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The Crystal Structure of a Tetranuclear Nickel(II) Cluster Compound, $Ni_4(OH)_4[C_6H_9(NH_2)_3]_4(NO_3)_4(H_2O)_7$

BENGT AURIVILLIUS

Division of Inorganic Chemistry 2, Chemical Center, The Lund Institute of Technology, P.O. Box 740, S-220 07 Lund 7, Sweden

Crystals of $Ni_4(OH)_4[C_6H_9(NH_2)_3]_4(NO_3)_4(H_2O)_7$ are monoclinic, space group $P2_1/m$ with the cell parameters $a=11.542(6)$, $b=14.204(1)$, $c=15.372(12)$ Å, $\beta=99.22(6)°$ (Hägg-Guinier powder diffractogram), $V=2487.6$ Å^3 and $Z=2$. The crystal structure has been determined from Patterson and Fourier methods and refined by least-squares to $R=0.064$ based on 4054 independent reflections (X-ray counter intensities).

The nickel atoms form clusters of four tetrahedrally arranged atoms each with interatomic distances varying between 3.16 and 3.20 Å. The shortest distance between nickel atoms belonging to different clusters is 9.02 Å. The Ni^{2+} and OH^- ions form a cubane-like structure with Ni – O distances of 2.07 – 2.10 Å.

The compound is an example of a complex between a metal atom and a stereo-specific ligand. The actual ligand, 1,3,5-triamino(*aaa*)-cyclohexane, and its nickel complex were first synthesized by Schwarzenbach and Egli, Zürich. 1,3,5-Triamino(*aaa*)-cyclohexane, denoted "tach" in this paper, has been used by Schwarzenbach [1] and Egli as a complexing agent. In "tach" the three NH_2-groups form an approximately equilateral triangle with the side 3.0 Å. "Tach" in this way offers three fixed ligands for octahedrally coordinated ions like Co(II), Ni(II) and Cu(II). The remaining three ligands of the octahedron may be supplied by OH^- ions. "Tach" acts here, according to Schwarzenbach as a stereo-specific ligand. The present investigation was started to elucidate the geometry of a complex ion containing per each nickel atom one OH^- ion and one "tach" molecule. The single crystals used for the structure determination were kindly supplied by G. Schwarzenbach.

EXPERIMENTAL

Crystal data. $Ni_4(OH)_4[C_6H_9(NH_2)_3]_4(NO_3)_4(H_2O)_7$, F.W. 1193.8. Space group $P2_1/m$ (No. 11);
$a=11.505(6)$, $b=14.203(1)$, $c=15.309(12)$ Å, $\beta=99.24(6)°$
(single-crystal diffractometer, Mo$K\alpha$, 30 reflections);
$a=11.542(6)$, $b=14.204(1)$, $c=15.372(12)$ Å, $\beta=99.22(6)°$, $V=2487.6$ Å^3
(Guinier-Hägg powder diffractogram, Cu$K\alpha_1$, 21 single indexed reflections).
$D_m=1.6$ g cm^{-3} (by flotation), $Z=2$, $D_x=1.594$ g cm^{-3}, $\mu=15.80$ cm^{-1} (Mo$K\alpha$).

The dimensions of the monoclinic unit cell were determined from least-squares analyses of the angular positions of 30 reflections registered on a single crystal diffractometer as well as of $\sin^2\theta$ values recorded in a Guinier-Hägg focussing camera with Cu$K\alpha_1$ radiation ($\lambda=1.54051$ Å) using KCl ($a=6.2930$ Å at 22 °C)

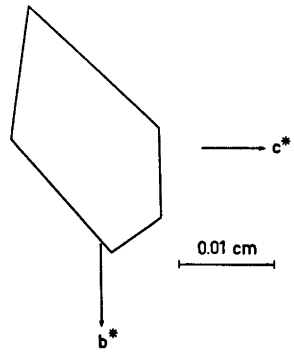

Fig. 1. Section perpendicular to the crystallographic *a*-axis of the single crystal used for the data collection. The directions of the reciprocal *b**- and *c**-axes are indicated.

as an internal standard. Slightly different values of the cell parameters were obtained, the largest deviation between the values being about 4σ. The discrepancy may partly be due to Mo$K\alpha_1$ and Mo$K\alpha_2$ not being resolved for the angles used, partly to systematic errors in the θ-values. The cell dimensions obtained from the powder diffractogram have been used consistently in this paper.

The blue transparent single crystal used had the form of an oblique prism with its edges extending along the a-axis and its basal planes lying in the bc-plane. The length of the prism parallel to the a-axis was 0.204 mm. A section through the prism at right angles to the a-axis (the b^*c^*-plane) is shown in Fig. 1. An approximate absorption correction was made on the basis of this drawing; the transmission factors varying between 0.76 and 0.85.

Preliminary Weissenberg photographs showed that the symmetry was monoclinic and that the only systematically missing reflections were $0k0$ with $k = 2n+1$, indicating the space groups $P2_1$ (No. 4) and $P2_1/m$ (No. 11).

Intensity data were collected on a computer-controlled four-circle diffractometer (CAD-4) equipped with a graphite monochromator (Mo$K\alpha$, $\lambda = 0.70930$ Å). The $\omega - 2\theta$ scan technique was used with a scan interval $\Delta\omega = (0.70 + 0.50 \tan\theta)°$. The background was measured for one quarter of the scan time at each end of the interval. In the range $3° < \theta < 35°$ 6164 independent reflections were recorded. The intensities of two control reflections were measured at regular intervals (124 times each). Based on these 248 values a scaling polynomial for the intensities was found, $I_{corr} = I_{obs}(1 - 0.2785 \times 10^{-3}h)$, where h (hours) is the time of exposure of the crystal. Out of the 6164 reflections, 1412 had zero or negative intensities and were therefore deleted. A further 698 reflections were given zero weight as $\sigma(I)/I > 3.09$. A total of 4054 reflections were used for the subsequent calculations after their intensities were corrected for Lorentz, polarization and absorption effects.

STRUCTURE DETERMINATION AND REFINEMENT

Assuming space group $P2_1/m$ all large maxima in a three-dimensional Patterson function could be explained as resulting from nickel-nickel vectors. Subsequent difference Fourier maps revealed the remaining non-hydrogen atoms. The parameters obtained were refined by least-squares calculations using anisotropic temperature factors for the nickel atoms and isotropic ones for the others. The function minimized was $\sum w_i(|F_o| - |F_c|)^2$, where $w_i^{-1} = \sigma^2(|F_o|^2)/4|F_o|^2 + 0.004|F_o|^2 + 5.0$. The final refinement converged at $R = 0.064$ and $R_w = 0.091$ (4054 independent reflections). The averages of $w_i(|F_o| - |F_c|)^2$ were approximately constant as a function of both $|F_o|$ and $\sin\theta$. The value of S, defined by $[\sum w_i(|F_o| - |F_c|)^2/(m-n)]^{1/2}$, where m and n are the numbers of observations and parameters varied, was 0.91. The form factors were those of the neutral atoms given by Hanson *et al.*[2]

Final positional and thermal parameters are given in Table 1. Lists of observed and calculated structure amplitudes are available from the author on request. As the structure so arrived at looked reasonable and as the thermal parameters were normal, no effort was made to refine the structure in space group $P2_1$. The positions of the hydrogen atoms were not determined.

Table 1. Final positional and thermal parameters for $Ni_4(OH)_4(C_6H_{15}N_3)_4(NO_3)_4(H_2O)_7$. Anisotropic temperature factors have been used for the nickel atoms and isotropic ones for the others. The expressions used for the temperature coefficients are $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ and $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$, respectively. The thermal parameters are in units 10^2 Å^2. Estimated standard deviations are given in parentheses. For U_{ij} see below.

