

Single-Crystal Neutron Structure Analysis of $(\text{NH}_4)_{21}[\text{H}_3\text{Mo}_{57}\text{V}_6(\text{NO})_6\text{O}_{183}(\text{H}_2\text{O})_{18}]\cdot 53 \text{H}_2\text{O}$

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The crystal structure of $(\text{NH}_4)_{21}[\text{H}_3\text{Mo}_{57}\text{V}_6(\text{NO})_6\text{O}_{183}(\text{H}_2\text{O})_{18}]\cdot 53 \text{H}_2\text{O}$, a supramolecular heteropoly cluster compound (space group $P6_3/mmc$, $Z=2$, final $R1=0.1302$ ($I>2\sigma(I)$) for 1745 unique reflections), was redetermined by single-crystal neutron diffraction studies at 20 K. The X-ray diffraction results reported in 1994 by Müller *et al.* (*Z. Anorg. Allg. Chem.* 620, 599) are confirmed. Additionally, we could localize many hydrogen positions not found so far and establish a phase transition near 240 K. Many of the ammonium ions, the ligand and hydrate H_2O molecules, and the hydroxy group are orientationally disordered, even at 20 K. The central cavity of the structure is built up by two twelve-membered rings consisting of six $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds each. These strong hydrogen bonds are obviously decisive for the stability of the cluster. The hydrate H_2O molecules are stronger-hydrogen-bond acceptor groups than the oxoligands of the cluster. © 2002 Elsevier Science (USA)

Key Words: molybdenum vanadium heteropolyanion cluster; single-crystal neutron diffraction; hydrogen bonds; phase transition.

INTRODUCTION

The determination of the structure and formula of giant transition metal-oxide cluster anions, in particular of the mixed valent type, is rather difficult, especially if the cation concentration is low and in the case of their disorder, but also if protonations are possible. Under such circumstances, the X-ray structure analysis (1) does not provide the information necessary for a complete determination of the formula: examples which we have had to deal with were crystalline compounds obtained from molybdenum blue solutions in which giant wheel cluster anions of the type Mo_{154} are present but also the $\{\text{M}_6\text{Mo}_{57}\}$ type clusters, which have remarkable multifunctional properties. In these cases, different types of spectroscopic studies, in addition to carefully performed analyses, have proved to be helpful. In the latter case we felt it was necessary to do, in addition, a single crystal neutron structure analysis in order to rule out

any final doubt with respect to the degree of protonation. The neutron diffraction experiments had to be performed at low temperatures (20 K). In the case of larger thermal motion of the hydrate H_2O molecules at higher temperatures, the hydrogen and oxygen position cannot be found unequivocally because the similar absolute values of the scattering lengths of hydrogen ($-3.739 \text{ fm}(2)$) and oxygen atoms ($+5.803 \text{ fm}$) can lead to cancellations of the peaks.

EXPERIMENTAL

The synthesis was performed according to Ref. (1). For the neutron experiment a single crystal with the dimensions $5.9 \times 5.2 \times 3.3 \text{ mm}^3$ was used and fixed with silica wool in a silica tube. The crystal was covered with a thin oil film of Santovac S5 fluid (Edward, H114-01-001) in order to prevent the loss of crystal water during the measurement. The measurement was executed on the D19 thermal-beam neutron diffractometer at the high-flux reactor of the Institute Laue-Langevin (ILL), Grenoble. This instrument is equipped with a $4 \times 64^\circ$ position-sensitive detector. The crystal was indexed at room temperature and then cooled to 20 K at 1 K min^{-1} with a Displex cryorefrigerator, while the strong 0 0 2 reflection was monitored. For the data collection a neutron wavelength of $\lambda = 153.50(3) \text{ pm}$ was used. Bragg intensities were integrated in three dimensions using the ILL program RETREAT (3). Neutron scattering lengths were taken from Sears (2). The structure was refined with the program SHELXL97 (4) with the atomic coordinates of X-ray structure at 173 K (1) as the starting model. The vanadium positions were fixed because it is difficult to obtain accurate vanadium parameters in a neutron experiment because of the small value of b_{coh} (-0.38 fm). With the help of difference Fourier methods it was possible to locate the hydrogen sites. During the refinement the O–H distances were fixed at 95 and 100 pm of ammonium ions and H_2O molecules, respectively.

TABLE 1

Crystal Data, Parameters Used for Data Collection, and R Values of the Neutron Single-Crystal Refinement of $(\text{NH}_4)_{21}[\text{H}_3\text{Mo}_{57}\text{V}_6(\text{NO})_6\text{O}_{183}(\text{H}_2\text{O})_{18}] \cdot 53 \text{ H}_2\text{O}$

$M/g \text{ mol}^{-1}$	10545
Space group, Z	$P6_3/mmc$ (No. 194), 2
Lattice constants/pm	$a = 2356.37(13)$ $c = 2690.55(19)$
Unit-cell volume/ 10^6 pm^3	12937.7
Calculated density/ Mg m^{-3}	2.711
Crystal size/ mm^3	$5.9 \times 5.2 \times 3.3$
Temperature/K	20
Wavelength/pm	153.50
Theta range/ $^\circ$	2.71–45.68
hkl ranges	$-15 \leq h \leq 20$, $-15 \leq k \leq 21$, $-22 \leq l \leq 25$
No. of reflections measured	5355
No. of unique reflections ($I \geq 2\sigma_i$)	1745
Parameters refined, restraints	412, 49
R (all reflections) ^a	$R1 = 0.1388$, $wR2 = 0.3201$
$R(I > 2\sigma(I))$ ^a	$R1 = 0.1302$, $wR2 = 0.3118$
Goodness of fit	1.064
Residual scattering density $\Delta\rho/\text{fm pm}^{-3}$	1.436×10^{-6} , -1.141×10^{-6}

$$^a w = [\sigma^2(F_o^2) + (0.1604 \cdot P)^2 + 1020.33 \cdot P] \text{ with } P = (F_o^2 + 2F_c^2)/3.$$

RESULTS

The cooling process was monitored by following the intensities of the 0 0 2 reflection. During cooling a hitherto unknown possible phase transition at 240 K was observed because the observed reflection displayed an increase of 20% in intensity. Therefore, it can be assumed that it is mainly due to the positions of the hydrogen atoms.

