Notes

Electronic Spectrum and Metal–Ligand Bonding Parameters of the $V(H_2O)_6^{3+}$ Ion

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The electronic spectrum of a crystal of $NH_4V(H_2O)_6(SO_4)_2{\cdot}6H_2O$ is reported and the transition energies interpreted in conjunction with previously reported magnetic susceptibility data using the angular overlap model. Satisfactory agreement with experiment can be obtained only if the π bonding in the plane of each water molecule is significantly weaker than that perpendicular to this plane.

The bonding in metal hydrates is of particular current interest as Beattie[1] has recently suggested that anisotropy in the π interaction may influence the type of alum structure adopted by different metal ions. However, recent studies of the bonding in bivalent metal hydrates using the angular overlap model (a.o.m.)[2–4] have suggested that better agreement with experiment is obtained if the π interaction is effectively isotropic about the metal–ligand bond axis, although interpretation of the experimental data has always been complicated by the presence of ligands other than water or by unequal metal–oxygen bond distances. In order to clarify these points we have measured the electronic spectrum of a single crystal of the cubic compound $NH_4V(H_2O)_6(SO_4)_2{\cdot}6H_2O$ and interpreted this using the a.o.m. This compound was chosen because it exhibits only a small trigonal distortion from octahedral symmetry[5,6] so that the energy-level splittings must be due to anisotropy in the metal–ligand π interaction. Also, the ground-state splitting has been observed directly in the Raman spectrum of this complex[7] and its low-temperature magnetic susceptibility has been reported,[8–10] which provides additional experimental data for the ligand-field analysis.

Experimental

Crystals of $NH_4V(H_2O)_6(SO_4)_2{\cdot}6H_2O$ were grown from aqueous solution as described previously.[7,11] The electronic spectrum was recorded at *ca.* 10 K using a Cary 17 spectrophotometer, the sample being cooled using a Cryodyne 22 closed-cycle cryostat.[12] To prevent dehydration, the sample was cooled to *ca.* 200 K before the cryostat was evacuated and the quality of the crystal was checked after the experiment using a polarising microscope.

Results and Discussion

Although the crystal structure of $NH_4V(H_2O)_6(SO_4)_2{\cdot}6H_2O$ has not been reported in detail, it has been suggested by Haussuhl[5] that it is isomorphous with the other vanadium(III) alums. The structure of caesium vanadium(III) alum has been reported[6] and the analogous potassium and rubidium salts have recently been found[13] to be isostructural with this, as predicted. The energy separation between the split components of the ground state was observed to be almost identical for the ammonium and caesium vanadium(III) alums by Best and Clark,[7] confirming that the disposition of the ligand molecules is very similar in the two compounds. In the alums the six $M{-}H_2O$ bonds are crystallographically equivalent and the trigonal distortion is invariably very small,[5,6,13,14] the angle O–M–O being 91° in $CsV(H_2O)_6(SO_4)_2{\cdot}6H_2O$.[6] The co-ordinated water molecules are related by an S_6 symmetry axis, adopting a 'paddle-wheel' conformation when viewed down the trigonal axis, and it is this arrangement which will cause a splitting of the parent octahedral states of the V^{3+} ion, if the π bonding is asymmetric about the V–O bond axis.

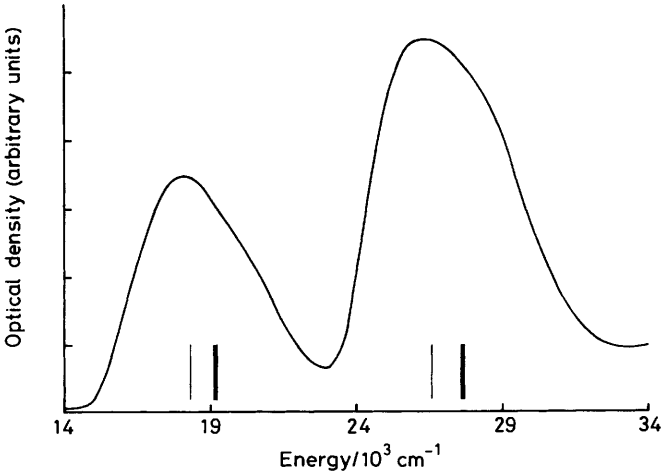

Figure 1. Spectrum of a crystal of $NH_4V(H_2O)_6(SO_4)_2{\cdot}6H_2O$ measured at *ca.* 10 K. Vertical lines represent values from calculation (i)

The electronic spectrum at *ca.* 10 K of a crystal of $NH_4V(H_2O)_6(SO_4)_2{\cdot}6H_2O$ is shown in Figure 1. This is quite similar to that reported for V^{3+} in aqueous solution at room temperature,[15] except that the peaks centred at *ca.* 18 000 and *ca.* 26 000 cm^{-1} each show distinct shoulders at higher energy. In the approximate D_{3d} point group of the $V(H_2O)_6^{3+}$ ion present in the alum salt, the $^3T_{2g}$ and $^3T_{1g}$ parent octahedral excited states split into $^3A_{1g}$ and ^3E_g, and $^3A_{2g}$ and ^3E_g, respectively, and the observed band splittings are presumably caused by this lowering in symmetry.

