



Fig. 2. The packing diagram for  $S_4N_4F_4$ . There are three unit cells along  $z$ .

**BONDLA** link of the **XRAY** suite of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and include the error contribution from the uncertainties in the unit-cell dimensions. Fig. 1 shows the molecular geometry and Fig. 2 the packing of the molecules in the unit cell; these figures were drawn using the program **SCHAKAL86** (Keller, 1986). Structural information has already been published (Wiegiers & Vos, 1961, 1963) and reference to Table 2 shows that within the errors of the

room-temperature study none of the bond angles change on cooling and none of the bonds are more than twice the e.s.d. removed from the room-temperature value. The low-temperature cell dimensions are reduced with respect to their room-temperature values by 0.1 Å in  $a$  (1.1%) and 0.1 Å in  $c$  (2.4%).

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## Structure of Hexaaquanickel(II) Bromate

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**Abstract.**  $[Ni(H_2O)_6](BrO_3)_2$ ,  $M_r = 422.60$ , cubic,  $Pa\bar{3}$ ,  $a = 10.2987(6)$  Å,  $V = 1092.3(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 824$ ,  $D_x = 2.57$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 90.79$  cm<sup>-1</sup>,  $T = 296$  K,  $R = 0.024$  for 360 unique reflections having  $I > \sigma_I$ . The single type of nickel ion is coordinated by six water-molecule O atoms, each at an observed distance of 2.061(2) Å, in an almost regular octahedral array.

The single type of bromate ion has an observed Br—O bond length of 1.655(2) Å and O—Br—O bond angle 104.25(9)°. Both the nickel–oxygen complex and the bromate ion were found to manifest rigid-body behavior. The Ni—O distance corrected for rigid-body motion is 2.065 Å, while the corrected Br—O bond length is 1.663 Å. Location and refinement of the two inequivalent H atoms permitted a detailed analysis of the hydrogen bonding, which occurs principally between the oxygen octa-

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hedron and the bromate groups. This structure is isomorphic to the structures of hexaaquanickel(II) chlorate and hexaaquacobalt(II) bromate which have been reported recently from this laboratory.

**Introduction.** Our interest in the transition metal-oxyhalogen salts stems in part from the fact that little (and sometimes erroneous) information is stated about them. The structure of hexaaquanickel(II) bromate was of particular interest because of possible structural comparisons of it both with the structure of its chlorate analogue and with the structures of other bromate salts recently determined in this laboratory.

**Experimental.** A nickel(II) bromate solution was produced by the metathetical reaction of aqueous analytical reagent grade nickel(II) sulfate in very nearly stoichiometric proportion with a saturated solution made from Strem Chemicals barium bromate. Following the removal of barium sulfate by filtration, the solution was evaporated at room temperature until bluish-green crystals, some regular octahedra and many hexagonal plates, were produced. The experimental sample was an irregular hexagonal chunk with principal dimensions approximately  $0.23 \times 0.31 \times 0.35$  mm. The crystal was coated with Apiezon L grease to retard possible loss or gain of water. The sample was analyzed at 296 K with a Rigaku AFC5S diffractometer utilizing graphite-monochromated Mo  $K\alpha$  radiation.

Unit-cell parameters were obtained from a symmetry-constrained least-squares fit of the setting angles for 25 centered reflections with  $28 < 2\theta < 30^\circ$ . Intensity data were measured for 2947 reflections (exclusive of standards) having  $+h$ ,  $+k$ ,  $\pm l$  ( $h_{\max} = 13$ ;  $k_{\max} = 12$ ;  $l: -13$  to  $+13$ ) and with  $2\theta$  values in the range  $4 \leq 2\theta \leq 55^\circ$ . The  $\omega$ - $2\theta$  scan technique was employed with scan widths  $(1.15 + 0.35 \tan \theta)^\circ$  in  $\omega$ , and a background/scan time ratio of 0.5. A variance was assigned to each reflection using the formula  $\sigma_I^2 = \sigma_{cs}^2(I) + (0.03I)^2$ , where  $\sigma_{cs}$  is based on counting statistics and  $I$  is the integrated intensity. Six standard reflections (202, 222, 002, 426, 551 and 162) were measured after every 150 reflections and showed a mean maximum non-systematic relative intensity variation of  $\pm 3.4\%$ . Accordingly, no decay correction was applied. The data were corrected for Lorentz and polarization effects. A  $\psi$ -scan absorption correction was applied based on  $\psi$ -scan data obtained just prior to intensity data collection; the range of transmission factors was 0.629–1.000, with an average value 0.843.