The refinement of the structure of the title compound in the centrosymmetric space group $P6_3/mmc$ (No. 194) with 412 parameters on the basis of 1745 unique reflections ($I \geq 2\sigma_i$) gave residuals $R1 = 13.02\%$, $wR2 = 31.18\%$, and $S = 1.064$. It was not possible to achieve better agreement because the number of unique reflections is too small to allow additional parameters to be refined. In particular, most H_2O molecules are disordered and this disorder cannot be modeled with the data available.

The crystal data and details concerning the intensity data collection and structure refinement are given in Table 1.¹ Atomic coordinates and isotropic thermal parameters as well as bond lengths and angles are given in Table 2 and 3.

¹Additional material to this paper can be ordered by referring to CSD 411895, the name of the main author, citations of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. The list of the F_o/F_c data is available from the author up to one year after the publication has appeared

TABLE 2

Final Atomic Co-ordinates and Equivalent Isotropic Displacement Parameters ($\times 10^4 \text{ pm}^2$) of $(\text{NH}_4)_{21}[\text{H}_3\text{Mo}_{57}\text{V}_6(\text{NO})_6\text{O}_{183}(\text{H}_2\text{O})_{18}] \cdot 53 \text{ H}_2\text{O}$ (Second Line: Single-Crystal X-Ray Data (1) in Italics $U_{\text{eq}} = B_{\text{eq}}/8\pi^2$)

Atom	Site	x	y	z	U_{eq}
Mo(1)	24 l	−0.0824(4)	0.3241(4)	0.6888(3)	0.027(2)
		<i>−0.0817(1)</i>	<i>0.3248(1)</i>	<i>0.6891(1)</i>	<i>0.028(1)</i>
Mo(2)	24 l	0.0413(3)	0.2579(3)	0.6900(3)	0.022(2)
		<i>0.0423(1)</i>	<i>0.2589(1)</i>	<i>0.6904(1)</i>	<i>0.023(1)</i>
Mo(3)	6 h	0.1827(3)	0.3653(7)	0.7500	0.018(4)
		<i>0.1829(1)</i>	<i>0.3658(1)</i>	<i>0.7500</i>	<i>0.020(1)</i>
Mo(4)	12 k	0.1779(3)	0.3559(5)	0.6302(4)	0.023(3)
		<i>0.1788(1)</i>	<i>0.3576(1)</i>	<i>0.6306(1)</i>	<i>0.021(1)</i>
Mo(5)	24 l	0.0714(4)	0.4068(4)	0.6143(3)	0.030(2)
		<i>0.0718(1)</i>	<i>0.4068(1)</i>	<i>0.6145(1)</i>	<i>0.026(1)</i>
Mo(6)	12 j	0.0670(5)	0.4622(5)	0.7500	0.030(3)
		<i>0.0682(1)</i>	<i>0.4634(1)</i>	<i>0.7500</i>	<i>0.024(1)</i>
Mo(7)	12 k	0.2481(2)	0.4962(5)	0.5678(4)	0.018(3)
		<i>0.2484(1)</i>	<i>0.4968(1)</i>	<i>0.5687(1)</i>	<i>0.020(1)</i>
V(1)	24 l	0.4259	0.5740	0.5710	0.018
V(2)	12 k	0.4207	0.5793	0.5928	0.011
N(100)	12 k	−0.0467(6)	0.4766(3)	0.6034(6)	0.101(5)
		<i>−0.0497</i>	<i>0.4752</i>	<i>0.5987</i>	
N	12 k	0.1537(2)	0.3073(4)	0.5772(4)	0.033(2)
		<i>0.1547(4)</i>	<i>0.3095(7)</i>	<i>0.5769(5)</i>	<i>0.027(4)</i>
O	12 k	0.1369(5)	0.2739(9)	0.5414(7)	0.061(5)
		<i>0.1369(5)</i>	<i>0.2738(9)</i>	<i>0.5410(5)</i>	<i>0.073(6)</i>
O(1)	24 l	−0.1123(4)	0.3772(5)	0.6874(4)	0.032(3)
		<i>−0.1110(5)</i>	<i>0.3785(5)</i>	<i>0.6871(4)</i>	<i>0.038(3)</i>
O(2)	12 j	−0.1206(6)	0.2785(7)	0.7500	0.033(4)
		<i>−0.1187(6)</i>	<i>0.2800(7)</i>	<i>0.7500</i>	<i>0.032(3)</i>
O(3)	24 l	−0.1332(4)	0.2637(4)	0.6487(3)	0.029(2)
		<i>−0.1319(4)</i>	<i>0.2640(4)</i>	<i>0.6496(3)</i>	<i>0.037(2)</i>
O(4)	24 l	−0.0266(4)	0.2674(4)	0.6956(3)	0.029(2)
		<i>−0.0258(4)</i>	<i>0.2686(4)</i>	<i>0.6959(3)</i>	<i>0.030(2)</i>
O(5)	24 l	−0.0072(4)	0.3738(4)	0.6470(3)	0.027(2)
		<i>−0.0055(4)</i>	<i>0.3743(4)</i>	<i>0.6477(3)</i>	<i>0.027(2)</i>
O(6)	12 j	−0.0129(6)	0.3862(6)	0.7500	0.024(3)
		<i>−0.0112(6)</i>	<i>0.3878(6)</i>	<i>0.7500</i>	<i>0.026(3)</i>
O(7)	12 j	0.0340(6)	0.2104(6)	0.7500	0.027(3)
		<i>0.0321(6)</i>	<i>0.2100(6)</i>	<i>0.7500</i>	<i>0.027(3)</i>
O(8)	24 l	0.0205(5)	0.1960(5)	0.6479(4)	0.034(3)
		<i>0.0211(5)</i>	<i>0.1976(4)</i>	<i>0.6492(3)</i>	<i>0.036(2)</i>
O(9)	12 k	0.1440(3)	0.2880(6)	0.6872(5)	0.028(3)
		<i>0.1439(3)</i>	<i>0.2878(6)</i>	<i>0.6867(4)</i>	<i>0.025(3)</i>
O(10)	24 l	0.0847(4)	0.3364(4)	0.6469(3)	0.022(2)
		<i>0.0845(4)</i>	<i>0.3372(4)</i>	<i>0.6473(3)</i>	<i>0.019(2)</i>
O(11)	12 j	0.0920(6)	0.3318(6)	0.7500	0.019(3)
		<i>0.0937(6)</i>	<i>0.3349(6)</i>	<i>0.7500</i>	<i>0.026(3)</i>
O(12)	24 l	0.1651(4)	0.4304(4)	0.6048(3)	0.024(2)
		<i>0.1658(4)</i>	<i>0.4318(4)</i>	<i>0.6052(3)</i>	<i>0.021(2)</i>
O(13)	12 k	0.2087(3)	0.4174(6)	0.6981(4)	0.019(3)
		<i>0.2091(2)</i>	<i>0.4183(5)</i>	<i>0.6993(4)</i>	<i>0.018(3)</i>
O(14)	24 l	0.0435(4)	0.3687(4)	0.5573(3)	0.024(2)
		<i>0.0444(4)</i>	<i>0.3689(4)</i>	<i>0.5579(3)</i>	<i>0.031(2)</i>
O(15)	24 l	0.0917(4)	0.4880(4)	0.6017(3)	0.024(2)
		<i>0.0928(4)</i>	<i>0.4889(4)</i>	<i>0.6026(3)</i>	<i>0.026(2)</i>
O(16)	24 l	0.1061(4)	0.4529(4)	0.6978(3)	0.023(2)
		<i>0.1069(4)</i>	<i>0.4531(4)</i>	<i>0.6986(3)</i>	<i>0.028(2)</i>
O(17)	6 h	0.1286(10)	0.5643(5)	0.7500	0.030(5)
		<i>0.1259(10)</i>	<i>0.5630(5)</i>	<i>0.7500</i>	<i>0.039(5)</i>

