Electronic Spectra and Crystal Structures of $[NH_4]_6[XMo_9O_{32}]\cdot 6H_2O$ (X = Ni^{IV} or Mn^{IV})*

Horst Stratemeier,[a] **Michael A. Hitchman,**[a] **David L. Kepert,**[b] **Brian W. Skelton,**[b]
Kathy E. Sugars[b] **and Allan H. White**[b]
[a] *Chemistry Department, University of Tasmania, P.O. Box 252C, Hobart, Tasmania (7001), Australia*
[b] *Chemistry Department, University of Western Australia, Nedlands, Western Australia (6009), Australia*

The crystal structures of the isomorphous compounds $[NH_4]_6[XMo_9O_{32}]\cdot 6H_2O$, (X = Ni or Mn) which crystallize in the rhombohedral space group $R32$, $Z = 1$ with $a = 10.084(2)$ Å, $\alpha = 104.31(2)°$ for X = Mn and $a = 10.087(4)$ Å, $\alpha = 104.35(3)°$ for X = Ni have been determined. The stereochemistry of the oxyanions is similar to that described previously for the manganese(IV) compound, with the Mn–O bond length [1.897(3) Å] being slightly longer than the Ni–O distance [1.872(2) Å], and both metal ions conforming to a crystallographic 32 ligand co-ordination geometry. The low-temperature polarized electronic spectra have been recorded, that of the manganese(IV) compound suggesting a ligand-field splitting parameter $\Delta = 22\,500\ \text{cm}^{-1}$, with the $^4T_2$ excited state exhibiting only a small trigonal splitting. The Racah interelectron repulsion parameter B is substantially reduced from the free-ion value, implying considerable covalence in the Mn^{IV}–O bonding. Although the spin-forbidden transitions cannot be fitted accurately using a single Racah parameter C, it is apparent that this undergoes only a modest reduction from the free-ion value. The electronic spectrum of the nickel(IV) compound is poorly resolved and suggests a ligand-field splitting parameter $\Delta \approx 21\,000\ \text{cm}^{-1}$.

Heteropolymolybdates have been extensively studied from early times,[1] though it is only recently that their structural chemistry has been investigated in detail.[2,3] The structure of $[MnMo_9O_{32}]^{6-}$ has been investigated several times by X-ray diffraction,[4–7] as has that of the ammonium salt of the corresponding nickel(IV) compound,[8] and their solution optical spectra have been reported.[9] However, the spectra could not be assigned unambiguously, and as the manganese compound is very dichroic it has been suggested[9] that the measurement of polarized crystal spectra might help resolve this problem. Such spectra should be of interest both because of the unusual oxidation state of the chromophores, and because these occupy trigonal sites formally somewhat similar to those of the Cr^{3+} ion in α-Al_2O_3 (ruby),[10] the optical properties of which have been the subject of intensive study.[11,12] The manganese(IV) ions in $[MnMo_9O_{32}]^{6-}$ are isoelectronic with the chromium(III) ions in ruby.

The present study reports the low-temperature d–d spectra of crystals of $[NH_4]_6[XMo_9O_{32}]\cdot 6H_2O$, where X = Ni or Mn. The nickel(IV) compound is isostructural with its manganese(IV) analogue, and to provide more precise data on the metal environments the crystal structures of the pair have been redetermined. The transition energies have been interpreted using the angular overlap model and the bonding parameters are compared with those reported for oxygen-donor ligands bound to metal ions in related systems.

Experimental

The compounds $[NH_4]_6[MnMo_9O_{32}]\cdot 6H_2O$ and $[NH_4]_6[NiMo_9O_{32}]\cdot 6H_2O$ were prepared by the method of Baker and Weakley[9] as deep red and black rhombohedral crystals, respectively.