In order to investigate the way in which the energy levels depend upon the bonding with the water molecules, the computer program package CAMMAG written by Gerloch and co-workers[16] was used to parameterise the metal–ligand interaction. Here, each independent metal–ligand bond is described using the three parameters e_σ, $e_{\pi x}$, and $e_{\pi y}$. These measure the σ- and π-bonding interactions with the water molecule, the latter referring to the effect parallel and perpendicular to the vector connecting the two hydrogen atoms. The overall energy levels in the complex were estimated using an angular-overlap matrix derived from the atomic co-ordinates and unit-cell parameters of $CsV(H_2O)_6(SO_4)_2{\cdot}6H_2O$.[6]

Agreement of the calculations with experiment could be

Table. Calculated and observed transition energies (cm^{-1}) with experimental uncertainties in parentheses

	^3E_g	$^3A_{1g}$	^3E_g	$^3A_{2g}$	^3E_g
Observed	1 830	17 300	19 500	25 300	27 800
	2 050	(±500)	(±500)	(±200)	(±200)
Calc. (i)	1 832	18 340	19 119	26 726	27 554
	1 942	18 345	19 120	26 732	27 567
	2 039		19 165		27 617
	2 050		19 207		27 667
Calc. (ii)	1 833	18 328	19 097	26 676	27 462
	1 942	18 333	19 098	26 683	27 475
	2 039		19 142		27 524
	2 050		19 184		27 574

obtained only using highly anisotropic π-bonding parameters. This is because the slight trigonal displacement of the ligand oxygen atoms (*ca.* 1°) is far too small * to affect significantly the energy levels, so that if $e_{\pi x} \simeq e_{\pi y}$ only small splittings of the parent octahedral states occur. Moreover, the correct ordering of the split ground-state levels could be achieved only with $e_{\pi y} > e_{\pi x}$, and agreement with experiment was found to be best if $e_{\pi y} - e_{\pi x} \approx 1\,000$ cm^{-1}. Calculated values of the spin-allowed transition energies, including the energy splittings due to spin–orbit coupling, are compared with those estimated from the observed spectrum by Gaussian analysis in the Table for two possible sets of bonding parameters (in cm^{-1}): (i) $e_\sigma = 7\,000$, $e_{\pi y} = 1\,000$, and $e_{\pi x} = 0$; (ii) $e_\sigma = 8\,530$, $e_{\pi y} = 2\,040$, and $e_{\pi x} = 1\,000$. Those estimated using parameter set (i) are shown in Figure 1. The proposed band assignments are shown in the Table (no other assignment is consistent with the observed splitting of the ground state). A Racah parameter $B = 644$ cm^{-1} and a spin–orbit coupling constant $\xi = 167$ cm^{-1} were used in the calculations. The energies of the transitions to the components of the higher ^3E_g level of the split $^3T_{1g}$ ground state of $NH_4V(H_2O)_6(SO_4)_2{\cdot}6H_2O$ have been reported,[7] and the calculated energy levels were also compared with these values (Table). Although the calculated excited-state splittings are smaller than those observed experimentally, the agreement is satisfactory for both sets of bonding parameters considering the rather large uncertainties in the band positions obtained from the Gaussian analysis. It is also possible that dynamic Jahn–Teller effects increase the splittings of the excited states somewhat. The calculated spin-allowed transition energies obtained using parameter set (i) are compared with the experimental band positions in Figure 1. A larger value of $e_{\pi y} - e_{\pi x}$ would produce bigger excited state splittings, but this would also produce a larger splitting of the ground state in disagreement with the results of Best and Clark[7] and with the magnetic measurements discussed below.

The magnetic moment μ of $NH_4V(H_2O)_6(SO_4)_2{\cdot}6H_2O$ has been measured over a temperature range by several workers,[8–10] and this provides a check on the reliability of the a.o.m. parameters derived from the electronic transition energies. The variation of μ calculated by CAMMAG using the a.o.m. parameters (i) above and an isotropic orbital-reduction coefficient $k = 0.85$ is compared with the reported experimental values in Figure 2. The agreement is excellent, and an almost equally good fit was obtained using the parameter set (ii). It may be noted that the temperature dependence of μ is quite sensitive to the zero-field splitting of the $^3A_{2g}$ ground state, estimated to be 4.95 ± 0.05 cm^{-1} in the present calculations.