TABLE 2—Continued

Atom	Site	x	y	z	U _{eq}
O(18)	12 k	0.0169(8)	0.5085(4)	0.6993(13)	0.099(10)
		0.0178(8)	0.5089(4)	0.7014(12)	0.146(14)
O(19)	12 k	0.2692(3)	0.5384(5)	0.6535(4)	0.019(3)
		0.2693(3)	0.5386(6)	0.6549(4)	0.026(3)
O(20)	12 k	0.2289(3)	0.4578(6)	0.5120(5)	0.026(3)
		0.2291(3)	0.4583(7)	0.5136(5)	0.035(3)
O(21)	24 l	0.3352(4)	0.5511(4)	0.5637(3)	0.020(2)
		0.3345(4)	0.5511(4)	0.5651(3)	0.024(2)
O(22)	12 k	0.4039(3)	0.5961(3)	0.6543(4)	0.025(3)
		0.4031(3)	0.5969(3)	0.6557(5)	0.026(3)
O(23)	12 k	0.4399(3)	0.5601(3)	0.5163(4)	0.022(3)
		0.4396(3)	0.5604(3)	0.5170(5)	0.034(3)
N(1)	6 h	-0.2060(7)	0.3970(3)	0.7500	0.069(5)
		-0.2090(14)	0.3955(7)	0.7500	0.050(7)
N(2) ^a	12 k	-0.1487(5)	0.1487(5)	0.7347(5)	0.053(8)
		-0.1459(8)	0.1459(8)	0.7500	0.072(10)
N(3) ^a	12 k	0.0633(5)	0.1267(10)	0.5784(9)	0.075(7)
		0.0607(10)	0.1214(21)	0.5780(15)	0.168(16)
N(4) ^a	24 l	0.5486(10)	0.6500(13)	0.4554(7)	0.119(9)
		0.5489(12)	0.6493(12)	0.4541(9)	0.128(8)
O(24) ^a	4 e	0	0	0.7880(40)	0.140(40)
		0	0	0.7096(22)	0.061(16)
O(25)	12 k	-0.1363(3)	0.1363(3)	0.6311(6)	0.053(5)
		-0.1341(6)	0.1341(6)	0.6330(9)	0.112(8)
O(26) ^a	12 k	0.0474(5)	0.0947(11)	0.7665(11)	0.057(17)
		0.0492(10)	0.0984(20)	0.7500	0.141(15)
O(27)	12 k	-0.2535(6)	0.2535(6)	0.6101(10)	0.135(12)
		-0.2548(10)	0.2548(10)	0.6150(14)	0.206(17)
O(28)	4 f	0.3333	0.6667	0.5056(10)	0.058(8)
		0.3333	0.6667	0.4941(26)	0.141(23)
O(29) ^a	24 l	-0.2218(15)	0.3470(20)	0.5557(12)	0.150(20)
		-0.2229(21)	0.3514(20)	0.5559(16)	0.108(14)
O(30) ^a	12 k	-0.2596(6)	0.2596(6)	0.7267(10)	0.063(12)
		-0.2617(11)	0.2617(11)	0.7371(15)	0.071(14)
O(31) ^a	24 l	0.6468(12)	0.7587(13)	0.4587(10)	0.079(9)
		0.6609(17)	0.7619(17)	0.4528(13)	0.216(16)
O(32) ^a	12 k	-0.0825(7)	0.0825(7)	0.7239(12)	0.077(14)
		-0.0830(12)	0.0830(12)	0.7325(18)	0.096(19)
O(33)	12 k	-0.0427(11)	0.0427(11)	0.6491(16)	0.169(14)
		-0.0481(17)	0.0418(17)	0.6447(26)	0.338(39)
O(34) ^a	12 i	0.5580(30)	0.5580(30)	0.5000	0.160(20)
		0.5608(34)	0.5608(34)	0.5000	0.416(48)
O(35)	4 f	-0.3333	0.3333	0.6750(50)	0.220(70)
		-0.3333	0.3333	0.6856(46)	0.310(62)
O(36)	12 i	0.7460(20)	0.7460(20)	0.5000	0.105(12)
		0.7095	0.7683	0.4508	0.149
H(1)	12 k	-0.0750(30)	0.4627(13)	0.6312(16)	0.152
H(2)	12 k	-0.0044(16)	0.4978(8)	0.6160(20)	0.152
H(3)	24 l	-0.0560(20)	0.5065(18)	0.5891(16)	0.152
H(171) ^a	12 k	0.1470(30)	0.5735(15)	0.7200(30)	0.046
H(181)	12 k	-0.0280(40)	0.4858(18)	0.7020(20)	0.148
H(182)	12 k	0.0240(30)	0.5122(16)	0.6580(20)	0.148
H(191)	12 k	0.2492(4)	0.4984(9)	0.6749(7)	0.028
H(192) ^a	24 l	0.3177(10)	0.5583(13)	0.6581(10)	0.028
H(221) ^a	24 l	0.3555(10)	0.5766(15)	0.6565(12)	0.037
H(222)	12 k	0.4169(5)	0.5831(5)	0.6853(7)	0.037
H(11)	12 k	-0.1733(18)	0.4134(9)	0.7253(13)	0.103
H(12)	12 j	-0.2230(20)	0.3518(10)	0.7500	0.103
H(21)	12 j	-0.1858(10)	0.1329(19)	0.7500	0.080
H(31) ^a	24 l	0.0984(18)	0.1500(30)	0.5940(20)	0.112
H(32) ^a	12 k	0.0410(20)	0.0820(40)	0.5380(30)	0.112