Electronic spectra were measured using polarized light on a Cary 17 spectrophotometer, the crystals being mounted by a technique described previously,[13] and cooled using a Cryodyne model 22 closed-cycle refrigerator. To avoid the possibility of the samples losing water, they were cooled to *ca.* 200 K before being subjected to a vacuum.

Crystallography.—Unique diffractometer data sets were measured at *ca.* 295 K within the limit $2\theta_{max} = 100°$ [monochromatic Mo-Kα radiation ($\lambda = 0.710\,69$ Å), $2\theta/\theta$ scan mode] yielding N independent reflections of which N_o with $I > 3\sigma(I)$ were used in the full-matrix least-squares refinement [statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.000\,08\sigma^4(I_{diff})$] after analytical absorption correction. Conventional residuals R, R' on $|F|$ are quoted. The value of R' for the manganese(IV) compound is relatively high, probably because the crystal used was considerably smaller than that of the nickel(IV) compound, leading to fewer observed reflections and poorer counting statistics, particularly on the weaker high-angle reflections. Neutral-atom complex scattering factors were used;[14] computation used the XTAL program system[15] implemented by S. R. Hall. No correction was applied for extinction. Coordinates are presented in a common rhombohedral setting to assist the spectroscopy (Table 1) with chirality determined from a ratio test. Hydrogen atoms were located; the site occupancy for the water molecules was constrained at 0.5 after initial refinement, as found in earlier studies.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond distances and angles.

Crystal/refinement data. $[NH_4]_6[XMo_9O_{32}]\cdot 6H_2O$, rhombohedral, space group $R32$ (no. 155, $D_3{}^7$), $Z = 1$. X = Mn, $M = 1\,646.7$, $a = 10.084(2)$ Å, $\alpha = 104.31(2)°$, $U = 909.4$ Å^3, $D_c = 3.01$ g cm^{-3}, $F(000) = 785$, $\mu_{Mo} = 32.1$ cm^{-1}, specimen $0.145 \times 0.170 \times 0.180$ mm, $A^*_{min,max} = 1.48, 1.80$, $N = 3372$, $N_o = 2947$, $R = 0.034$, $R' = 0.054$; X = Ni, $M = 1650.4$, $a = 10.087(4)$ Å, $\alpha = 104.35(3)°$, $U = 909.5$ Å^3, $D_c = 3.01$ g cm^{-3}, $F(000) = 788$, $\mu_{Mo} = 33.8$ cm^{-1}, specimen $0.260 \times 0.235 \times 0.221$ mm, $A^*_{min,max} = 1.69, 2.28$, $N = 3424$, $N_o = 3238$, $R = 0.026$, $R' = 0.028$.

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Non-hydrogen atom coordinates for $[NH_4]_6[XMo_9O_{32}]\cdot 6H_2O$

	X = Mn			X = Ni		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
X	0	0	0	0	0	
Mo(1)	−0.115 81(3)	−0.149 47(3)	−0.341 48(3)	0.115 24(2)	0.149 53(2)	0.340 79(2)
Mo(2)	0	0.200 69(2)	($\bar{y}$)	0	−0.199 75(2)	($\bar{y}$)
O(1)	0.015 0(3)	−0.158 9(3)	−0.135 6(2)	−0.015 8(2)	0.155 3(2)	0.134 9(2)
O(2)	0.025 1(3)	0.025 0(3)	−0.316 6(3)	−0.025 1(2)	−0.024 8(2)	0.315 5(2)
O(3)	−0.259 8(3)	−0.152 4(4)	−0.475 6(3)	0.259 0(2)	0.152 2(2)	0.475 6(2)
O(4)	−0.261 0(3)	(*x*)	(*x*)	0.261 0(2)	(*x*)	(*x*)
O(5)	−0.146 4(5)	0.209 8(4)	−0.322 7(4)	0.148 0(2)	−0.206 8(2)	0.322 3(2)
O(6)	−0.053 5(5)	−0.277 1(4)	−0.426 5(4)	0.051 7(2)	0.278 1(2)	0.425 3(2)
N(1)	0	−0.557 1(5)	−0.442 9(5)	0	0.558 4(3)	0.441 7(3)
N(2)	−0.301 1(7)	−0.698 9(7)	0	0.301 3(4)	0.698 7(4)	0
O(7)	−0.408(1)	−0.738(1)	−0.267(2)	0.421 3(9)	0.750 7(8)	0.274(1)
O(8)	−0.445(2)	−0.438(2)	−0.666(2)	0.443(1)	0.444(1)	0.651(1)

Table 2 The manganese/nickel environments

Distance/Å or angles/°	X = Mn	X = Ni
X–O(1)	1.897(3)	1.872(2)
O(1)–X–O(1^{I})	86.7(1)	87.08(7)
O(1)–X–O(1^{II})	86.2(1)	86.51(7)
O(1)–X–O(1^{III})	101.6(1)	100.25(7)
O(1)–X–O(1^{IV})	168.8(1)	170.00(7)

Transformations of the asymmetric unit: I, z, x, y; II, $\bar{y}, \bar{x}, \bar{z}$; III, $\bar{z}, \bar{y}, \bar{x}$; IV, $\bar{x}, \bar{z}, \bar{y}$.

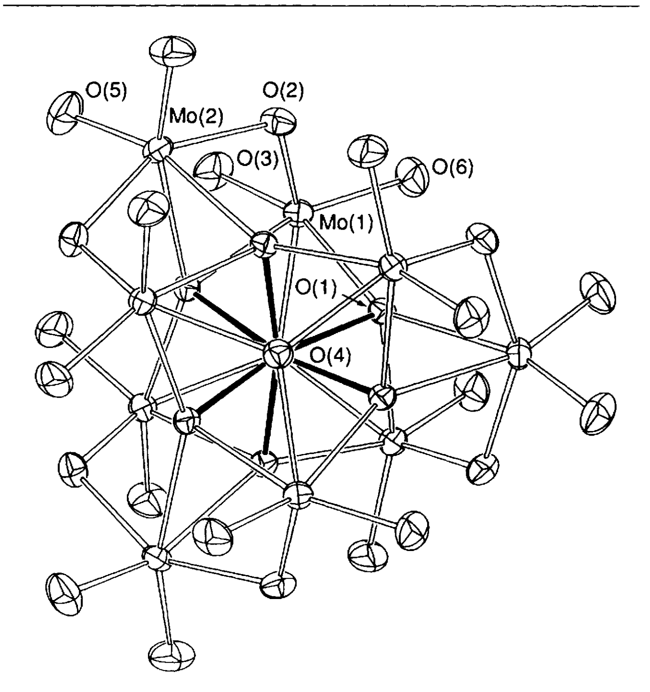

Fig. 1 Projection of the complex manganese anion down its three-fold axis, with 50% thermal ellipsoids; bonds to the manganese atom, which lies directly below O(4), are shown as solid lines

Results and Discussion

Crystal Structures.—The overall crystal packing and stereochemistries of the polyanions were found to be as reported previously in X-ray studies of $[NH_4]_6[MnMo_9O_{32}]\cdot 6H_2O$[5] and its potassium analogue.[6,7] The non-hydrogen atomic coordinates are given in Table 1, and the geometry of the manganese(IV) anion is illustrated in Fig. 1 showing clearly the distortion from ideal octahedral geometry about the metal ion, the feature most pertinent to the present study. The bond lengths and angles defining the stereochemistry of the manganese(IV) and nickel(IV) ions are given in Table 2.

