$Zn[Si(SiMe_3)_3]_2$ (1a). A solution of $ZnCl_2$ (0.57 g, 4.2 mmol) and $(THF)_3LiSi(SiMe_3)_3$ (4.00 g, 8.40 mmol) in diethyl ether (30 mL) was stirred at room temperature for 10 h. After removal of volatiles under dynamic vacuum, the colorless residue was extracted into pentane (50 mL). Concentrating (to ca. 5 mL) and cooling to −45 °C for 12 h gave the product as colorless hexagonal plates (1.91 g, 81%), mp 194–195 °C. Anal. Calcd for $C_{18}H_{54}Si_8Zn$: C, 38.6; H, 9.71. Found: C, 38.6; H, 9.63. Mass spectrum (*m/e*): calcd for $C_{18}H_{54}Si_8Zn$, 560; found, 560 (most abundant peak with correct isotope envelope). IR (Nujol, CsI; cm^{-1}): 1385 m, 1298 w, 1250 s, 1223 s, 1085 br w, 1035 w, 825 br s, 737 m, 680 s, 618 s, 445 m, 407 m, 306 w.

$Cd[Si(SiMe_3)_3]_2$ (1b). The above procedure was repeated with $CdCl_2$ (0.19 g, 1.0 mmol) and $(THF)_3LiSi(SiMe_3)_3$ (1.00 g, 2.13 mmol) in diethyl ether (20 mL). The solution was stirred for 18 h and then worked up as above to give 0.45 g (74%) of pale green crystals, mp 154–160°C dec. Anal. Calcd for $C_{18}H_{54}CdSi_8$: C, 35.6; H, 8.96. Found: C, 35.6; H, 8.99. IR (Nujol, CsI; cm^{-1}): 1384 m, 1298 w, 1250 s, 1235 s, 1090 br w, 1037 m, 830 br s, 738 m, 678 s, 616 s, 450 m, 390 m, 295 w.

$Hg[Si(SiMe_3)_3]_2$ (1c). A solution of $HgBr_2$ (0.38 g, 1.1 mmol) and $(THF)_3LiSi(SiMe_3)_3$ (1.00 g, 2.1 mmol) in diethyl ether was stirred for 45 min. Workup as above yielded 0.41 g (56%) of pale yellow crystals, mp 199–200 °C. Anal. Calcd for $C_{18}H_{54}HgSi_8$: C, 31.1; H, 7.82. Found: C, 30.8; H, 7.80. IR (Nujol, CsI; cm^{-1}): 1382 m, 1297 w, 1248 s, 1233 s, 828 br s, 735 m, 678 s, 614 s, 451 m, 382 m, 290 w.

$Zn[Si(SiMe_3)_3]_2(bpy)$ (2a). Pentane (30 mL) was added to a mixture of $Zn[Si(SiMe_3)_3]_2$ (0.20 g, 0.36 mmol) and bipyridine (0.056 g, 0.36 mmol). After the mixture was stirred for 10 min, the purple solution was filtered and concentrated to ca. 5 mL in vacuo. Cooling to −45 °C gave purple crystals (mp 180–183 °C) of the product in 77% yield (0.20 g). Anal. Calcd for $C_{28}H_{62}N_2Si_8Zn$: C, 46.9; H, 8.72. Found: C, 46.7; H, 8.79. IR (Nujol, CsI; cm^{-1}): 1589 m, 1432 s, 1302 m, 1230 br s, 1146 m, 1006 m, 830 br s, 751 s, 730 s, 672 s, 608 s, 431 m, 407 m.

$Cd[Si(SiMe_3)_3]_2(bpy)$ (2b). The above method was followed with $Cd[Si(SiMe_3)_3]_2$ (0.20 g, 0.33 mmol) and bipyridine (0.051 g, 0.33 mmol). Bright red crystals (mp 147–148 °C) were isolated in 60% yield (0.15 g). Anal. Calcd for $C_{28}H_{62}CdN_2Si_8$: C, 44.0; H, 8.18. Found: C, 43.8; H, 8.21. IR (Nujol, CsI; cm^{-1}): 1585 m, 1545 w, 1430 s, 1201 m, 1228 s, 1145 m, 999 m, 830 br s, 750 s, 730 s, 672 s, 617 s, 438 m, 400 m.

