the splitting of which ought to be comparable to that found for vanadium(III) in its caesium sulphate alum (1950 cm^{-1}). Spin–orbit coupling will then act to lift the degeneracy of the ground term. While magnetic and single-crystal EPR studies have been conducted on $CsTi(SO_4)_2 \cdot 12H_2O$ the interpretation of these results is contradictory. The magnetochemistry of $CsTi(SO_4)_2 \cdot 12H_2O$ has been interpreted assuming that the trigonal field of the alum site gives an orbital singlet. However, the temperature dependence of the magnetic moment suggests the involvement of another state between 100 and 300 cm^{-1} higher in energy, the parentage of this state being the e_g component of the t_{2g} (O_h) orbitals. This implies that the trigonal-field splitting is less than about 500 cm^{-1}. The alternative description of the electronic structure of titanium(III) in which the trigonal field of the alum site gives an orbital doublet is however supported by the EPR data. The g values obtained for single-crystal $CsTi(SO_4)_2 \cdot 12H_2O$ ($g_\parallel = 1.25$, $g_\perp = 1.14$) are considerably lower than those obtained for the amorphous solid ($g_\parallel = 1.994$, $g_\perp = 1.986$). This substantial lowering of the g value from 2.0023 for the alum suggests that the ground term is indeed derived from an orbital doublet.

The contention that the trigonal-field splitting of titanium(III) is at least comparable to that of vanadium(III) receives support from *ab initio* configuration interaction calculations[24] of $[Ti(OH_2)_6]^{3+}$ which give an optimised geometry of *all-vertical* D_{3d} symmetry with a trigonal-field splitting of 5646 cm^{-1}, *i.e.* e_π = 1882 cm^{-1}. The magnitude of this splitting is larger than that for vanadium(III), and this reinforces the expectation of a large trigonal-field splitting for titanium(III) in $CsTi(SO_4)_2 \cdot 12H_2O$ (> 3150 cm^{-1}) rather than the 100—300 cm^{-1} derived from the magnetochemistry. Further support for the larger value of the trigonal splitting comes from single-crystal EPR and multiple-scattering Xα calculations of the second-row transition-metal ruthenium(III) in $CsRu(SO_4)_2 \cdot 12H_2O$ which yield an e_π value of 1633 cm^{-1}.[22]

Conclusion

Correlations between the molecular and electronic structure of tervalent hexaaqua cations are revealed by precise structural information. Of particular importance is the relationship between the twist angle of the water molecule and the energy of the components of the t_{2g} (O_h) orbitals. Such interactions are effective in terms of perturbing the degeneracy of the t_{2g} orbitals and may be described within the Jahn–Teller formalism. In complexes where the metal–ligand π bonding is anisotropic, asymmetry in the occupation of the t_{2g} orbitals may influence the structure. Transition-metal aqua ions provide an important demonstration of this effect.

While our understanding of the details of the metal–ligand interactions is far from complete, the structural chemistry of the tervalent cation in the caesium sulphate β alum lattice is comparatively well defined. The tervalent cations are well separated in the lattice is comparatively well defined. The tervalent cations are well separated in the lattice (8.7 Å) and the hexaaqua cation has a regular MO_6 framework which is only slightly tilted with respect to the unit-cell axes. The co-ordinated water molecule adopts the trigonal-planar conformation with $\varphi = -18$ to $-23°$. The hydrogen bonds emanating from this water molecule are strong, being approximately linear with $r(O \cdots O)$ distances in the range 2.60—2.68 Å, The interpretation of the electronic and spectroscopic properties of the tervalent cations in the caesium sulphate β alum lattice must be conducted within this framework.

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