The symmetry of the space group requires all Mn–O bond lengths to be equivalent for the manganese(IV) complex; the observed distance [1.897(3) Å] is similar to that reported previously[5] for the same compound [1.90(1) Å], and perhaps marginally shorter than those reported for the analogous potassium salt [1.91(1) and 1.93(1) Å].[6] The geometry of the nickel(IV) complex is similar to that reported previously.[8] The Ni–O distance is somewhat shorter [1.872(2) Å] than the manganese(IV) distance, as is to be expected. However, it is interesting that while the Mn^{IV}–O distance is significantly shorter than that [1.959] Å(3) involving the isoelectronic chromium(III) ion in $CsCr(SO_4)_2\cdot 12H_2O$, the Ni^{IV}–O distance is identical to that [1.873(5) Å] of the Co^{III}–O bonds in $CsCo(SO_4)_2\cdot 12H_2O$.[16] Possibly a shorter Ni^{IV}–O bond is precluded by the rigidity of the molybdate framework of the polyanion, though as noted below the ligand-field splitting of the nickel(IV) ion in $[NH_4]_6[NiMo_9O_{32}]\cdot 6H_2O$ is only marginally smaller than expected.

The $X^{IV}O_6$ octahedra undergo a significant angular distortion, with three O–X–O angles opening from 90 to 101.6(1)° in the case of Mn^{IV} and 100.25(7)° for Ni^{IV}; a slightly larger distortion is expected for the former metal ion because of the greater Mn–O bond distance. The remaining O–X–O angles reduce by an approximately equal amount [86.7(1), 86.2(1) for Mn^{IV} and 87.08(7), 86.51(7)° for Ni^{IV}].

Electronic Spectra.—The compounds form with the crystallographically equivalent (100), (010), *etc.* crystal faces well developed, the morphology being confirmed by X-ray diffraction. The manganese(IV) compound formed crystals sufficiently large (diameter *ca.* 0.3 mm) to allow cleavage of sections thin enough to give good optical spectra. Several of these were studied at room temperature and *ca.* 15 K using polarized light, and typical low-temperature spectra with the electric vector along the two extinction directions of the crystal face are shown in Fig. 2. The room-temperature spectra were similar, except that the bands were somewhat broader and less well resolved. The nickel(IV) compound formed much smaller crystals, and absorbed light more strongly, and good quality, reproducible spectra could not be obtained. While the overall form of the spectra was consistent, the relative intensities and shapes of the bands observed for different samples varied somewhat. Typical spectra measured at *ca.* 15 K are shown in Fig. 3, though it should be noted that the unusual shape observed for the band centred at *ca.* 18 000 cm^{-1} in A polarization suggests that the intensity of this may well be underestimated due to stray light effects.[13]

For the two extinction directions of the (100) crystal face the

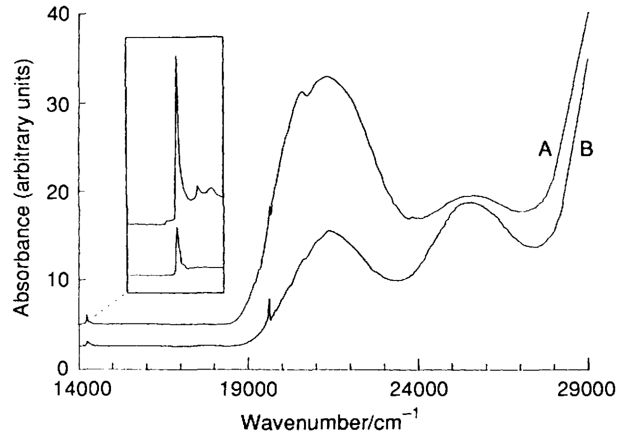

Fig. 2 Polarized electronic spectra measured at *ca.* 15 K of the (100) face of $[NH_4]_6[MnMo_9O_{32}]\cdot 6H_2O$ with the electric vector along the extinction direction in the plane containing the three-fold axis of the MnO_6 polyhedron (B) and normal to this plane (A); see text for the molecular projections of the two spectra. The insert shows an enlargement of the region 13 890–15 875 cm^{-1}