Reaction of 1a with HCl. A 5-mm septum-capped NMR tube was charged with **1a** (0.020 g, 0.035 mmol) and benzene-d_6 (0.4 mL). Dry HCl gas (5 cm^3, excess) was then added to the NMR tube with a gastight syringe. Reaction occurred immediately to produce a white precipitate (presumably $ZnCl_2$) and $HSi(SiMe_3)_3$ as the only product detected by ^1H NMR.

Reaction of 1a with H_2O. To a 5-mm septum-capped NMR tube containing **1a** (0.020 g, 0.035 mmol) and benzene-d_6 (0.4 mL) was added H_2O (3 μL, 0.17 mmol). Over the course of a few hours, the reaction proceeded to give an insoluble white material and $HSi(SiMe_3)_3$ (by ^1H NMR).

Collection of Diffraction Data. Crystal data and the parameters used during the collection of diffraction data are collected in Table II. A colorless crystal of **1a** was sealed in a glass capillary. **1a** was found to crystallize in the triclinic space group $P\bar{1}$. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with $14° < 2\theta < 21°$. No absorption correction was needed (regular crystal shape, $\mu = 9.3$ cm^{-1}). The structure displayed an unusually high thermal activity in the methyl groups, and the absence of diffraction data beyond $2\theta = 42°$ and the very low density ($D = 1.00$ cm^{-3}) are in keeping with a very loose lattice packing. The particularly high thermal parameters for the methyl groups of Si(3) may additionally contain unresolved rotational disorder.

Solution and Refinement of the Structure. The structure was solved intuitively, with Zn placed at ($^1/_2$, $^1/_2$, $^1/_2$). The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and were refined anisotropically. Hydrogen atom positions were calculated and fixed in idealized positions (d(C–H) = 0.96 Å; thermal parameters equal 1.2 times the isotropic equivalent for the carbon to which it was attached). The final difference Fourier synthesis showed only a diffuse background (maximum 0.63 e/Å^3). An inspection of F_o vs. F_c values and trends based upon sin θ, Miller index, or parity group failed to reveal any systematic error. All computer programs used in the data collection and refinement are contained in the Nicolet (Madison, WI) program package SHELXTL (version 5.1).

Atomic coordinates are provided in Table III and bond distances and angles in Table IV. Additional data are available as supplementary material.

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Registry No. **1a**, 108168-22-5; **1b**, 108168-23-6; **1c**, 61576-80-5; **2a**, 108150-76-1; **2b**, 108150-77-2; $(THF)_3LiSi(SiMe_3)_3$, 81859-95-2.

Supplementary Material Available: Table 2S, listing anisotropic thermal parameters, and Table 3S, listing hydrogen atom coordinates and their isotropic thermal parameters (2 pages); Table 1S, listing calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Cesium Molybdenum Alum, $Cs[Mo(H_2O)_6](SO_4)_2 \cdot 6H_2O$, at 110 K

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Received December 30, 1986

The X-ray crystal structure of cesium molybdenum alum provides the first structural characterization of the hexaaquamolybdenum(III) ion: Mo–O is 2.089 (1) Å. The alum belongs to the β class and has the cubic cell dimension $a = 12.442$ (1) Å at 110 K. Refinement of the structure (space group $Pa\bar{3}$) was made on the basis of 2791 reflections to $R = 0.0214$. A general discussion of the conformations of transition-metal hexaaqua ions is given. The occurrence of pyramidally ligating water molecules in certain α-alums is ascribed to a partial avoidance of π overlap with low-spin d^6 metal ions. The angular overlap model has been used to calculate the electronic stabilization energies of different conformations of d^n hexaaqua ions containing planarly ligating water molecules. In the alums, however, the conformation taken by the hexaaqua ions is that which fits the hydrogen-bonding pattern of the structure.

The hexaaquamolybdenum(III) ion has recently[1,2] been isolated in the solid state by preparation of cesium molybdenum alum, $Cs[Mo(H_2O)_6](SO_4)_2 \cdot 6H_2O$, whose low-temperature X-ray crystal structure is reported here. The structure gives a characterization of the $[Mo(H_2O)_6]^{3+}$ ion and extends the large series of cesium alum structure determinations already made.[3,4] These alum structures are important in the study of hexaaqua ions because the alums for many trivalent metal ions are the only compounds in which the hexaaqua ions may be isolated. It has thus been

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[†] Chemistry Department I.