TABLE 2—Continued

Atom	Site	x	y	z	U _{eq}
H(41) ^a	24 l	0.5680(30)	0.6860(30)	0.4340(20)	0.179
H(42) ^a	24 l	0.5180(30)	0.6540(30)	0.4760(20)	0.179
H(43) ^a	24 l	0.5260(30)	0.6100(20)	0.4370(20)	0.179
H(44) ^a	24 l	0.5810(30)	0.6490(40)	0.4760(20)	0.179
H(251) ^a	24 l	-0.1771(16)	0.1130(20)	0.6096(15)	0.079
H(252)	12 k	-0.1377(9)	0.1377(9)	0.6674(7)	0.079
H(261) ^a	12 j	0.0770(50)	0.1377(19)	0.7500	0.110
H(271) ^a	24 l	-0.2350(50)	0.2920(30)	0.5870(30)	0.202
H(272)	12 k	-0.2315(10)	0.2315(10)	0.6260(30)	0.202
H(281) ^b	12 k	0.3520(9)	0.7040(19)	0.5290(17)	0.087
H(301)	6 h	-0.2406(8)	0.2406(8)	0.7500	0.094
H(302) ^a	12 j	-0.2974(17)	0.2360(30)	0.7500	0.094
H(311) ^a	24 l	0.6110(20)	0.7610(30)	0.4770(20)	0.119
H(312) ^a	24 l	0.6220(30)	0.7127(17)	0.4460(20)	0.119
H(321)	6 h	-0.1001(11)	0.1001(11)	0.7500	0.115
H(322) ^c	24 l	-0.0351(18)	0.1110(50)	0.7330(40)	0.115
H(331)	24 l	-0.0872(18)	0.0110(30)	0.6380(30)	0.254
H(341) ^a	24 l	0.5750(60)	0.6060(3)	0.4980(60)	0.234
H(351)	4 f	-0.3333	0.3333	0.6640(40)	0.080
H(361)	24 l	0.7470(30)	0.7290(30)	0.5020(20)	0.157

^aRefinement by assuming an occupation factor of 1/2 for this site.^bRefinement by assuming an occupation factor of 2/3 for this site.^cRefinement by assuming an occupation factor of 1/4 for this site.

DISCUSSION

A. Heavy Atom Structure

The heavy atom structure of the cluster anion (see Fig. 1), which was already due to the single-crystal X-ray structure analysis (1), exhibits an enormous variety of different polyhedra: *three* MoO₆ (Mo3 and symmetry equivalent positions as in the subsequent cases), *six* (O=)MoO₄(H₂O) (Mo7), *twenty-four* (O=)MoO₅ (Mo2, Mo5), *twelve* (O=)₂MoO₄ (Mo1) and *six* (O=)VO₄(H₂O) octahedra (V1) as well as *six* pentagonal Mo(NO)O₆ bipyramids (Mo4) and *three* O₃{Mo(μ-H₂O)₂(μ-OH)-Mo}₃ units (Mo6) consisting of face-sharing double octahedra. The crystal structure analysis shows that the anion consists of large {Mo₁₅^{VI}(MoNO)₂³⁺O₅₈(H₂O)₂}²⁰⁻ ({Mo₁₇}) units. This can be seen nicely in the polyhedral plots of Fig. 1. In the cluster anion (see Fig. 1), six {(H₂O)VO}₂²⁺ (the shortest V^{IV}...V^{IV} distance is 655.9 pm (X-ray data (1)) and three {Mo^V(μ-H₂O)₂(μ-OH)Mo^V}⁹⁺ cationic groups link the three {Mo₁₇} units (corresponding distances between the metal centers: Mo^V...Mo^V 335.0 and Mo^V...V^{IV} 534.7 pm).

The cluster anion shows H₂O ligands occupying terminal positions of the octahedra: The *twelve* terminal H₂O ligands (O19 and O22 as well as symmetry equivalent positions), coordinated to *six* molybdenum(VI) and *six* vanadium(IV) centers (trans to (=O)), point to the concave side of the {Mo₁₇} units, whereby two *twelve*-membered rings arranged around the >6(S₃) axis are

TABLE 3
Selected Atomic Distances (pm) and Angles (°) of
(NH₄)₂₁[H₃Mo₅₇V₆(NO)₆O₁₈₃(H₂O)₁₈₁·53H₂O