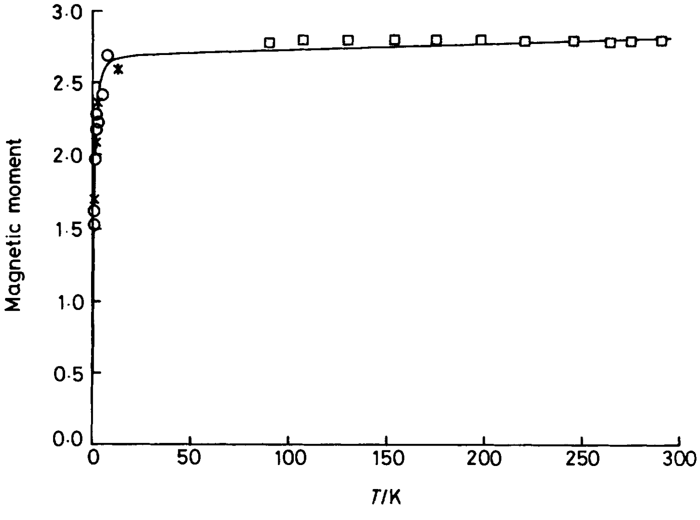

Figure 2. Magnetic moment of $NH_4V(H_2O)_6(SO_4)_2{\cdot}6H_2O$ calculated with bonding parameters (i) using CAMMAG. The experimental data of Fritz and Pinch,[8] Figgis *et al.*,[9] and van der Handel and Siegert[10] are shown as circles, squares, and stars, respectively

Discussion of the Bonding Parameters.—In previous studies the effects of the large orbital splitting of the ground state on the magnetic properties[9] and Raman spectrum[7] have been interpreted in terms of a trigonal component of the ligand field. However, this is at variance with the small trigonal distortion of the primary co-ordination sphere.[17] The present calculations suggest instead that the orbital splittings must be caused by highly anisotropic π bonding with the water molecules, with $e_{\pi y} - e_{\pi x} \approx 1\,000$ cm^{-1}. Applying an upper limit of $e_{\pi y} = 0.25\, e_\sigma$, as suggested by several theoretical and experimental studies,[18–20] implies that $e_{\pi y}$ lies in the range 1 500 ± 500 cm^{-1}, so that $e_{\pi x}$ must be quite small (500 ± 500 cm^{-1}). This is consistent with a simple covalent model of the interaction between water and the V^{3+} ion, with the oxygen p_x orbital being unavailable to bond with the metal because of its involvement in bonding to the hydrogen atoms. The estimate of $e_\sigma = 7\,700 \pm 700$ cm^{-1} seems reasonable, being, as expected, considerably larger than the values reported for this ligand bonded to various bivalent ions (3 000—5 000 cm^{-1})[21] and quite similar to those derived from analysis of the electronic spectra of two mixed-ligand chromium(III) complexes (*ca.* 7 500 cm^{-1}).[22,23] Values of $e_\sigma = 7\,000$ cm^{-1} and $e_{\sigma y} = 1\,000$ cm^{-1} have been reported recently[24] for the bonding parameters of the water molecules in the complex *trans*-$[V(C_2O_4)_2(H_2O)_2]^-$, though here, as in other similar studies,[18] it was assumed in the analysis that $e_{\pi x} = 0$.

The significant π anisotropy deduced in the present study lends credence to the proposal that anisotropy in the metal–ligand π bond influences the type of alum structure adopted by transition-metal ions.[1] It is also noteworthy that, ignoring the slight trigonal distortion of the oxygen positions, if the metal–ligand π bonding *were* isotropic, the ground state of the V^{3+} ion would be orbitally degenerate and subject to a Jahn–Teller distortion. The highly anisotropic π interaction means that a concerted rotation of the water hydrogen atoms about the V–O bond axes is equivalent to a torsional vibration which removes the Jahn-Teller degeneracy. The observed splitting of the ground state (*ca.* 1 940 cm^{-1}) is in fact comparable to the splittings caused by displacements along Jahn-Teller active stretching modes deduced[25] for similar complexes with ligands forming isotropic π bonds with metal ions having orbital triplet ground states.

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* Test calculations showed that a distortion of the $V{-}OH_2$ bond vectors greater than 10° from the octahedral angle of 90° is necessary to cause splittings of the observed magnitude.[17]

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