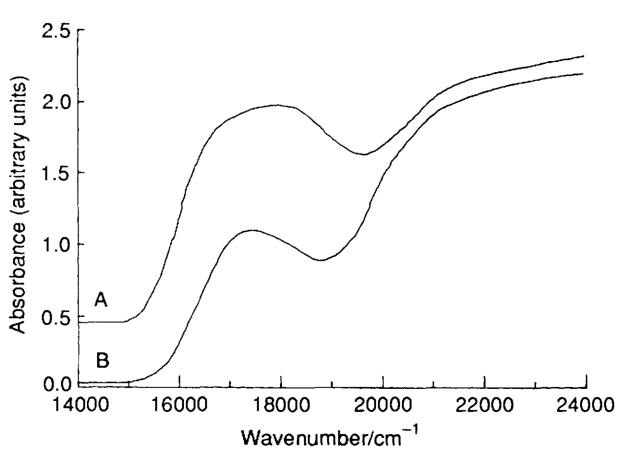

Fig. 3 Polarized electronic spectra measured at *ca.* 15 K of the (100) face of $[NH_4]_6[NiMo_9O_{32}]\cdot 6H_2O$ with A and B defined as in Fig. 2

electric vector is parallel (A) and perpendicular (B) to the bisector of the angle between two sides of the rhombohedral unit cell. The X^{IV} metal ions lie on crystallographic sites of D_3 symmetry, with the three-fold symmetry axis, *z*, of the molecular coordinate system lying on the body-diagonal of the unit cell (Fig. 1). For polarization A the electric vector makes the molecular projections $0.47z^2 + 0.53(xy)^2$, while for polarization B it lies exactly in the *xy* plane.

For a manganese(IV) complex of D_3 symmetry the ground state transforms as $^4A_2$ and the excited states of $^4T_{2g}$ and $^4T_{1g}$ symmetry in a regular octahedral complex split into states of ^4E and $^4A_1$ and ^4E and $^4A_2$ symmetry, respectively. For electric dipole transitions, the selection rules indicate that $^4A_2 \longrightarrow {}^4E$ is allowed in *xy* polarization, and $^4A_2 \longrightarrow {}^4A_1$ in *z* polarization. Considering first the relatively intense, broad bands which may be assigned to spin-allowed transitions, the spectrum of $[NH_4]_6[MnMo_9O_{32}]\cdot 6H_2O$ in B polarization shows bands centred at 21 390 and 25 510 cm^{-1}. Following the above selection rules, these may be assigned to transitions to the ^4E components of the $^4T_2$ and $^4T_1$ excited states, respectively. In A polarization, the rather intense, broad band centred at *ca.* 21 345 cm^{-1} may be assigned to the *z*-allowed $^4A_2 \longrightarrow {}^4A_1$ transition. The bulk of the intensity of the relatively weak band centred at 25 535 cm^{-1} in A polarisation must be due to the *xy*-allowed $^4A_2 \longrightarrow {}^4E$ transition (the relative intensity compared with that of the band at 25 510 cm^{-1} in B polarization is approximately equal to the ratio of the *xy* molecular projections, *i.e.* 0.5:1). The electric-dipole forbidden $^4A_2 \longrightarrow {}^4A_2$ transition is thus not resolved.

The trigonal splitting of the $^4T_2$ excited state, *ca.* 45 cm^{-1}, is therefore very small, being similar to the estimated experimental uncertainty of the band maxima (*ca.* 50 cm^{-1}). Relatively small splittings of this excited state have also been observed for the chromium(III) ions in ruby (450 cm^{-1}),[12,17] the tris(oxalato)chromate(III) complex, $[Cr(ox)_3]^{3-}$ (304 cm^{-1}),[18] and the tris(ethane-1,2-diamine)chromium(III) complex, $[Cr(en)_3]^{3+}$ (*ca.* 50 cm^{-1}).[19]