The intensity data were consistent with Laue group  $m\bar{3}$  and, on the basis of systematic absences, space group  $Pa\bar{3}$  (No. 205) but in a non-standard setting. Following index transformation to the

Table 1. *Final positional parameters and equivalent isotropic and isotropic displacement parameters for hexaaquanickel(II) bromate at 296 K with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}/B(\text{\AA}^2)$
Ni	0	0	0	1.41 (2)
Br	0.26016 (3)	0.26016	0.26016	1.52 (2)
O(1)	0.1679 (2)	0.1567 (2)	0.3414 (2)	2.2 (1)
O(2)	0.0345 (2)	-0.0303 (2)	0.1948 (2)	2.0 (1)
H(1)	0.047 (4)	0.023 (3)	0.231 (4)	2.1 (10)†
H(2)	-0.040 (4)	-0.050 (4)	0.228 (4)	4.2 (11)†

† Refined isotropically.

Table 2. *Bond lengths (Å) and angles (°) for hexaaquanickel(II) bromate with e.s.d.'s in parentheses*

	Observed distance (Å)	Rigid-body distance (Å)		Observed angle (°)
Coordination polyhedron: rigid body I				
Ni—O(2)	2.061 (2)	2.065	O(2)—Ni—O(2)'	180
O(2)—O(2)'	4.122 (4)	4.131	O(2)—Ni—O(2)''	90.33 (9)
O(2)—O(2)''	2.924 (4)	2.930	O(2)—Ni—O(2)'''	89.67 (9)
O(2)—O(2)'''	2.906 (4)	2.911		
Bromate ion: rigid body II				
Br—O(1)	1.655 (2)	1.663	O(1)—Br—O(1)''	104.25 (9)
Br—Ni	4.6407 (6)			
Br—Ni''	4.4024 (3)			
Water molecule				
O(2)—H(1)	0.68 (3)		H(1)—O(2)—H(2)	99 (5)
O(2)—H(2)	0.87 (4)			

Code for symmetry-related atoms: (–)  $x, y, z$ ; (i)  $-x, -y, -z$ ; (ii)  $z, x, y$ ; (iii)  $-z, -x, -y$ ; (iv)  $\frac{1}{2} + x, \frac{1}{2} - y, -z$ .

standard setting, analysis proceeded as described for hexaaquacobalt(II) bromate (Blackburn, Gallucci & Gerkin, 1990). Full-matrix least-squares refinement was performed using the *TEXSAN* structure analysis package (Molecular Structure Corporation, 1989) to minimize the function  $\sum \sigma_F^{-2} (|F_o| - |F_c|)^2$ , in which  $\sigma_F = \sigma_I/2FLp$ . Neutral-atom scattering factors and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71, 148) for Ni, Br and O; the scattering factor for H was taken from Stewart, Davidson & Simpson (1965).

$R_{int}$  was found to be 0.050 for 488 sextuplets, and the results for the final refinement cycle using all unique reflections with  $I > \sigma_I$  were: 360 independent observations; 33 variables;  $R = 0.024$ ;  $wR = 0.027$ ;  $S = 1.16$ ;  $(\Delta/\sigma)_{\max} < 0.01$ . The refined value of the secondary-extinction coefficient was  $2.58(12) \times 10^{-6}$ . Maximum and minimum peaks on the final electron density difference map had values  $+0.43$  and  $-0.41 \text{ e \AA}^{-3}$ , respectively: the maximum was located at  $x = y = z = 0.31$ ,  $\sim 0.9 \text{ \AA}$  from Br; the minimum was located at  $x = 0.31, y = 0.06, z = 0.26$ , which is not within  $1.5 \text{ \AA}$  of any atom. (For the final refinement cycle for 309 independent observations

Table 3. *Hydrogen-bond parameters for hexaaquanickel(II) bromate with e.s.d.'s in parentheses*