Atom	x	y	z	U
Ni(1)	0.17135(6)	0.13864(5)	0.26150(4)	(2.17)
Ni(2)	0.40977(9)	¼	0.32133(6)	(2.22)
Ni(3)	0.28806(9)	¼	0.11933(6)	(2.10)
OH^- ions				
O(1)	0.3356(3)	0.1556(3)	0.2226(2)	2.58(8)
O(2)	0.2377(5)	¼	0.3436(4)	2.71(11)
O(3)	0.1329(5)	¼	0.1739(3)	2.47(11)

Table 1. Continued.

"Tach" molecule 1 bonded to Ni(1)				
N(11)	0.0085(5)	0.1374(4)	0.3073(3)	3.58(11)
N(12)	0.1013(5)	0.0365(4)	0.1657(3)	3.61(11)
N(13)	0.2317(5)	0.0279(4)	0.3491(3)	3.55(11)
C(11)	−0.0433(6)	0.0431(5)	0.3209(4)	3.92(14)
C(12)	−0.0728(6)	−0.0096(5)	0.2332(4)	4.23(15)
C(13)	0.0360(6)	−0.0437(5)	0.1967(4)	3.72(14)
C(14)	0.1170(6)	−0.1006(5)	0.2662(4)	4.17(15)
C(15)	0.1476(6)	−0.0502(5)	0.3556(4)	3.84(14)
C(16)	0.0382(6)	−0.0138(5)	0.3888(4)	3.99(15)
"Tach" molecule 2 bonded to Ni(2)				
N(21)	0.4684(5)	0.1470(4)	0.4179(3)	3.39(11)
N(22)	0.5796(7)	¼	0.2839(5)	3.7(2)
C(21)	0.5877(6)	0.1607(5)	0.4734(4)	3.68(14)
C(22)	0.6814(6)	0.1609(5)	0.4141(4)	3.98(15)
C(23)	0.6826(8)	¼	0.3586(6)	3.8(2)
C(24)	0.5884(9)	¼	0.5273(6)	4.2(2)
"Tach" molecule 3 bonded to Ni(3)				
N(31)	0.2290(5)	0.1480(4)	0.0220(3)	3.57(11)
N(32)	0.4551(6)	¼	0.0807(5)	3.20(15)
C(31)	0.2645(6)	0.1609(5)	−0.0672(4)	3.56(13)
C(32)	0.3984(6)	0.1608(5)	−0.0589(4)	4.14(15)
C(33)	0.4559(8)	¼	−0.0175(6)	3.4(2)
C(34)	0.2109(9)	¼	−0.1112(6)	4.0(2)
Nitrate ions				
N(4)	0.4684(7)	0.0415(6)	0.7347(5)	6.5(2)
O(41)	0.3648(8)	0.0487(6)	0.7312(5)	10.0(2)
O(42)	0.5126(8)	0.0569(6)	0.6694(6)	10.3(3)
O(43)	0.5229(8)	0.0101(6)	0.8040(6)	10.2(2)
N(5)	0.9025(9)	¼	0.9841(6)	5.5(2)
O(51)	0.7980(9)	¼	0.9412(6)	7.3(2)
O(52)	0.9489(6)	0.1740(4)	1.0031(4)	7.7(2)
N(6)	0.0379(8)	¼	0.5494(6)	4.6(2)
O(61)	0.0843(12)	¼	0.4855(9)	10.8(4)
O(62)	−0.0664(12)	¼	0.5468(8)	10.4(4)
O(63)	0.0969(10)	¼	0.6205(7)	9.0(3)
Water molecules				
O(W1)	0.8176(8)	¼	0.1713(6)	6.5(2)
O(W2)	0.7042(6)	0.0655(5)	0.9398(4)	7.5(2)
O(W3)	0.6569(6)	0.0988(5)	0.1168(4)	7.7(2)
O(W4)	0.2846(6)	0.1135(5)	0.5414(4)	7.3(2)

Anisotropic thermal parameters for the nickel atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	2.07(4)	2.26(4)	2.21(3)	−0.17(3)	0.32(3)	0.17(3)
Ni(2)	1.91(5)	2.74(5)	2.03(5)	0	0.07(4)	0
Ni(3)	2.23(5)	2.31(5)	1.80(5)	0	0.36(4)	0

Table 2. Selected interatomic distances (Å) and angles (°) in the crystal structure of $Ni_4(OH)_4(C_6H_{15}N_3)_4(NO_3)_4(H_2O)_7$. The sign ′ denotes atoms symmetry related to those given in Table 1.

Ni–Ni distances < 9.00 Å		
Ni(1)–Ni(3)	3.168(2)	
Ni(1)–Ni(1′)	3.164(1)	
Ni(1)–Ni(2)	3.180(2)	
Ni(2)–Ni(3)	3.196(3)	

Ni–O(OH⁻) distances < 3.50 Å		
Ni(1)–O(3)	2.079(3)	
Ni(1)–O(1)	2.091(4)	
Ni(1)–O(2)	2.091(4)	
Ni(2)–O(2)	2.068(6)	
Ni(2)–O(1)	2.102(4)	2×
Ni(3)–O(1)	2.083(4)	2×
Ni(3)–O(3)	2.096(6)	

Ni–N(NH_2) distances < 3.50 Å		
Ni(1)–N(11)	2.110(5)	
Ni(1)–N(13)	2.114(5)	
Ni(1)–N(12)	2.132(5)	
Ni(2)–N(21)	2.117(5)	2×
Ni(2)–N(22)	2.129(8)	
Ni(3)–N(32)	2.106(7)	
Ni(3)–N(31)	2.116(5)	2×

The cubane-like clusters $Ni_4(OH)_4^{4+}$

O–Ni–O		Ni–O–Ni	
O(2)–Ni(1)–O(3)	80.5(2)	Ni(1)–O(1)–Ni(2)	98.6(2)
O(2)–Ni(1)–O(1)	79.9(2)	Ni(1)–O(1)–Ni(3)	98.8(2)
O(3)–Ni(1)–O(1)	80.6(2)	Ni(2)–O(1)–Ni(3)	99.6(2)
O(2)–Ni(2)–O(1)	80.1(2)	Ni(1)–O(2)–Ni(1′)	98.3(2)
O(2)–Ni(2)–O(1′)	80.1(2)	Ni(1)–O(2)–Ni(2)	99.7(2)
O(1)–Ni(2)–O(1′)	79.3(2)	Ni(1′)–O(2)–Ni(2)	99.7(2)
O(1)–Ni(3)–O(1′)	80.1(2)	Ni(1)–O(3)–Ni(1′)	99.1(2)
O(1)–Ni(3)–O(3)	80.4(2)	Ni(1)–O(3)–Ni(3)	98.7(2)
O(1′)–Ni(3)–O(3)	80.4(2)	Ni(1′)–O(3)–Ni(3)	98.7(2)

The "tach" molecules

Molecule 1

C(11)–C(12)	1.530(10)	C(16)–C(11)–C(12)	111.7(6)
C(12)–C(13)	1.534(10)	C(11)–C(12)–C(13)	113.4(6)
C(13)–C(14)	1.532(10)	C(12)–C(13)–C(14)	110.8(5)
C(14)–C(15)	1.540(9)	C(13)–C(14)–C(15)	113.8(6)
C(15)–C(16)	1.525(9)	C(14)–C(15)–C(16)	111.9(6)
C(16)–C(11)	1.521(9)	C(15)–C(16)–C(11)	113.9(5)
C(11)–N(11)	1.495(9)	C(12)–C(11)–N(11)	110.6(5)
C(13)–N(12)	1.487(9)	C(16)–C(11)–N(11)	110.7(5)
C(15)–N(13)	1.488(9)	C(12)–C(13)–N(12)	111.2(5)
		C(14)–C(13)–N(12)	110.1(5)
		C(14)–C(15)–N(13)	110.3(5)
		C(16)–C(15)–N(13)	110.7(5)

Molecule 2

C(21)–C(22)	1.523(9)	2×	C(21)–C(24)–C(21′)	113.8(8)	
C(22)–C(23)	1.527(9)	2×	C(24)–C(21)–C(22)	112.5(6)	2×
C(21)–C(24)	1.514(8)	2×	C(21)–C(22)–C(23)	114.0(6)	2×
			C(22)–C(23)–C(22′)	111.8(8)	

Table 2. Continued.

C(21)–N(21)	1.512(8)	2×	C(24)–C(21)–N(21)	110.0(6)	2×
C(23)–N(22)	1.515(12)		C(22)–C(21)–N(21)	109.4(5)	2×
			C(22)–C(23)–N(22)	110.3(5)	2×
Molecule 3					
C(31)–C(32)	1.530(9)	2×	C(31)–C(34)–C(31′)	112.8(8)	
C(31)–C(34)	1.520(8)	2×	C(34)–C(31)–C(32)	111.8(6)	2×
C(32)–C(33)	1.522(9)	2×	C(31)–C(32)–C(33)	113.6(6)	2×
			C(32)–C(33)–C(32′)	112.7(8)	
C(31–N(31)	1.504(8)	2×	C(32)–C(31)–N(31)	110.1(5)	2×
C(33)–N(32)	1.511(11)		C(34)–C(31)–N(31)	110.9(6)	2×
			C(32)–C(33)–N(32)	110.2(5)	2×
The nitrate ions					
Ion 1					
N(4)–O(41)	1.192(12)		O(41)–N(4)–O(42)	119.8(9)	
N(4)–O(42)	1.218(12)		O(41)–N(4)–O(43)	116.1(9)	
N(4)–O(43)	1.230(12)		O(42)–N(4)–O(43)	123.7(9)	
Ion 2					
N(5)–O(51)	1.279(14)		O(52)–N(5)–O(52′)	124.5(1.1)	
N(5)–O(52)	1.220(8)	2×	O(52)–N(5)–O(51)	117.7(5)	2×
Ion 3					
N(6)–O(61)	1.191(16)		O(61)–N(6)–O(62)	123.7(1.2)	
N(6)–O(62)	1.199(16)		O(61)–N(6)–O(63)	119.3(1.2)	
N(6)–O(63)	1.192(14)		O(62)–N(6)–O(63)	116.9(1.1)	
Possible hydrogen bond contacts < 3.00 Å					
O(W2)–O(43)	2.821(11)		O(W2)–O(W3)	2.898(10)	
O(51)–O(W2)	2.835(8)	2×	O(1)–O(43)	2.931(10)	
O(W1)–O(W3)	2.873(9)	2×	O(43)–O(W3)	2.999(11)	

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The coordination of nickel. The three-dimensional Patterson function, the symmetry, the cell volume and the observed density showed that the unit cell contains eight nickel atoms. The determination of the structure (the non-hydrogen atoms) made clear that the unit cell content is two formula units $Ni_4(OH)_4$-

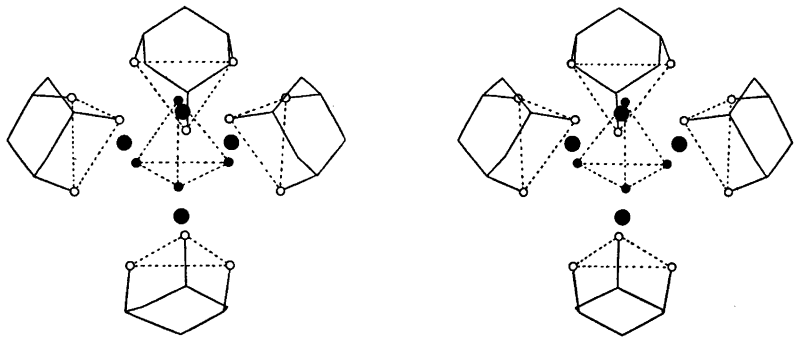

Fig. 2. Stereo view of one complex ion $Ni_4(OH)_4(C_6H_{15}N_3)_4^{4+}$. Large filled circles denote nickel atoms, small filled ones hydroxide ions and empty ones amino groups. The $(OH^-)_4$ tetrahedron is marked out by dotted lines. Dotted lines are also drawn between nitrogen atoms bonded to the same nickel atom.

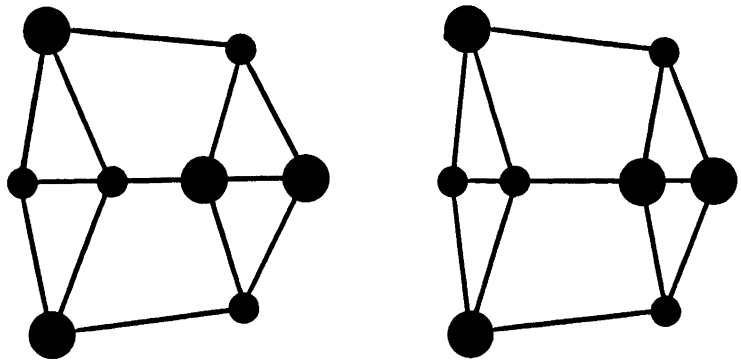

Fig. 3a. Stereo view of the cubane-like structure of $Ni_4(OH)_4^{4+}$ in the present compound. Large filled circles denote nickel atoms and small ones hydroxide ions. Ni – O(OH^-) bonds are shown by full lines.

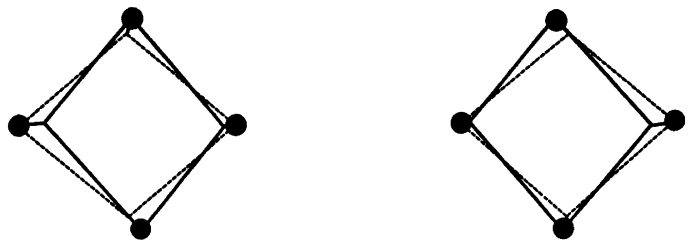

Fig. 3b. Stereo view of the cubane-like structure of the $Ni_4(OCH_3)_4^{4+}$ ion in $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$. The circles indicate nickel atoms. Full and dotted lines indicate Ni – O(OCH_3^-) bonds.

$(C_6H_{15}N_3)_4(NO_3)_4(H_2O)_7$, a composition which was not unreasonable with respect to the stability measurements performed by Schwarzenbach.[1]

Four and four of the nickel atoms form clusters, the atoms arranged in form of nearly regular tetrahedra, *cf.* Table 2 and Fig. 2. Within the tetrahedra the Ni – Ni distances vary between 3.168(2) and 3.196(3) Å, whereas the shortest distance between Ni atoms belonging to different tetrahedra is 9.016(8) Å.

The hydroxide oxygen atoms O(OH^-) also form nearly regular tetrahedra (Fig. 2) with distances O – O varying between 2.682(8) and 2.697(8) Å (the O – O distances are not listed in Table 2).

The nickel atoms and the O(OH^-) atoms form together a cubane-like structure (Fig. 3a). Distances and angles within the "cube" are given in Table 2. None of the six planes defining the "cube" is, however, exactly planar. The deviations of the atoms from the respective best planes range between 0.08 and 0.09 Å. Within the "cube" the Ni – O – Ni angles vary between 98.3(2) and 99.7(2)°, whereas the O – Ni – O angles vary between 79.3(2) and 80.6(2)°.

The nickel atoms are octahedrally coordinated by three hydroxide oxygen atoms O(OH^-) and three amino nitrogen atoms N(NH_2). The Ni – O(OH^-) distances vary between 2.068(6) and 2.102(4) Å and the Ni – N(NH_2) distances between 2.106(7) and 2.132(5) Å. The distances are normal as compared to the values 2.085(2) and 2.11(4) Å, respectively, given in the International Tables.[3]

The same kind of nickel tetramer as found here has previously been described for tetrakis-[(μ_3-methoxy-2,4-pentanedionatomethanol)-nickel(II)], $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$.[4] Both in this compound and in the present one the Ni – Ni distances are slightly larger than 3 Å. There is thus no reason to assume metal-metal bonding. The cubane-like structure of the

Table 3. Comparison between mean values of distances (Å) and angles (°) in 1,3,5-triamino(*aaa*)-cyclohexane, "tach", and cyclohexylammonium chloride.[5] The *e.s.d*'s given in parentheses refer to one single measurement.

	C–C	C–N	C–C–C	C–C–N
"Tach" molecule 1	1.530(10)	1.490(9)	112.6(6)	110.7(5)
"Tach" molecule 2	1.521(9)	1.513(12)	113.1(8)	109.9(6)
"Tach" molecule 3	1.524(9)	1.506(11)	112.7(8)	110.4(6)
Cyclohexylammonium chloride	1.515(10)	1.488(8)	111.4(5)	110.0(5)

acetylacetonate nickel(II) tetramer (Fig. 3b) is somewhat less deformed than the corresponding part in the present compound. The magnetic properties of the acetylacetonate nickel(II) tetramer have been investigated by Martin and coworkers.[4] Similar investigations on Ni "tach" are in progress.[5]

The "tach" molecules. The "tach" molecules contain the cyclohexane rings in the *chair* conformation. Three crystallographically different "tach" molecules occur in the unit cell. For two of them (molecules 2 and 3, *cf.* Table 2) the four carbon atoms forming the bottom of the chair lie by symmetry in one plane; for the third (molecule 1) their maximum deviations from the best plane are 0.01 Å. The "tach" molecules are thus not twisted. All distances and angles in the molecules are normal as compared to corresponding values in cyclohexylammonium chloride [6] (Table 3).

Possible hydrogen bonds. As mentioned earlier the positions of the hydrogen atoms were not determined. Possible hydrogen bond contacts shorter than 3.00 Å are given in Table 2 and indicated by dotted lines in Fig. 4. As seen from the drawing there are no short N–H···O or N–H···N bonds. The unit cell contains eight nitrate ions, denoted ions 1, 2 and 3, and 14 water molecules, denoted O(W1), O(W2), O(W3) and O(W4) (*cf.* Table 2). Two nitrate ions (ion 3) and four water molecules O(W4) have no short contacts O–H···O. On the other hand four nitrate ions (ion 1) and two nitrate ions (ion 2) may be linked by two water molecules O(W1), four O(W2) and four O(W3) by hydrogen bonds O–H···O.

The nitrate oxygen O(43) (ion 1) may also be linked to the hydroxide oxygen atoms O(1) of $Ni_4(OH)_4^{4+}$ and in this way the tetramers will occur in pairs joined *via* hydrogen bonds.

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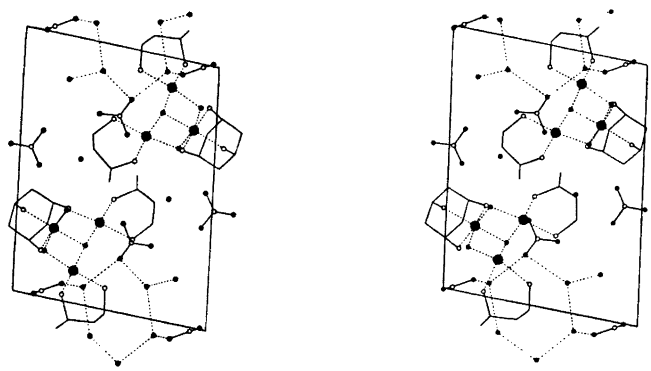

Fig. 4. Stereo view of the content of one unit cell of $Ni_4(OH)_4(C_6H_{15}N_3)_4(NO_3)_4(H_2O)_7$. Large filled circles indicate nickel atoms, small filled ones oxygen atoms and small open ones nitrogen atoms. Dotted lines indicate Ni–O(OH^-) bonds as well as possible hydrogen bonds.

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