Symmetry co-ordinates:			
i: $x, I+x-y, z$	ii: $x, I+x-y, 3/2-z$	iii: $I+x-y, I-y, I-z$	iv: $I-y, I+x-y, z$
v: $y-x, I-x, z$	vi: $y-I, y-x, I-z$	vii: $-y, -x, z$	viii: $x, y, 3/2-z$
ix: $y, x, I-z$			
NH ₄ ⁺ ions:			
N(100)–H(1)	94(2)	H(1)–N(100)–H(2)	105(6)
N(100)–H(2)	93(2)	H(1)–N(100)–H(3)	102(3)
N(100)–H(3)	92(2)	H(2)–N(100)–H(3)	111(3)
N(100)–H(3) ⁱ	92(2)	H(1)–N(100)–H(3) ⁱ	102(3)
		H(2)–N(100)–H(3) ⁱ	111(3)
		H(3)–N(100)–H(3) ⁱ	124(3)
H(1)···O(1)	231.1	N(100)–H(1)···O(1)	136.2
H(1)···O(1) ⁱ	231.1	N(100)–H(1)···O(1) ⁱ	136.2
H(2)···O(18)	227.1	N(100)–H(2)···O(18)	123.2
H(2)···O(15)	242.2	N(100)–H(2)···O(15)	133.6
H(2)···O(15) ⁱ	242.2	N(100)–H(2)···O(15) ⁱ	133.6
N(1)–H(11)	94(2)	H(11)–N(1)–H(12)	106(2)
N(1)–H(11) ⁱⁱ	94(2)	H(11)–N(1)–H(12) ⁱⁱ	106(2)
N(1)–H(12)	93(2)	H(11) ⁱⁱ –N(1)–H(12)	106(2)
N(1)–H(12) ⁱⁱ	93(2)	H(11) ⁱⁱ –N(1)–H(12) ⁱⁱ	106(2)
		H(11)–N(1)–H(11) ⁱⁱ	90(2)
		H(12)–N(1)–H(12) ⁱⁱ	135(2)
H(11)···O(1)	224.9	N(1)–H(11)···O(1)	135.4
H(11)···O(1) ⁱ	224.9	N(1)–H(11)···O(1) ⁱ	135.4
H(11) ⁱⁱ ···O(1)	224.9	N(1)–H(11) ⁱⁱ ···O(1)	135.4
H(11) ⁱⁱ ···O(1) ⁱ	224.9	N(1)–H(11) ⁱⁱ ···O(1) ⁱ	135.4
H(12)···O(30)	199.5	N(1)–H(12)···O(30)	161.7
H(12)···O(30) ⁱⁱ	199.5	N(1)–H(12)···O(30) ⁱⁱ	161.7
H(12) ⁱⁱ ···O(30)	199.5	N(1)–H(12) ⁱⁱ ···O(30)	161.7
H(12) ⁱⁱ ···O(30) ⁱⁱ	199.5	N(1)–H(12) ⁱⁱ ···O(30) ⁱⁱ	161.7
N(4)–H(41)	94(2)	H(41)–N(4)–H(42)	109(2)
N(4)–H(42)	96(2)	H(41)–N(4)–H(43)	111(2)
N(4)–H(43)	95(2)	H(41)–N(4)–H(44)	110(2)
N(4)–H(44)	95(2)	H(42)–N(4)–H(43)	109(2)
		H(42)–N(4)–H(44)	109(2)
		H(43)–N(4)–H(44)	110(2)
H(41)···O(31)	191.0	N(4)–H(41)···O(31)	113.9
H(41)···O(3) ⁱⁱⁱ	244.9	N(4)–H(41)···O(3) ⁱⁱⁱ	153.6
H(42)···O(29) ⁱⁱⁱ	219.9	N(4)–H(42)···O(29) ⁱⁱⁱ	121.9
H(42)···O(23)	232.3	N(4)–H(42)···O(23)	116.8
H(44)···O(34)	204.4	N(4)–H(44)···O(34)	114.3
H(44)···O(14) ^{iv}	241.3	N(4)–H(44)···O(14) ^{iv}	146.2
Ligand H ₂ O molecules and hydroxy groups:			
O(17)–H(171)	88(7)	Mo(6)–O(17)–H(171)	105(2)
H(171)···O(22) ^v	200.7	O(17)–H(171)···O(22) ^v	177.8
O(18)–H(181)	93(8)	H(181)–O(18)–H(182)	103(5)
O(18)–H(182)	113(8)		
H(181)···O(1)	235.8	O(18)–H(181)···O(1)	135.1
H(181)···O(1) ⁱ	235.8	O(18)–H(181)···O(1) ⁱ	135.1
H(181)···O(15)	245.2	O(18)–H(182)···O(15)	133.2
H(181)···O(15) ⁱ	245.2	O(18)–H(182)···O(15) ⁱ	133.2
O(19)–H(191)	100(2)	H(191)–O(19)–H(192)	105(2)
O(19)–H(192)	100(2)		
H(191)···O(13)	176.6	O(19)–H(191)···O(13)	165.5
H(192)···O(22)	176.5	O(19)–H(192)···O(22)	169.4
O(22)–H(221)	100(2)	H(221)–O(22)–H(222)	106(2)
O(22)–H(222)	99(2)		
H(221)···O(19)	176.6	O(22)–H(221)···O(19)	173.4
H(222)···O(17) ^{iv}	190.2	O(22)–H(222)···O(17) ^{iv}	171.2
Hydrate H ₂ O molecules:			
O(25)–H(251)	102(2)	H(251)–O(25)–H(252)	123(3)
O(25)–H(252)	98(2)		
H(251)···O(31) ^{vi}	237.0	O(25)–H(251)···O(31) ^{vi}	151.3
O(27)–H(271)	100(2)	H(271)–O(27)–H(272)	129(7)
O(27)–H(272)	99(2)		
H(271) ^{viii} ···O(29)	144.9	O(27)–H(271)···O(29)	167.6

TABLE 3—Continued

H(271)···O(29) ^{viii}	144.9	O(27)–H(271) ^{viii} ···O(29) ^{viii}	167.6
H(272)···O(3)	213.7	O(27)–H(272)···O(3)	134.0
H(272)···O(3) ^{vii}	213.7	O(27)–H(272)···O(3) ^{vii}	134.0
O(28)–H(281)	99(2)	H(281)–O(28)–H(281) ^{iv}	82(2)
H(281)···O(21) ⁱ	231.0	O(28)–H(281)···O(21) ⁱ	143.4
H(281)···O(21) ^{iv}	231.0	O(28)–H(281)···O(21) ^{iv}	143.4
O(30)–H(301)	100(2)	H(301)–O(30)–H(302)	81(4)
O(30)–H(302)	100(2)		
H(301)···O(2)	250.2	O(30)–H(301)···O(2)	121.4
H(301)···O(2) ^{vii}	250.2	O(30)–H(301)···O(2) ^{vii}	121.4
O(31)–H(311)	101(2)	H(311)–O(31)–H(312)	101(6)
O(31)–H(312)	100(2)		
H(311)···O(20) ^{iv}	198.5	O(31)–H(311)···O(20) ^{iv}	177.4
O(32)–H(321)	101(2)	H(321)–O(32)–H(322)	96(7)
O(32)–H(322)	100(2)		
H(322)···O(7)	213.6	O(32)–H(322)···O(7)	139.9
H(322)···O(26) ^{vii}	215.4	O(32)–H(322)···O(26) ^{vii}	133.7
H(322)···O(26)	232.8	O(32)–H(322)···O(26)	136.7
O(33)–H(331)	98(2)	H(331)–O(33)–H(331) ^{vii}	136(6)
O(33)–H(331) ^{vii}	98(2)		
H(331)···O(8)	230.1	O(33)–H(331)···O(8)	143.1
H(331) ^{vii} ···O(8) ^{vii}	230.1	O(33)–H(331) ^{vii} ···O(8) ^{vii}	143.1
O(34)–H(341)	99(2)	H(341)–O(34)–H(341) ^{ix}	72(6)
O(34)–H(341) ^{ix}	99(2)		
H(341)···O(14) ^{iv}	218.3	O(34)–H(341)···O(14) ^{iv}	124.5
H(341) ^{ix} ···O(14) ^v	218.3	O(34)–H(341) ^{ix} ···O(14) ^v	124.5

formed through hydrogen bonding. Another remarkable structural feature is the existence of six bridging H₂O ligands. They occupy bridging positions between each of the neighbouring molybdenum(V) centers so that three {Mo(μ-H₂O)₂(μ-OH)Mo} units—composed of face-sharing double octahedra—result.

The rather unique large central cavity is spanned by the oxygen atoms of an O₃₃ polyhedron (see Fig. 2). This solid can be considered as being built up by the following oxygen atoms: twelve (O22 and O19 as well as symmetry equivalent positions as in the subsequent cases) from the terminal H₂O ligands attached to the vanadium(IV) (VI) and molybdenum(VI) centres (Mo7) (thus forming the above mentioned two six-membered rings), three (O17) from the μ-OH groups of the three {Mo(μ-H₂O)₂(μ-OH)Mo} units, twelve μ₂-bridging ones (O16) bound to Mo5 and Mo6, as well as an additional six (O13) μ₂-bridging ones between Mo3 and Mo4.

It is important to note that the cation lattice is disordered, so that we are not able to distinguish between NH₄⁺ cations and H₂O molecules on the basis of the single-crystal X-ray structure analysis and, therefore, the number of NH₄⁺ ions and lattice H₂O molecules could only be determined by additionally paying strict attention to the elemental analysis (nitrogen value!) and to the thermogravimetric measurements. (The number of NH₄⁺ cations for such large compounds can only be given to a certainty of roughly ±1 NH₄⁺).

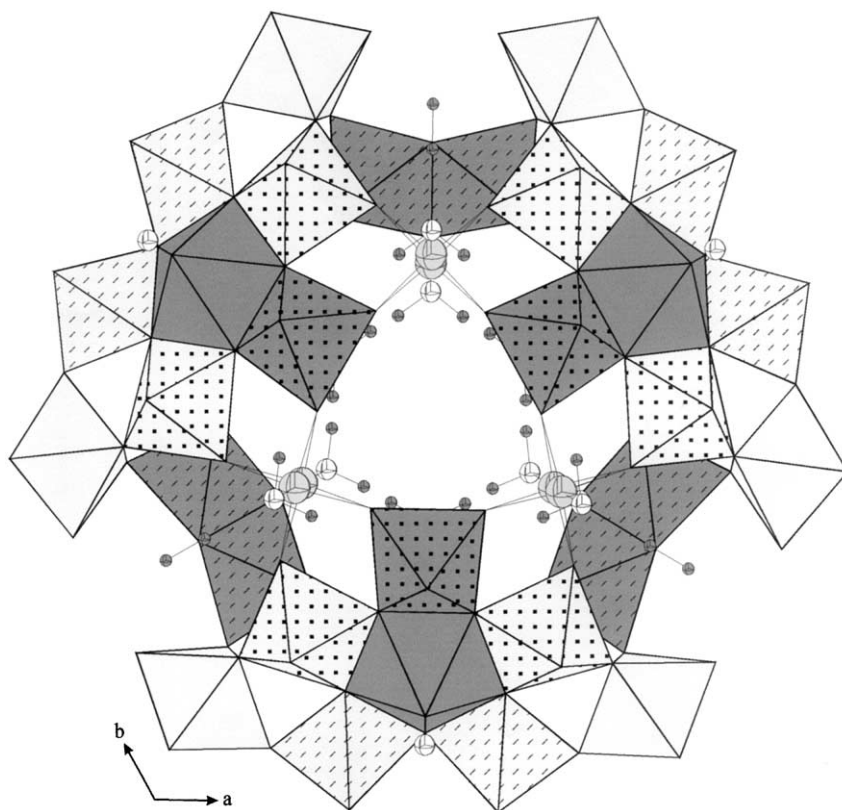


FIG. 1. Polyhedral representation of the cluster anion: Mo(1) octahedra ($(\text{O}=\text{MoO}_4)$), light gray Mo(2) octahedra ($\text{O}=\text{MoO}_5$), light gray with strokes; Mo(4), pentagonal bipyramids, ($\text{Mo}(\text{NO})\text{O}_6$), dark gray; Mo(5), octahedra, ($\text{O}=\text{MoO}_5$), light gray with dots; Mo(6) face-shared double octahedra ($\text{O}_3\{\text{Mo}(\mu\text{-H}_2\text{O})_2(\mu\text{-OH})\text{Mo}\}\text{O}_3$), dark gray with strokes; Mo(7) octahedra ($\text{O}=\text{MoO}_4(\text{H}_2\text{O})$), dark gray with dots; vanadium atoms; large light gray circles; oxygen atoms, white circles; hydrogen atoms; small dark gray circles.

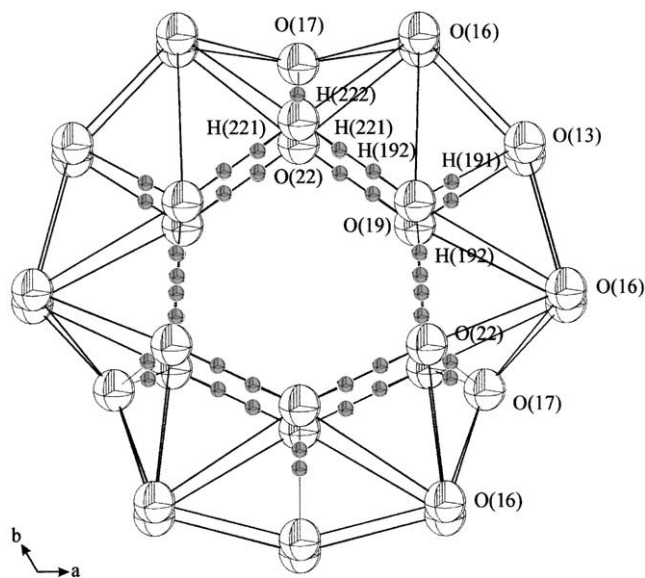


FIG. 2. Central (formal) cavity of the cluster anion spanned by 33 oxygen atoms (see text).

B. Location of the Hydrogen Atoms

(a) *The central cavity and the OH and H₂O ligands.* The central cavity discussed above, which is spanned by *twelve* ligand H₂O molecules (6 H₂O(22) and 6 H₂O(19) in the form of a hexagonal prism, is built up by two *twelve*-membered rings consisting of *six* O–H···O hydrogen bonds each (see Fig. 2). The hydrogen-bond schemes of the *two* kinds (O19) and O22) of H₂O molecules involved are shown in Fig. 3. The hydrogen bonds of these ligand H₂O molecules (type *J* after Chidambaran *et al.* (5)) are relatively strong inside the rings with H···O hydrogen-bond distances of 176.6 and 176.5 pm. They are obviously decisive for the stability of the whole supramolecular cluster system. The hydrogen bonds to the oxo ligands (O13) and the hydroxy ligands (O17) in the periphery of the central cage are similar in strength ($r_{\text{H}\cdots\text{O}} = 176.6$ and 190.2 pm, respectively).

As shown in Figs. 2 and 3, the hydrogen atoms inside the *twelve*-membered ring (H192) and (H221) are disordered. This means that there are *two* different kinds of such rings,

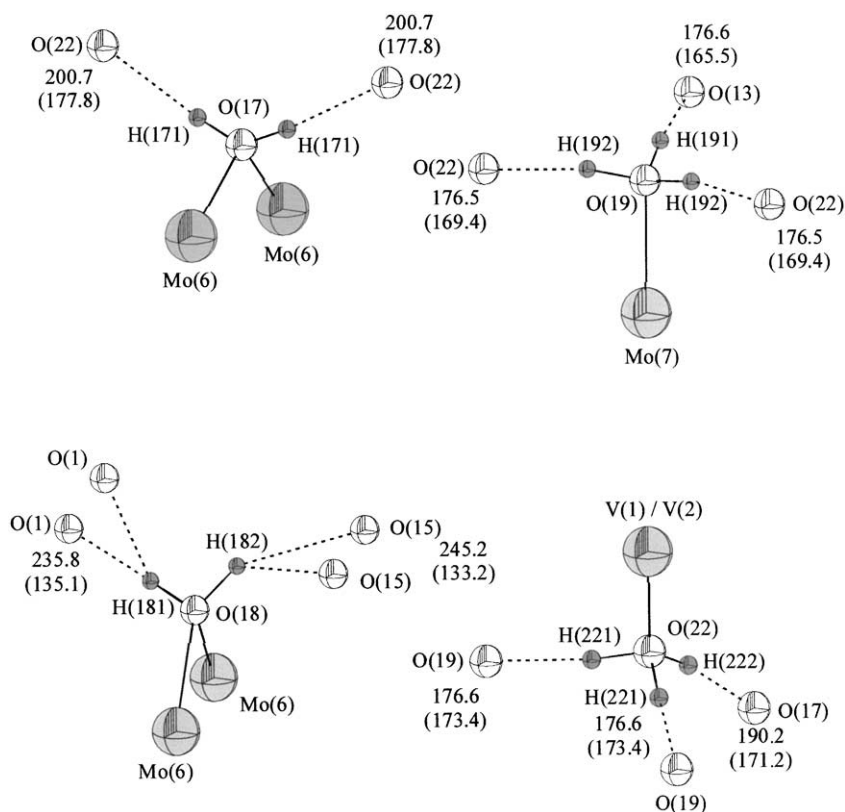


FIG. 3. Co-ordination geometry of the hydroxy ligands and ligand H_2O molecules of $(\text{NH}_4)_{21}[\text{H}_3\text{Mo}_5\text{V}_6(\text{NO})_6\text{O}_{183}(\text{H}_2\text{O})_{18}] \cdot 53 \text{H}_2\text{O}$ (dashed lines: possible hydrogen bonds; $\text{H} \cdots \text{O}$ distances in pm; $\text{O}-\text{H} \cdots \text{O}$ angles (in $^\circ$) in parentheses).

i.e., one with the mentioned hydrogen atoms at the left side of the H_2O oxygen atom and one with the hydrogen atoms at the right side. The hydrogen bonds of the ligands at the

outside of the central cavity such as $\text{H}_2\text{O}18$ (type B (5) and $\text{O}17\text{H}$ are very weak ($r_{\text{H} \cdots \text{O}} = 235.8$ (H181) and 245.2 pm (H182), and 200.7 pm (H171), respectively). As shown in

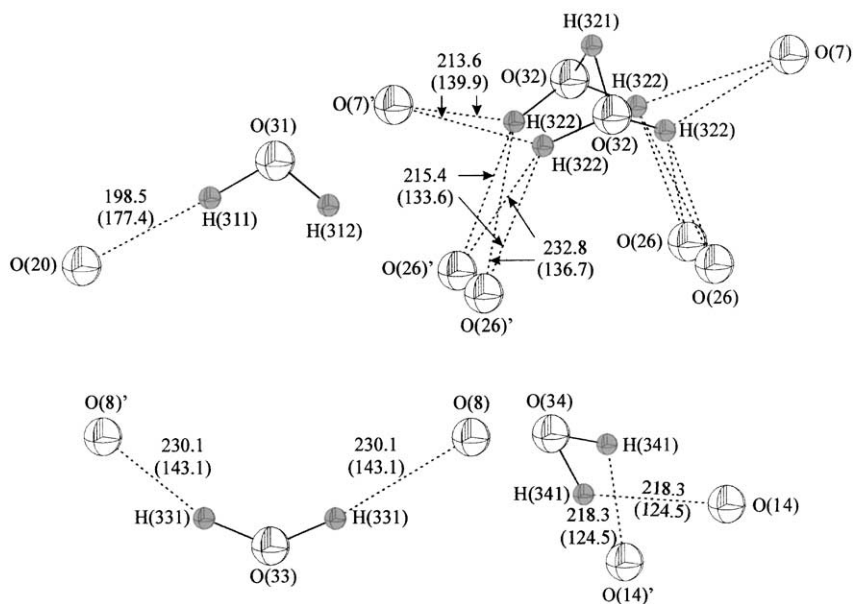


FIG. 4. Co-ordination geometry of the hydrate H_2O molecules of $(\text{NH}_4)_{21}[\text{H}_3\text{Mo}_5\text{V}_6(\text{NO})_6\text{O}_{183}(\text{H}_2\text{O})_{18}] \cdot 53 \text{H}_2\text{O}$ (oxygen atoms labeled with primes belong to adjacent cluster anions; for further explanations see Fig. 3).

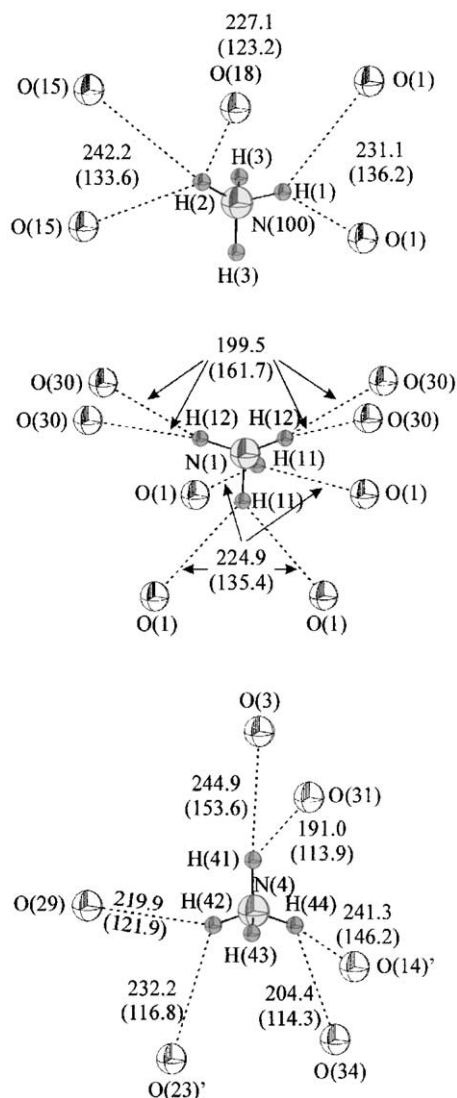


FIG. 5. Co-ordination geometry of the ammonium ions of $(\text{NH}_4)_{21}[\text{H}_3\text{Mo}_{57}\text{V}_6(\text{NO})_6\text{O}_{183}(\text{H}_2\text{O})_{18}] \cdot 53\text{H}_2\text{O}$ (for further explanations see Fig. 3).

Fig. 3, the hydrogen atoms of H_2O_{18} are obviously not disordered in contrast to that of the hydroxy ligand (O17H).

(b) *The hydrate H_2O molecules.* The refinement of the hydrate H_2O molecules outside the cluster anion, i.e. those due to O25–O36, was not possible in a satisfactory manner. This is obviously caused by some amount of thermal motion despite the very low measuring temperature. The hydrogen bond schemes of some of these H_2O molecules with linear, bent, and bifurcated bonds are shown in Fig. 4. As mentioned above these hydrate H_2O molecules are mostly orientationally disordered with one or two hydro-

gen atoms on partially occupied split positions. Whether some H_3O^+ oxonium ions are present as well cannot be unequivocally decided. The respective hydrogen-bond distances range from $r_{\text{H}\cdots\text{O}} = 144.9$ pm (H271) to $r_{\text{H}\cdots\text{O}} = 237.0$ pm (H251). This means hydrogen bonds of extremely different strength, i.e., from for H_2O molecules unusually strong bonds to very weak ones (6). These hydrogen bonds, especially the intercluster bonds, i.e., those between different cluster anions (see Fig. 5), contribute significantly to the stability of the supramolecular compound under discussion. Some H_2O hydrogen atoms, however, such as H252 and H312, seem not to be involved in any hydrogen bond. (This is supported by infrared spectroscopic data (7), which display OH stretching modes > 3650 cm^{-1} at the high wavenumber flank of the broad, in the whole rather featureless band in the range 3700 – > 3000 cm^{-1} .)

(c) *The ammonium ions.* The bonding schemes of the ammonium ions (see Fig. 5) are similar to those of the hydrate H_2O molecules. The NH_4^+ ions are obviously disordered in a similar way to the hydrate H_2O molecules. They form $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds of different strengths to both cluster-anion oxygen atoms and hydrate H_2O molecules. The respective $\text{H}\cdots\text{O}$ distances range from 191.0 pm (H41) to 242.2 pm (H3) with some hydrogen atoms such as H3 and H43 not being involved in hydrogen bonds. Altogether, it seems that the hydrate H_2O molecules are stronger hydrogen bond acceptor groups or are more basic than the oxoligands of the cluster (6, 8) and, hence, in the mean the $\text{N}-\text{H}\cdots\text{OH}_2$ hydrogen bonds are stronger than the $\text{N}-\text{H}\cdots\text{O}-\text{MO}_x$ ones.

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