Water oxygen— acceptor oxygen	Distance (Å)	Proton— acceptor oxygen	Observed distance (Å)	Neutron-adjusted† distance (Å)	Observed O—H—O angle (°)	
O(2)—O(1) <sup>v</sup>	2.761 (3)	H(2)—O(1) <sup>v</sup>	1.96 (4)	1.87	O(2)—H(2)—O(1) <sup>v</sup>	153 (4)
O(2)—O(1)	2.806 (3)	H(1)—O(1)	2.18 (3)	1.91	O(2)—H(1)—O(1)	156 (4)
O(2)—O(2) <sup>iii</sup>	2.907 (4)	H(2)—O(2) <sup>iii</sup>	2.58 (4)	2.56	O(2)—H(2)—O(2) <sup>iii</sup>	103 (3)
O(2)—O(2) <sup>vi</sup>	2.924 (4)	H(1)—O(2) <sup>vi</sup>	2.80 (3)	2.80	O(2)—H(1)—O(2) <sup>vi</sup>	94 (3)
O(2)—O(1) <sup>vii</sup>	3.235 (3)	H(1)—O(1) <sup>vii</sup>	2.84 (4)	2.70	O(2)—H(1)—O(1) <sup>vii</sup>	120 (4)
		H(2)—O(1) <sup>vii</sup>	2.81 (4)	2.78	O(2)—H(2)—O(1) <sup>vii</sup>	112 (4)

Code for symmetry-related atoms: (–)  $x, y, z$ ; (iii)  $-z, -x, -y$ ; (v)  $-y, -\frac{1}{2} + z, \frac{1}{2} - x$ ; (vi)  $y, z, x$ ; (vii)  $-\frac{1}{2} + z, x, \frac{1}{2} - y$ .

† See text for details.

with  $I > 3\sigma$ ;  $R = 0.018$ ;  $wR = 0.025$ ;  $S = 1.17$ . Similarly, for the 390 independent observations with  $I > 0$ ,  $R = 0.028$ ,  $wR = 0.027$ ;  $S = 1.13$ . These latter two refinements were performed for comparison purposes only.)

Final atomic parameters and their e.s.d.'s are given in Table 1.\* Selected interatomic distances and angles in the nickel coordination polyhedron, in the bromate ion and in the water molecule are given with their e.s.d.'s in Table 2.

Rigid-body analysis of the nickel–oxygen complex and the bromate ion was performed using *THMA11* (Trueblood, 1986), based on the work of Schomaker & Trueblood (1968). The average magnitude of the differences in the mean-square displacement amplitudes (MSDA) along the interatomic vectors for the two unique atom pairs of the bromate ion was found to be  $8(16) \times 10^{-4} \text{ \AA}^2$ ; the corresponding value for the four unique atom pairs of the nickel–oxygen complex was found to be  $20(12) \times 10^{-4} \text{ \AA}^2$ . We concluded that Hirshfeld's (1976) rigid-bond test, as described by Dunitz, Schomaker & Trueblood (1988), is satisfied for the nickel–oxygen complex and for the bromate ion. Rigid-body-corrected bond lengths are given in Table 2; corrected angles differed typically from observed angles by less than their e.s.d.'s and were therefore not tabulated.

**Discussion.** Hexaaquanickel(II) bromate, hexaaquanickel(II) chlorate and hexaaquacobalt(II) bromate are isomorphous. A unit cell of the cobalt isomorph is shown as Fig. 1 by Blackburn, Gallucci & Gerkin (1990).

The nickel coordination polyhedron has, by symmetry, a single Ni—O(2) distance and thus departs only in an angular sense, but by at most  $0.33^\circ$  and thus less than  $4\sigma$  of the relevant angles, from regular octahedral geometry. Corrected for rigid-body

motion, the Ni—O(2) distance becomes  $2.065 \text{ \AA}$ ; the corresponding rigid-body-corrected value  $2.060 \text{ \AA}$  has been reported for hexaaquanickel(II) chlorate (Gallucci & Gerkin, 1990).

The bromate ion has, by symmetry, a single Br—O(1) distance [observed value:  $1.655(2) \text{ \AA}$ ] and an O(1)—Br—O(1) angle measuring  $104.25(9)^\circ$ . Corresponding values reported for the bromate ion in hexaaquacobalt(II) bromate are  $1.653(2) \text{ \AA}$  and  $104.07(9)^\circ$  (Blackburn, Gallucci & Gerkin, 1990). In the present case, however, the bromate ion was found to behave as a rigid body; the corrected Br—O(1) distance is  $1.663 \text{ \AA}$ .

The observed H—O—H angle, within its uncertainty, falls in the range  $100.4\text{--}109.9^\circ$  given by Chiari & Ferraris (1982) for inorganic hydrates of class *J* (Ferraris & Franchini-Angela, 1972) to which this water belongs.