The relatively sharp peak centred at 14 265 cm^{-1} in both A and B polarization is due to the transitions to the spin–orbit components of the ^2E state, the half-width (*ca.* 40 cm^{-1}) being too large to allow these to be resolved. The analogous transitions occur as very sharp lines in the spectra of ruby,[11,12] and the trigonal complexes $[Cr(ox)_3]^{3-}$ and $[Cr(en)_3]^{3+}$.[18,19] Sharp lines at 14 866 and 14 786 cm^{-1} in the fluorescence spectrum of Mn^{4+} doped into α-Al_2O_3 have been assigned to transitions from these levels.[20] The weak peaks at 14 903 and 15 314 cm^{-1} which are observed predominantly in *z* polarization (Fig. 2) are assigned as transitions to the ^2E and $^2A_2$ components of the $^2T_1$ state; while it is possible that the latter peak is due to the first member of a vibrational progression built upon an electronic origin at 14 903 cm^{-1}, the calculations described below suggest that the ^2E component of the $^2T_1$ state should lie *ca.* 230 cm^{-1} below the $^2A_2$ level, supporting the former assignment. The sharp peak at 19 640 cm^{-1}, which is predominantly *xy* polarized, is assigned to the transition to the $^2A_1$ component of the $^2T_2$ excited state, while the feature at 20 600 cm^{-1} which is largely *z* polarized is due to the transition to the ^2E component of this level. However, the close proximity of the latter transition to the band maximum of the $^4A_2 \longrightarrow {}^4A_1({}^4T_2)$ transition makes it likely that a strong antiresonant interaction will occur, so that in fact it is probably the *dip* at 20 750 cm^{-1} which corresponds to the $^4A_2 \longrightarrow {}^2A_1({}^2T_2)$ transition energy, rather than the peak maximum at 20 600 cm^{-1}. Similar antiresonance has also been observed for the corresponding $^4A_2 \longrightarrow {}^2T_2$ transition of $[Cr(en)_3]^{3+}$.[19] In overall terms, the assignment of the spectrum is in agreement with that proposed by Weakley.[21]

The spectrum of $[NH_4]_6[NiMo_9O_{32}]\cdot 6H_2O$ shows a reasonably well resolved peak centred at 17 400 cm^{-1} in B polarisation. In A polarization the band broadens, becomes asymmetric and more intense, and the maximum apparently moves somewhat to higher energy, though this could be an artifact of the intense absorption commencing at *ca.* 20 000 cm^{-1} (Fig. 3). The ground state of a low-spin nickel(IV) complex of D_3 symmetry is of $^1A_1$ symmetry, and as the transition to the ^1E component of the first excited state ($^1T_1$) is electric dipole allowed in *xy* polarization the band centred at 17 400 cm^{-1} in the B spectrum may be assigned to this transition, with the band centred at *ca.* 18 000 cm^{-1} in A polarization being assigned to the transition to the $^1A_2({}^1T_1)$ state, which is electric dipole allowed in *z* polarization.

The band assignments and energies of the band maxima are listed in Table 3 for both compounds. The positions of the peaks agree well with those reported previously for solutions of the polyanions, and these are also given in the Table for comparison.

Metal–Ligand Bonding Parameters.—The computer program CAMMAG, developed by Gerloch and co-workers,[22] was used to estimate the metal–ligand and interelectron repulsion parameters for the compounds. This program calculates the excited-state energies taking as input the angular overlap[23] σ- and π-bonding parameters e_σ and $e_{\pi x}$, $e_{\pi y}$, the interelectron repulsion parameters *B* and *C*, and the co-ordination geometry defined by the metal and ligand positions obtained from the crystal structure determination.

Presumably because of the relatively small deviation from a regular octahedral co-ordination geometry, the calculated

Table 3 Experimental and calculated transition energies (cm^{-1}) for the compounds

	Observed			
	Crystal			
Assignment	Polarization A	Polarization B	Solution[a]	Calculated[b]
(*a*) $[NH_4]_6[MnMo_9O_{32}]\cdot6H_2O$				
$^4A_2 \longrightarrow {}^2E$	14 265	14 265	14 300	13 613
$^2T_1(^2E)$	14 903		15 100	13 917
$^2T_1(^2A_2)$	15 314			14 154
$^2T_2(^2A_1)$	19 640	19 640		20 665
$^2T_2(^2E)$	20 600		20 600	21 414
$^4T_2(^4E)$		21 390	21 300	21 278
$^4T_2(^4A_1)$	21 345			21 558
$^4T_1(^4A_2)$				25 409
$^4T_1(^4E)$	25 535	25 510	~25 500	26 049
(*b*) $[NH_4]_6[NiMo_9O_{32}]\cdot6H_2O$				
$^1A_1 \longrightarrow {}^1T_1(^1E)$		17 400	17 600	17 746
$^1T_1(^1A_2)$	*ca.*18 000			17 859

[a] Data from ref. 9. [b] Calculated using the computer program CAMMAG; see text for details.

transition energies were found to be sensitive only to the *difference* between the σ- and π-bonding parameters. For this reason, the ratio between e_σ and $e_{\pi x} = e_{\pi y} = e_\pi$ was set equal to 4:1, the value observed for several oxygen-donor ligands.[24]

For the manganese(IV) compound the energy of the first spin-allowed transition depends only upon the metal–ligand bonding parameters, and the observed energy yields the parameters $e_\sigma = 11\,250$ cm^{-1} and $e_\pi = 2\,812.5$ cm^{-1}. The energy separation Δ between the e_g and t_{2g} orbitals in a regular octahedral complex is given by[23] $\Delta = 3e_\sigma - 4e_\pi$. This implies the overall ligand-field splitting parameter $\Delta = 22\,500$ cm^{-1}, which is in good agreement with the sparse data available for other manganese(IV) compounds; for instance, $\Delta \approx 21\,800$ cm^{-1} for $[MnF_6]^{2-}$,[25] while $\Delta = 21\,300$ cm^{-1} for Mn^{4+} doped into α-Al_2O_3.[20] As expected, the splitting is significantly greater than that observed for the isoelectronic di- and tri-valent metal ions with oxygen ligands, thus the hexahydrate ions of V^{II} and Cr^{III} have $\Delta = 12\,600$ and $17\,400$ cm^{-1}, respectively.[26]

In agreement with experiment, a rather small splitting due to the trigonal component of the ligand field is calculated for the $^4T_2$ excited state of $[NH_4]_6[MnMo_9O_{32}]\cdot6H_2O$, 280 cm^{-1} neglecting spin–orbit coupling, with the ^4E component being lower in energy than $^4A_1$. The sign of the splitting differs from that deduced from experiment, though the observed value, *ca.* 45 cm^{-1}, is so small that it is of only marginal significance. A larger splitting is predicted for the $^4T_1$ excited state, 640 cm^{-1}, but this cannot be compared with experiment because the electric-dipole forbidden transition to the $^4A_2$ component of $^4T_1$ is not resolved.

To a good approximation, the energy separation between the $^4T_1$ and $^4T_2$ states depends only on the Racah parameter *B*, and the observed transition energy suggests the value $B = 400$ cm^{-1}. This implies that *B* is reduced to 37% of the free-ion value (1088 cm^{-1}),[27] suggesting considerable covalent character in the Mn^{IV}–O bonding. A reduction in *B* to 51% of the free-ion value has been derived from the corresponding energy separation in the optical spectrum of $[MnF_6]^{2-}$,[25] and as the fluoro complex is expected to be more ionic the comparison seems reasonable. A significant proportion of these decreases is probably due to a reduction of the effective nuclear charge on the metal ion, rather than delocalization of the electrons onto the ligands; a value of $B = 760$ cm^{-1} has been estimated for the isoelectronic vanadium(II) ion.[27] The energies of all the spin-forbidden transitions could not be fitted accurately using a single value for the second Racah parameter. A value of $C = 3500$ cm^{-1} overestimates the energies of the components of the $^2T_2$ excited state by *ca.* 1000 cm^{-1}, but underestimates those of the ^2E and $^2T_1$ states by *ca.* 800 cm^{-1} (Table 3). The inability to reproduce the energies of a range of spin-forbidden transitions using a single value of *C* is not uncommon, and this feature has been discussed in detail by Ferguson.[28] Taking $C = ca.$ 3500 cm^{-1} implies a reduction to *ca.* 80% of the free-ion value,[27] a much smaller difference than that observed for *B*. As the spin-forbidden transitions largely occur within the metal t_2 orbitals, which participate far less strongly in covalent bonding than the e orbitals involved in the spin-allowed transitions, it is to be expected that *C* should be reduced from the free-ion value by a smaller amount than *B*, and this has been confirmed in numerous other studies.[28]

The EPR spectrum of Mn^{4+} doped into $[NH_4]_6[NiMo_9O_{32}]\cdot6H_2O$ has been reported by Byfleet *et al.*,[29] and analysed in terms of a zero-field splitting parameter $|D| = 0.861$ cm^{-1}, a ground-state splitting of 1.722 cm^{-1}. However, using perturbation formulae it was found[29] that an anomalously large trigonal splitting of the excited state, 7000 cm^{-1}, was required to explain the zero-field splitting. The present calculations yield a ground-state splitting equal to that above assuming an effective spin–orbit coupling constant $\zeta = 280$ cm^{-1}. Such a value seems reasonable, since although the free-ion value for Mn^{4+} has been estimated[27] as 420 cm^{-1} this is very sensitive to the effective nuclear charge, being reduced to 260 cm^{-1} for a nuclear charge of +3.[27]

The energy of the $^1A_1 \longrightarrow {}^1T_1$ transition of the nickel(IV) compound depends not only upon Δ, but also, to a lesser extent, upon the Racah parameter *B*. Since only one transition is observed it is impossible to determine both Δ and *B* independently. Taking a value of *B* identical to that in the managanese(IV) compound yields the estimates $e_\sigma \approx 10\,500$ cm^{-1}, $e_\pi \approx 2625$ cm^{-1}, with $\Delta \approx 21\,000$ cm^{-1}. The fact that $[NH_4]_6[NiMo_9O_{32}]\cdot6H_2O$ has a somewhat smaller Δ value than the corresponding manganese(IV) compound is consistent with the relative lengths of the X^{IV}–O bonds in the two compounds. As discussed above, while the Ni^{IV}–O bonds are shorter than those to Mn^{IV}, the difference is not as great as expected. The Δ value of the present nickel(IV) compound is similar to that for the $[NiF_6]^{2-}$ complex (*ca.* 20 500 cm^{-1}),[30] and somewhat greater than that estimated[31] for the hydrate of the corresponding, isoelectronic cobalt(III) ion, *ca.* 19 210 cm^{-1}. It is normally expected that the ligand-field splitting is greater for a tetravalent metal ion than for the corresponding isoelectronic trivalent metal ion. However, it should be noted that in the present case the Ni^{IV}–O and Co–O bond lengths are similar, and the contraction of the d orbitals due to the higher charge on the former metal ion might be expected to produce a *smaller* Δ value for the nickel(IV) compound. All in all, the optical spectra suggest that any lengthening of the Ni^{IV}–O bonds due to the rigid nature of the Mo^{VI}–O framework is only marginal. The calculations predict that the $^1T_1$ excited state of the nickel(IV) compound should be split by a rather small amount (*ca.* 113 cm^{-1}). While the observed spectra suggest a somewhat larger splitting (*ca.* 600 cm^{-1}), the poor quality of the spectra render this conclusion uncertain.

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