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(1) Brorson, M.; Schäffer, C. E. *Acta Chem. Scand., Ser. A* **1986**, *A40*, 358–360.

(2) Since the publication of ref 1 the magnetic susceptibility of the alum has been measured from 5 K to room temperature. The observed susceptibility is $\chi = 5.67 \times 10^{-3}$ cgsu mol^{-1} at 298 K, which corresponds to the magnetic moment of $[Mo(H_2O)_6]^{3+}$ being $\mu_{eff} = 3.77$ μ_B when correction for diamagnetism has been made.

(3) Beattie, J. K.; Best, S. P.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 2105–2111.

0020-1669/87/1326-2109$01.50/0

Table I. Crystallographic Data for Cesium Molybdenum Alum

formula	$Cs[Mo(H_2O)_6](SO_4)_2 \cdot 6H_2O$
fw	637.15
space group	$Pa\bar{3}$
a, Å	12.442 (1)
V, Å^3	1926.3
Z	4
d(calcd), g cm^{-3}	2.197
cryst size, mm	octahedron edge = 0.064
μ, cm^{-1}	28.054
2θ range, (°) deg	0–30
range of indices	hkl, 0–17
no. of obsvns	3274
Results from Refinement Including Extinction	
no. of unique data	2791
no. of data with $F > 3\sigma(F)$	1439
R	0.0214
R_w	0.0226
w	$(\sigma^2(F) + 0.005F^2)^{-1}$
g	0.844 (3) × 10^{-4}

found[3,4] that the M^{III}–OH_2 units of the $[M^{III}(H_2O)_6]^{3+}$ ions are *pyramidal* in the cesium alums of cobalt, rhodium, and iridium, but *planar* in the other cesium alums. A possible explanation for these findings will be given here in terms of the electron configuration of the metal ion. Furthermore, the electronic energy differences between different conformations[5] of a hexaaqua ion containing planarly ligating water will be discussed in a ligand-field context by using the angular overlap model. These conformations differ by the relative orientations of the six water molecule planes.

Experimental Section

Preparation. Alum crystals were prepared from sodium hexakis(formato)molybdate(III) and cesium sulfate in *p*-toluenesulfonic acid as described in ref 1.

Crystallography. Oxidation of the alum by the atmosphere during the X-ray data collection did not take place since the crystal was cooled down to 110 K in a stream of evaporating dinitrogen. From a preliminary data collection on another specimen from the batch it was known that the integrated intensities were affected by extinction. Hence the crystal was dipped in liquid dinitrogen several times to increase the mosaic spread. The diffraction data were collected on a Nonius-CAD4 diffractometer using monochromatized Mo Kα radiation (λ = 0.71069 Å) and performing $\omega/2\theta$ scans. The cell dimension was determined from a least-squares fit to the positions of 25 reflections. The maximum scan time used was 180 s. For determination of the backgrounds the scans were extended 25% on each side of the peak. Three reflections were measured every 10000 s to check for decay of the crystal, which, however, did not appear to take place. Crystallographic data are given in Table I. The data were corrected for Lorentz, polarization, and absorption effects. The structure was easily solved by using knowledge of other alum structures.[3] Least-squares refinements of F's were performed by using the programs of the SDP package.[6] The discrepancy indices, $R = \sum||F_o| - k|F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - k|F_c|)^2/\sum w|F_o|^2)^{1/2}$, obtained were 0.0274 and 0.0277, refining 50 variables and using 466 unique observations ($I/\sigma(I) > 2$) after averaging (R_{int} = 0.018 on F's). However, some reflections were still affected by extinction. Inspection of the ψ scans of several low-order reflections revealed no significant variation, indicating the extinction to be essentially isotropic. Hence refinements were made by including isotropic extinction parameters[7] using the program MOLLY[8] (no multipole refinement) and the scattering factors of Cromer and Mann.[9] Several models for the secondary extinction were tried out. The best fit was obtained with the mosaic spread, described by a Lorentzian distribution function, being the main contributor to the extinction. The final discrepancy parameters are given in Table I. Non-hydrogen atoms were refined anisotropically while the isotropic thermal parameters of the hydrogen atoms were fixed.

Table II. Positional Parameters for Cesium Molybdenum Alum

	x	y	z
Cs	0.500	0.500	0.500
Mo	0.000	0.000	0.000
S	0.3273 (1)	0.3273 (1)	0.3273 (1)
O1	0.2587 (2)	0.2587 (2)	0.2587 (2)
O2	0.2811 (1)	0.3339 (1)	0.4365 (1)
O3	0.5536 (1)	0.2938 (1)	0.6594 (1)
O4	0.1679 (1)	−0.0019 (1)	−0.0010 (1)
H31	0.526 (3)	0.281 (3)	0.705 (3)
H32	0.610 (2)	0.284 (3)	0.678 (3)
H41	0.202 (3)	−0.048 (3)	0.017 (2)
H42	0.204 (3)	0.047 (3)	−0.022 (2)

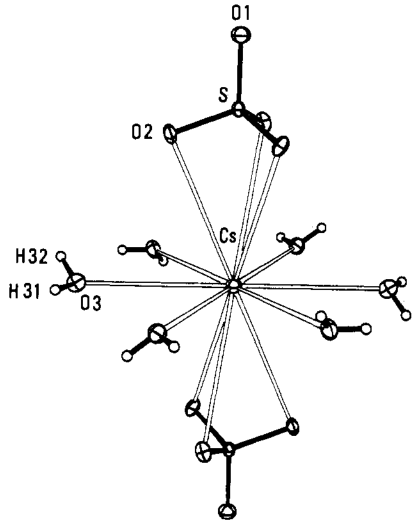

Figure 1. Environment of the cesium ion in cesium molybdenum alum. The cesium ion, whose site symmetry is S_6, has 12 oxygen atom neighbors: six from the water of crystallization and six from the two sulfate groups on the crystallographic 3-fold axis. The β structure of the cesium molybdenum alum is established by the fact that the six water oxygen atoms (almost) lie in the same plane.

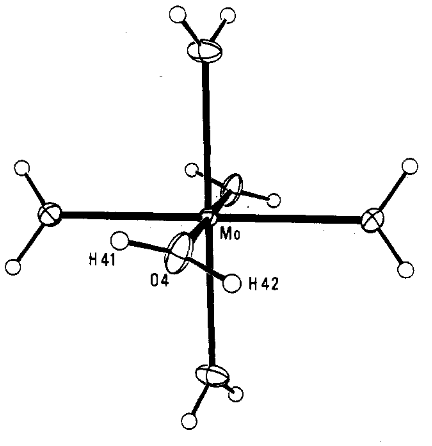

Figure 2. The $[Mo(H_2O)_6]^{3+}$ ion as found in the alum. The three cyclically permutable crystal axes are approximately parallel to the 4-fold axes of the MoO_6 octahedron and have on the figure their positive ends directed out, right, and up, respectively.

Results

The space group symmetry imposes some restrictions on the atomic coordinates in the alum structure: cesium and molybdenum are located on completely symmetry-fixed positions with site symmetry S_6 ($\bar{3}$) while sulfur and one of the sulfate group oxygen atoms are located on the crystallographic 3-fold axis. The positional parameters obtained by the refinement are given in Table

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(4) Armstrong, R. S.; Beattie, J. K.; Best, S. P.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1973–1975.

(5) Cotton, F. A.; Fair, C. K.; Lewis, G. E.; Mott, G. N.; Ross, F. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 5319–5323.

(6) Structure Determination Package, Enraf-Nonius, Delft, Holland.

(7) Becker, P. J.; Coppens, P. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 129–147.

(8) Hansen, N. K.; Coppens, P. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1978**, *A34*, 909–921.

(9) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321–324.

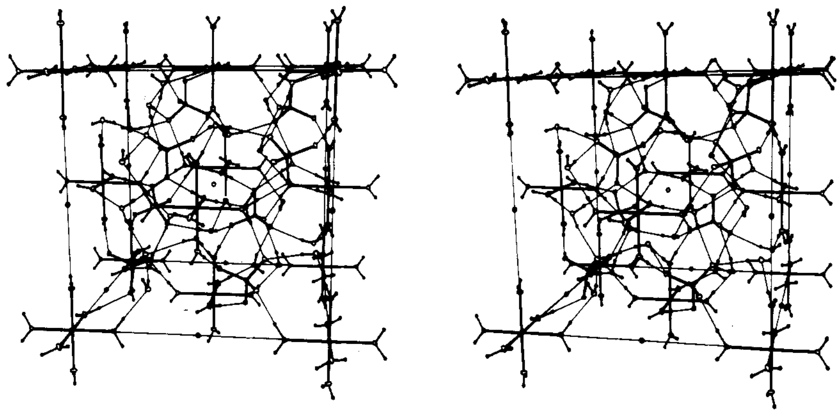

Figure 3. Stereoscopic view of the unit cell. Hydrogen bonds are represented by thin lines. Notice, in particular, that the conformations taken by the $[Mo(H_2O)_6]^{3+}$ ions are those that fit the hydrogen-bonding pattern.

Table III. Bond Lengths (Å) and Angles (deg) for Cesium Molybdenum Alum[a]

Mo–O4	2.089 (1)	S–O1	1.478 (1)
Cs–O2	3.509 (1)	S–O2	1.478 (1)
Cs–O3	3.311 (1)		
O3–H31	0.68 (4)	O4–H41	0.75 (3)
O3–H32	0.75 (4)	O4–H42	0.80 (3)
O4–Mo–O4′	91.00 (6)	O1–S–O2	109.83 (5)
O3–Cs–O3′	60.02 (4)	O2–S–O2′	109.11 (8)
O2–Cs–O3	80.49 (3)		
H31–O3–H32	101 (5)	H41–O4–H42	110 (4)
	Hydrogen Bonds		
O3–O2	2.776 (2)	O3—H31–O2	170 (4)
O3–O1	2.827 (2)	O3–H32–O1	173 (3)
O4–O3	2.602 (2)	O4–H41–O3	176 (3)
O4–O2	2.638 (2)	O4–H42–O2	175 (3)

[a] The angle between a Mo–O4 bond and its associated crystal axis is 0.74 (4).

II, bond lengths and angles, in Table III, and thermal parameters, in Table SI.

Alums are divided into three classes: α, β, and γ. The γ class, whose only member is sodium (aluminum) alum, is characterized by the orientation of the sulfate group, which here has the oxygen on the 3-fold axis directed toward the univalent metal ion. In the α- and β-alums this oxygen is directed toward the trivalent metal ion, and the univalent metal ion has 12 neighboring oxygen atoms: six belonging to two sulfate groups and six belonging to the water of crystallization. The geometry of these latter six oxygen atoms about the univalent metal ion has been suggested[3] as a structural criterion for distinguishing between α- and β-alums: In the α-alums the oxygen atoms of the six water molecules form a puckered ring around the metal while the ring in β-alums is almost planar. According to this criterion the cesium molybdenum alum is assigned to the β class (Figure 1).

The molybdenum atom lies on a S_6 site, but the six oxygen atoms by which it is coordinated are very close to forming a regular octahedron (Figure 2). The Mo–O distance in $[Mo(H_2O)_6]^{3+}$ is 2.089 (1) Å, which may, for example, be compared to the values 2.155 (3) and 2.18 (1) Å found[10] for water–oxygen molybdenum(III) bonds in $(NH_4)_2[MoX_5(H_2O)]$ (X = Cl, Br).

The low-temperature data collection has helped to sharpen the directions in space of the O–H bonds. These directions, which by the X-ray technique are better determined than the O–H bond lengths, determine the water ligation symmetry. As in the other[3] cesium β-alums it is found here that the water molecules are planarly ligating to the trivalent metal ion. This is borne out in the fact that the sum of the three angles subtended at the oxygen atom is 360 (4)°, i.e. within the standard deviation equal to the value characteristic of a planar $Mo–OH_2$ unit.

Discussion

In ref 3 possible structural criteria that might accomplish a division of non-γ alums into an α and a β class were discussed. It was found that the geometry of the six water molecule oxygen atoms around the univalent metal ion divided the structures known into distinct classes. The cesium cobalt alum was, as the only cesium alum, placed in the α class, but the other criteria considered all placed it in an intermediate position between distinct α and β classes.[11] The fact that the same is the case for the structures[4] of cesium rhodium and cesium iridium alums suggests a subdivision of the α class into α′ and α″ where the α′ class contains all α-alums except the cesium alums of cobalt, rhodium, and iridium, which instead belong to the α″ class.

The alums of the α″ class contain $[M^{III}(H_2O)_6]^{3+}$ ions whose $M–OH_2$ units are pyramidal. The angle, θ_{wag},[12] between the M–O bond and the water molecule plane is approximately 30°, i.e. intermediate between the value $\theta_{wag} = 0°$ for planarly ligating water and the value $\theta_{wag} \approx 55°$ for tetrahedrally ligating water. The occurrence of pyramidal $M–OH_2$ units is often related to the acceptance of a hydrogen bond by the oxygen atom (cf., for example, Figure 1 where O3 accepts a hydrogen bond from H41). However, the oxygen atoms coordinated to the trivalent metal ion do not accept hydrogen bonds in the alums, and an explanation for the pyramidally ligating water in the α″ alums is probably best found in the electronic structure of the metal ion.

In an octahedrally coordinated d-block transition-metal ion the orbitals transforming as e_g may form σ bonds (but not π bonds) to the ligands, and the orbitals transforming as t_{2g} may form π bonds (but not σ bonds) to the ligands. The overlap between the t_{2g} orbitals of the metal ion and the π-donating orbital of a water molecule depends on the angle θ_{wag} in such a way that a maximum overlap is obtained when the water is planarly ligating and a minimum is obtained when it is tetrahedrally ligating. In the α′- and β-alums the π donation from water to the t_{2g} orbitals is energetically favorable, and the overlap is maximized by a planar ligation. In the α″-alums, however, the trivalent metal ions have the electron configuration $(t_{2g})^6$ corresponding to a *filled* t_{2g} orbital level. Therefore π donation from water may be unfavorable and thus (partially) avoided by approaching a ligation symmetry that is tetrahedral.

Hexaaqua ions containing planarly ligating water may take different conformations due to the free rotation about the M–O bonds. Three high-symmetry rotamers are possible (ref 5, Figure 1): a T_h conformation, an all-horizontal D_{3d} conformation, and an all-vertical D_{3d} conformation. The two D_{3d} conformations, which differ by the orientations of the water molecules relative to the 3-fold axis, may alternatively be described by the adjectives longitudinal and latitudinal, respectively. The D_{3d} conformations may be obtained from the T_h conformation by a set of symmetry

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(10) Cavell, R. G.; Quail, J. W. *Inorg. Chem.* **1983**, *22*, 2597–2599.

(11) These criteria were (a) the sulfur atom fractional coordinate, (b) the orientation of the $[M^{III}(H_2O)_6]^{3+}$ octahedron relative to the crystal axes, and (c) the distance ratio between $M^I–O$ bonds to sulfate and to water.

(12) Hunt, J. P.; Friedman, H. L. *Prog. Inorg. Chem.* **1983**, *30*, 359–387.

coupled rotations of the six water molecules about the M–O bonds. Each water molecule is rotated 45°, but depending on the overall direction of the six coupled rotations, one arrives at either the all-horizontal or the all-vertical conformation. In the $[Mo(H_2O)_6]^{3+}$ ion the angle of rotation is 22 (3)° and the conformation is intermediate between the T_h and the all-horizontal D_{3d} conformations (cf. Figure 2).

Generally, the symmetry lowering from T_h to D_{3d} splits the triply degenerate t_{2g} orbital level into a nondegenerate $a_{1g}(D_{3d})$ level and a doubly degenerate $e_g(D_{3d})$ level. The absolute magnitude of this splitting amounts to $3e_{\pi\perp}$ in an angular overlap model[13] description, where $e_{\pi\perp}$ is the parameter associated with the water π orbital, which is perpendicular to the molecular plane, and where $e_{\pi\parallel}$ is assumed to vanish. As also found[5] by other methods the energetic ordering of the orbital levels is opposite in the two conformations: In the all-horizontal conformation the $e_g(D_{3d})$ level is the lower; in the all-vertical conformation the $a_{1g}(D_{3d})$ level is the lower. In the AOM description the splitting of the t_{2g} orbital level follow the barycenter principle, i.e. the $a_{1g}(D_{3d})$ level has the relative energy $\pm 2e_{\pi\perp}$ and the $e_g(D_{3d})$ level the relative energy $\mp e_{\pi\perp}$. On the basis of the ligand field stabilization energies associated with the D_{3d} field component one would expect[5] d^1 transition-metal hexaaqua ions to take the all-vertical conformation, d^2 ions to take the all-horizontal conformation, and d^3 ions to be equally stable in any of the three conformations and in fact in any conformation. The fact that cesium titanium[14] (d^1), cesium vanadium[3] (d^2), and cesium chromium[3] (d^3) alums, as well as the alums of closed-shell trivalent metal ions, have trivalent metal ions in conformations that are very similar to that of $[Mo(H_2O)_6]^{3+}$ (Figure 2) indicates, however, that the electronic structure has little influence on the conformation found in the alums. Rather it is the hydrogen-bonding pattern of the crystal that determines the conformation of these planarly ligated hexaaqua ions (Figure 3).

Acknowledgment. We are grateful to Flemming Hansen for technical assistance and to the Danish Natural Science Research Council for financial support (Grant No. 11-4894 to M.B. and Grants Nos. 11-2360 and 11-1837, which provided the diffractometer and the low-temperature equipment).

Supplementary Material Available: Table SI, listing thermal parameters (1 page); a table of structure factors (6 pages). Ordering information is given on any current masthead page.

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(14) Sygusch, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 662–665.

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Vanadium-51 NMR Spectroscopy of Tungstovanadate Polyanions. Chemical Shift and Line-Width Patterns for the Identification of Stereoisomers[1]

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Vanadium-51 NMR spectra are reported for several tungstovanadate polyoxoanions, including $V_xW_{6-x}O_{19}^{(2+x)-}$ (x = 1–3), α-$SiV_xW_{12-x}O_{40}^{(4+x)-}$ (x = 1–3), β_1-, β_2-, and β_3-$SiVW_{11}O_{39}^{5-}$, α-$PV_2W_{10}O_{40}^{5-}$ (mixture of isomers), $VV_2W_{10}O_{40}^{5-}$ (mixture of isomers), and $VV_3W_9O_{40}^{6-}$ (mixture of isomers). Two-bond coupling of ^{51}V to ^{183}W was resolved in spectra of $VW_5O_{19}^{3-}$ and α-$BVW_{11}O_{40}^{6-}$. The pH dependence of the chemical shift permits evaluation of pK_a's for $HV_2W_4O_{19}^{3-}$ and for α- and β-$HSiV_3W_9O_{40}^{6-}$. There is a linear correlation between δ and the square root of the line width for structurally related anions such as $RVW_{11}O_{40}^{n-}$ (R = H_2, B, Si, P). As more adjacent VO_6 octahedra are incorporated into a polyanion structure, both line width and chemical shift increase. The effect on line width is greater if the VO_6 octahedra share corners, and the effect on δ is greater if the VO_6 groups share edges. This pattern enables the identification of resonance lines for the 1,2- and 1,4-isomers of $PV_2W_{10}O_{40}^{5-}$ and $VV_2W_{10}O_{40}^{5-}$ in spectra of samples containing all possible stereoisomers and of the line for the 1,4,9-isomer of $VV_3W_9O_{40}^{6-}$ in a mixture of at least 13 isomers.

Characterization and structural identification of solute species by NMR spectroscopy is dramatically advancing the field of heteropoly- and isopolyanion chemistry. In particular, chemical shifts of ^{17}O NMR lines,[2] relative line intensities,[3] and connectivity patterns revealed by $^{183}W\cdots{}^{183}W$ coupling[4] are powerful structure indicators. However, both ^{17}O and ^{183}W are difficult nuclei to observe on account of low natural abundance or low inherent sensitivity, and satisfactory NMR spectra require the use of concentrated solutions and long accumulation times. In contrast, ^{51}V is an abundant, NMR-sensitive nucleus[5] and spectra are easily and rapidly recorded by normal FT techniques on millimolar solutions. Indeed, several earlier ^{51}V NMR studies of polyvanadates were made by using CW techniques.[6] At present there is no satisfactory correlation between structure and ^{51}V spectral parameters for polyanion solutions. We have therefore investigated several series of tungstovanadate heteropolyanions, including mixtures of stereoisomers, to seek structure–spectra correlation patterns and to explore the value of ^{51}V NMR spectra in this field.

Experimental Section

Preparation of Compounds. Hexametalate Salts. Tetra-*n*-butylammonium pentatungstovanadate was prepared according to Flynn's

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