Our analysis of the hydrogen bonding is based partially on treatments of hydrogen bonding by Jeffrey (1987) and Chiari & Ferraris (1982). Neutron-adjusted hydrogen positions (see Gallucci & Gerkin, 1990) were used in the hydrogen-bonding analysis. Hydrogen-bonding parameters are given in Table 3.

The hydrogen-bonding situation is, as would be expected, nearly identical to that for the isomorphs hexaaquanickel(II) chlorate and hexaaquacobalt(II) bromate. For hexaaquacobalt(II) bromate and hexaaquanickel(II) bromate, for example, corresponding H—O(acceptor) distances differ by no more than  $0.07 \text{ \AA}$  and corresponding O(water)—H—O(acceptor) angles differ by no more than  $5^\circ$ , approximately their standard deviations. To summarize briefly: there are twelve strong hydrogen bonds linking the polyhedron to the surrounding bromate ions; in addition, there are two weaker hydrogen bonds within the same coordination polyhedron and a single bifurcated bond to a bromate–oxygen acceptor. Figs. 2 and 3 presented by Blackburn, Gallucci & Gerkin (1990) for hexaaquacobalt(II) bromate illustrate this hydrogen-bonding situation. We note in particular the presence of three-center/bifurcated hydrogen bonding (Jeffrey & Maluszynska, 1986) in these isomorphous structures.

\* Lists of structure factors, anisotropic displacement parameters and supplementary material relating to the rigid-body analysis have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54004 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

It is of interest that of the three salts of the form  $[M(H_2O)_6](XO_3)_2$  whose structures we have determined, this is the first case in which the halate ion displayed rigid-body motion. In all three cases, the metal–oxygen complex manifested rigid-body motion.

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## Crystal Chemistry of *cyclo*-Hexaphosphates. XX. Structure of Cerium *cyclo*-Hexaphosphate Decahydrate

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**Abstract.**  $Ce_2P_6O_{18} \cdot 10H_2O$ ,  $M_r = 934.22$ , orthorhombic,  $P2_12_12$ ,  $a = 13.522$  (5),  $b = 13.105$  (9),  $c = 6.938$  (3) Å,  $V = 1230$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.523$  Mg m<sup>-3</sup>,  $\lambda(Ag K\alpha) = 0.5608$  Å,  $\mu = 2.125$  mm<sup>-1</sup>,  $F(000) = 900$ , room temperature, final  $R = 0.036$  for 3450 independent reflections. The title compound and the previously described  $Ca_2(NH_4)_2P_6O_{18} \cdot 6H_2O$  [Averbuch-Puchot (1990). *Acta Cryst.* **C46**, 2005–2007] have some common features, but they are not isostructural. Of the approximately 55 known *cyclo*-hexaphosphates, these two compounds are unique examples of structures exhibiting a  $P_6O_{18}$  ring anion with twofold internal symmetry. The coordination around the Ce atom forms a three-capped trigonal prism.  $CeO_9$  polyhedra interconnect  $P_6O_{18}$  rings in a three-dimensional way.

**Introduction.** This work is part of a systematic investigation of *cyclo*-hexaphosphates of mono-valent, divalent, trivalent and mixed cations.  $Ce_2$ -

$P_6O_{18} \cdot 10H_2O$  is the fourth structural type observed so far in the domain of trivalent cation *cyclo*-hexaphosphates, the previous ones being represented by  $Cr_2P_6O_{18}$  (Bagieu-Beucher & Guitel, 1977),  $Nd_2P_6O_{18} \cdot 12H_2O$  (Trunov, Chudinova & Borodina, 1988) and  $Cr_2P_6O_{18} \cdot 21H_2O$  (Bagieu-Beucher, Averbuch-Pouchot & Rzaigui, 1991). Up to now the existence of isotopic salts has been reported only for the first structure type, namely  $Al_2P_6O_{18}$  (Kanene, Konstant & Krasnikov, 1985) and  $Ga_2P_6O_{18}$  (Chudinova, Grunze & Guzeva, 1987).

**Experimental.** The chemical preparation of the title compound has already been described in a general article about the synthesis of rare-earth *cyclo*-hexaphosphates (Rzaigui, 1991). Crystal size:  $0.16 \times 0.14 \times 0.13$  mm. Density not measured. Philips PW 1100 diffractometer, graphite monochromator. 18 reflections ( $10.9 < \theta < 13.1^\circ$ ) for refining unit-cell dimensions.  $\omega$  scan, scan width:  $1.20^\circ$ , scan speed: