regular than the 'occupied' octahedra in the mercury salt, the converse is true in the nickel salt: the 'occupied' octahedra are compressed along z and are more nearly regular than the 'unoccupied' octahedra (O–O octahedral distances are as follows: nickel salt: occupied: 2·840 and 2·948 Å, unoccupied: 2·840 and 3·231 Å; mercury salt: occupied: 3·188 and 3·430 Å, unoccupied: 3·188 and 3·059 Å).

As the numerical values make clear, the 'occupied' nickel salt octahedra depart substantially less from regularity than do the 'occupied' mercury salt octahedra.

The anion stacks are essentially geometrically identical in the two structures within the qualifications given above.

The Ni–O(water) distance in the present salt, 2·047 (2) Å, accords well with values from other recent determinations of Ni^{II}–O(water) distances, e.g. 2·06 Å (average) in room-temperature nickel(II) nitrate hexahydrate (Bigoli, Braibanti, Tiripicchio & Camellini, 1971) and 2·064 Å in room-temperature nickel(II) iodide hexahydrate (Louër, Grandjean & Weigel, 1973).

Finally, the Br–O distance in the perbromate ion in the present salt, 1·603 (3) Å, is found to be in very good agreement, e.g., with the room-temperature value, 1·608 (3) Å, found for barium perbromate trihydrate (Gerkin et al., 1988). The difference between these best values, though of little statistical significance, is consistent with an average linear thermal expansion coefficient of the order $20 \times 10^{-6}\,deg^{-1}$, a quite plausible value.

References

Alcock, N. W. (1970). Crystallographic Computing, edited by F. R. Ahmed, pp. 271–278. Copenhagen: Munksgaard.

Bigoli, F., Braibanti, A., Tiripicchio, A. & Camellini, M. T. (1971). Acta Cryst. B27, 1427–1434.

Cromer, D. T. & Liberman, D. (1970). J. Chem. Phys. 53, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). Acta Cryst. A24, 321–324.

Cromer, D. T. & Waber, J. T. (1965). Acta Cryst. 18, 104–109.

Gerkin, R. E., Reppart, W. J. & Appelman, E. H. (1988). Acta Cryst. C44, 960–962.

Johansson, G. & Sandström, M. (1978). Acta Chem. Scand. Ser. A, 32, 109–113.

Johnson, C. K. (1971). ORTEPII. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Louër, M., Grandjean, D. & Weigel, D. (1973). J. Solid State Chem. 7, 222–228.

Meulenaer, J. de & Tompa, H. (1965). Acta Cryst. 19, 1014–1018.

Sheldrick, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. W. & Hall, S. R. (1972). The XRAY system–version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

Structure of Tripotassium Monohydroxo(pentahydroxoundecaoxoheptaborato)platinate(IV) Trihydrate

By Helmut Behm

Crystallography Laboratory, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Abstract. $K_3[Pt\{B_7O_{11}(OH)_5\}(OH)].3H_2O$, $M_r = 720\cdot13$, orthorhombic, Pnma, $a = 19\cdot283$ (3), $b = 11\cdot480$ (2), $c = 8\cdot106$ (2) Å, $V = 1794\cdot4$ (4) Å^3, $Z = 4$, $D_x = 2\cdot66\,Mg\,m^{-3}$, $\lambda(CuK\alpha) = 1\cdot54184$ Å, $\mu(CuK\alpha) = 22\cdot12\,mm^{-1}$, $F(000) = 1368$, $T = 293$ K, final conventional $R = 0\cdot027$ for 1458 observed reflections. The structure contains isolated mononuclear $[Pt\{B_7O_{11}(OH)_5\}(OH)]$ complexes, which are held together by potassium ions and water molecules. The borate complex, with seven boron atoms, acts as a pentadentate ligand which encloses the Pt nucleus on one side. The coordination sphere of the Pt atom is an almost regular octahedron, built up by five oxygen atoms of the borate complex and one additional OH group. The structure reported here is the first platinum borate. It is the first instance of a true heptaborate which forms a novel type of molecular structure. The proton distribution in the structure cannot be described by the borate rules given by Christ & Clark [Phys. Chem. Miner. (1977), 2, 59–87].

Introduction. The present investigation is part of a series of studies of transition-metal borate structures. Several new borate complexes with various transition metals, such as Cu, Co and U, were synthesized and their structures reported (Behm, 1983a,b, 1985; Behm & Smykalla, 1987).

It seems obvious that the forming of these new borate complexes is strongly influenced by and related to the type of the transition-metal ions. To study the influence of size, charge and electronic properties of the metal ions in forming such complexes in aqueous alkali borate solutions, the system Pt–K,Na-borate–H_2O has been investigated. From a solution containing Pt^{IV} and K pentaborate, crystals were obtained. Its structure was determined.

Experimental. *Preparation.* $K_3[Pt\{B_7O_{11}(OH)_5\}(OH)]$.-$3H_2O$ was synthesized from an aqueous solution of potassium pentaborate, to which, under stirring, a solution of K_2PtCl_6 was added. After several months under slow evaporation a few yellow crystals were observed, embedded among the predominant colourless potassium pentaborate crystals. The yellow Pt borate crystals were isolated. They seem to be stable in air. Their composition was established by the X-ray structure determination.

Crystal size $0.13 \times 0.14 \times 0.11$ mm, graphite crystal monochromator, Nonius CAD-4 single-crystal diffractometer, unit-cell dimensions from 25 reflections with $13° < \theta < 53°$. Intensity data of 6252 reflections (*hkl* from −23, −14, 0 to 16, 14, 9, up to $\theta = 65°$), using the ω–2θ scan with a scan angle of $1.65°$ and a variable scan rate with a maximum scan time of 15 s per reflection. The intensity of the primary beam was checked by three reference reflections every 30 min. The final drift correction factors were between 1.00 and 1.05. A smooth curve was used to correct for this drift. Profile analysis (Lehmann & Larsen, 1974; Grant & Gabe, 1978). Absorption correction using the *XRAY* system (1976) (part *ABSORB*), with the Gaussian quadrature method, $9 \times 9 \times 9$ sampling points. Symmetry-equivalent reflections averaged, $R_{merge} = \Sigma(F_o - <F_o>)/\Sigma F_o = 0.044$, 1620 unique reflections of which 1458 with $F_o > 6\sigma(F_o)$. Lorentz and polarization corrections.

The structure was solved with Patterson methods, using the automated program system *PATSYS* (Behm & Beurskens, 1985), which combines *SHELX*84 (Sheldrick, 1984) and *DIRDIF* (Beurskens *et al.*, 1982). All nonhydrogen atoms were obtained in a single automatic run. The structure was refined by full-matrix least squares on $|F_o|$ values, using *SHELX* (Sheldrick, 1976). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Isotropic refinement converged to $R = 0.11$. An attempt to refine the structure in the related non-centrosymmetric space group $Pn2_1a$ showed strong

Table 1. *Fractional positional and thermal parameters (with e.s.d.'s)*

$$U_{eq} = \tfrac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{eq}(Å^2 \times 10^2)$
Pt1	0.11696 (1)	0.2500	0.54859 (3)	1.02 (1)
K1	0.39333 (7)	0.5102 (1)	0.4195 (2)	3.66 (4)
K2	0.0721 (1)	0.7500	0.3260 (3)	4.71 (8)
O1	0.1802 (2)	0.3734 (4)	0.6359 (4)	2.1 (1)
O2	0.0530 (2)	0.3776 (4)	0.4748 (4)	2.0 (1)
O3	0.1654 (3)	0.2500	0.3277 (6)	1.7 (1)
O4	0.2658 (2)	0.3549 (4)	0.4186 (5)	3.3 (1)
O5	0.0752 (2)	0.3526 (3)	0.1820 (4)	2.1 (1)
O6	0.2696 (3)	0.2500	0.1701 (6)	1.6 (1)
O7	0.1607 (3)	0.2500	0.0320 (5)	1.6 (1)
O8	0.2798 (2)	0.4909 (4)	0.6228 (5)	3.6 (1)
O9	0.2669 (3)	0.2500	−0.1133 (7)	4.4 (2)
O10	0.0158 (2)	0.5135 (3)	0.2741 (4)	2.4 (1)
O11	0.0645 (2)	0.2500	0.7671 (6)	1.3 (1)
O12	0.3876 (2)	0.3873 (5)	0.1038 (8)	4.9 (2)
O13	0.4325 (5)	0.2500	0.462 (1)	7.1 (4)
B1	0.2394 (3)	0.4031 (6)	0.5594 (7)	1.9 (2)
B2	0.0486 (3)	0.4115 (6)	0.3143 (7)	1.8 (2)
B3	0.2430 (4)	0.2500	0.335 (1)	1.5 (2)
B4	0.2308 (5)	0.2500	0.030 (1)	2.2 (3)
B5	0.1188 (4)	0.2500	0.183 (1)	2.0 (3)

correlations between related parameters. No deviation from centrosymmetry could be recognized. Therefore the refinement was continued in *Pnma*. At this stage an additional empirical absorption correction was applied (Walker & Stuart, 1983), resulting in a further decrease of R to 0.043 (correction factors were in the range 0.75–1.56).

The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. From a difference Fourier map all hydrogen atoms could be located. During the final stages of the refinement the positional and anisotropic parameters of the non-hydrogen atoms and the isotropic temperature factors of the hydrogen atoms were refined. The positional parameters of the hydrogen atoms were fixed at the positions found in the difference Fourier map. The final conventional agreement factors were $R = 0.027$ and $wR = 0.035$ for the 1458 'observed' reflections and 165 variables. The function minimized was $\Sigma w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0.00016F_o^2]$ with $\sigma(F_o)$ from counting statistics. The maximum shift over e.s.d. ratio in the last full-matrix least-squares cycle was less than 0.1. The final difference Fourier map showed peaks of about $1.0 e Å^{-3}$ close to the Pt atom. Plots were made with *PLUTO* (Motherwell, 1976), geometry data were calculated using *PARST* (Nardelli, 1983).

Discussion. Final positional and thermal parameters are given in Table 1.* Molecular geometry data are

---

* Lists of structure factors, anisotropic thermal parameters, hydrogen atoms and hydrogen bonds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44980 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected distances* (Å) *and angles* (°) (*with e.s.d.'s*)

Pt1—O1	1·999 (4)	O1—Pt1—O1'	90·3 (2)
Pt1—O1'	1·999 (4)	O1—Pt1—O2	87·9 (2)
Pt1—O2	2·006 (4)	O1—Pt1—O2'	176·6 (1)
Pt1—O2'	2·006 (4)	O1—Pt1—O3	91·8 (1)
Pt1—O3	2·020 (5)	O1—Pt1—O11	89·7 (1)
Pt1—O11	2·039 (5)	O2—Pt1—O2'	93·8 (2)
K1—O5	2·716 (4)	O2—Pt1—O3	91·1 (1)
K1—O8	2·750 (4)	O2—Pt1—O11	87·4 (1)
K1—O10	2·836 (4)	O3—Pt1—O11	177·8 (2)
K1—O12	2·924 (6)	O1—B1—O4	126·8 (5)
K1—O1	3·013 (4)	O1—B1—O8	119·6 (5)
K1—O4	3·037 (4)	O4—B1—O8	113·5 (5)
K1—O7	3·081 (3)	O2—B2—O5	125·8 (5)
K1—O13	3·101 (3)	O2—B2—O10	120·0 (5)
K1—O11	3·125 (3)	O5—B2—O10	114·2 (5)
K1—O10'	3·378 (4)	O3—B3—O4	108·8 (4)
K2—O11	2·740 (5)	O3—B3—O6	108·7 (6)
K2—O12	2·857 (6)	O4—B3—O4'	112·3 (7)
K2—O12'	2·857 (6)	O4—B3—O6	109·1 (4)
K2—O13	2·952 (10)	O6—B4—O7	122·6 (7)
K2—O10	2·954 (4)	O6—B4—O9	115·7 (7)
K2—O10'	2·954 (4)	O7—B4—O9	121·7 (8)
K2—O9	3·145 (7)	O3—B5—O5	111·1 (4)
K2—O2	3·251 (4)	O3—B5—O7	109·1 (6)
K2—O2'	3·251 (4)	O5—B5—O5'	108·9 (6)
B1—O1	1·343 (7)	O5—B5—O7	108·3 (4)
B1—O4	1·367 (7)	B3—O3—B5	129·8 (6)
B1—O8	1·373 (7)	B1—O4—B3	127·8 (5)
B2—O2	1·361 (7)	B2—O5—B5	127·9 (5)
B2—O5	1·366 (7)	B3—O6—B4	125·7 (6)
B2—O10	1·371 (7)	B4—O7—B5	124·1 (6)
B3—O6	1·433 (9)	Pt1—O1—B1	122·4 (3)
B3—O4	1·449 (6)	Pt1—O2—B2	122·2 (4)
B3—O4'	1·449 (6)	Pt1—O3—B3	115·2 (3)
B3—O3	1·497 (9)	Pt1—O3—B5	114·9 (3)
B4—O7	1·352 (11)		
B4—O9	1·352 (10)		
B4—O6	1·362 (10)		
B5—O5	1·448 (6)		
B5—O5'	1·448 (6)		
B5—O7	1·468 (9)		
B5—O3	1·475 (10)		

collected in Table 2. The crystallographic numbering scheme of the borate–platinum complex is given in Fig. 1; a projection of the structure is given in Fig. 2.

The crystal structure belongs to the class of soroborates. It contains the first real isolated hepta-borate, in the notation given by Christ & Clark (1977) 7: 5Δ + 2T. The borate molecule itself is built up of two tetrahedral and five trigonal planar coordinated boron atoms. One single trigonal and two tetrahedral boron atoms form a six-membered ring, if the oxygen atoms are also counted. The two tetrahedral boron atoms B(3) and B(5) are bonded to four additional BO$_3$ groups, thereby forming a cage. Five oxygen atoms of this borate molecule, four of the additional BO$_3$ groups and the oxygen atom bonded between the two tetrahedral boron atoms form together with an additional OH group an almost ideal octahedron, at the centre of which lies the Pt^{IV} nucleus. This pentadentate chelate complex shows a strong relation to the class of cryptate compounds.

The Pt—O distances in the octahedron are between 1·999 (4) and 2·039 (5) Å. These values are comparable with those found in chemically related com-

pounds containing Pt(OH)$_6$ or PtO$_6$ complexes, as in [NH$_4$]$_2$[Pt(OH)$_6$], K$_2$[Pt(OH)$_6$] (Bandel, Platte & Trömel, 1982) or in K$_6$Na$_2$[PtW$_6$O$_{24}$].12H$_2$O (Lee, Ichida, Kobayashi & Sasaki, 1984) with six symmetrically equivalent Pt—O distances of 2·017 (7), 2·016 (8) and 2·01 (2) Å respectively. The interatomic distances and angles in the tetrahedral BO$_4$ groups of the complex are in the ranges 1·433 (9) to 1·497 (9) Å and 108·3 (4) to 112·3 (7)°, respectively. The distances and angles in the BO$_3$ groups are 1·343 (7) to 1·373 (7) Å and 113·5 (5) to 126·8 (5)°. This rather wide spread in the angles of the BO$_3$ groups indicates considerable stress in the borate molecule to allow for an almost ideal octahedral coordination sphere around the central Pt nucleus.

All oxygen atoms of the BO$_3$ groups which do not complex or are not bonded to a BO$_4$ group are
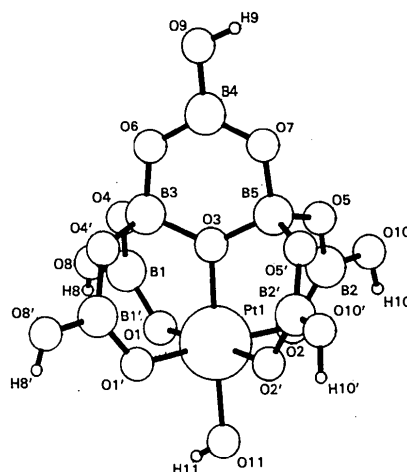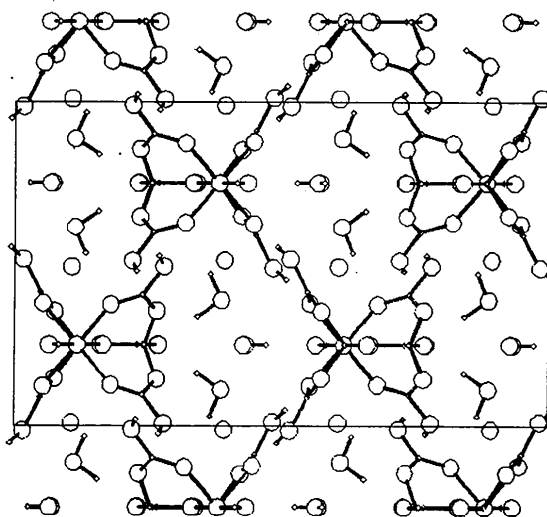

Fig. 1. Crystallographic numbering scheme.

Fig. 2. Projection of the unit cell along the *c* axis. *a* is to the right and *b* is down.

protonated. The idealized symmetry of the borate molecule, ignoring the hydrogen atoms, is $mm2$ (C_{2v}) and, including the hydrogen atoms, the symmetry is m (C_s). The site symmetry in the space group is also m, which is a remarkable feature for a larger borate molecule, as has been pointed out by Zobetz (1982).

The Pt borate complexes are held together by a network of hydrogen bonds and the potassium–oxygen polyhedra. All hydrogen atoms in the structure, the hydrogen atoms of the hydroxyl groups as well as those of the water, participate in the hydrogen-bond network. The individual distances and angles have been deposited. Between the Pt borate complexes the potassium cations are located in such a way that all oxygen atoms in the structure, except that bonded between the two tetrahedral boron atoms and the oxygen O(6), build up the oxygen coordination polyhedra around the potassium cations. K(1) has a tenfold coordination which can be considered as a strongly distorted bicapped square antiprism. K(2) has a ninefold coordination which may best be described as a distorted tricapped trigonal prism. Both cation polyhedra are strongly connected in two dimensions by sharing several corners and edges; they build up double layers in the bc plane.

References

BANDEL, G., PLATTE, C. & TRÖMEL, M. (1982). *Acta Cryst.* B38, 1544–1546.

BEHM, H. (1983a). *Acta Cryst.* C39, 20–22.

BEHM, H. (1983b). *Acta Cryst.* C39, 1156–1159.

BEHM, H. (1985). *Acta Cryst.* C41, 642–645.

BEHM, H. & BEURSKENS, P. T. (1985). *Z. Kristallogr.* 170, 10.

BEHM, H. & SMYKALLA, C. (1987). *Z. Kristallogr.* In the press.

BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M, VAN DEN HARK, TH. E. M., PRICK, P. A. J., NOORDIK, J. H., BEURSKENS, G., GOULD, R. O. & PARTHASARATHI, V. (1982). *Conformation in Biology*, edited by R. SRINIVASAN & R. H. SARMA, pp. 389–406. New York: Adenine Press.

CHRIST, C. L. & CLARK, J. R. (1977). *Phys. Chem. Miner.* 2. 59–87.

GRANT, D. F. & GABE, E. J. (1978). *J. Appl. Cryst.* 11, 114–120.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

LEE, U., ICHIDA, H., KOBAYASHI, A. & SASAKI, Y. (1984). *Acta Cryst.* C40, 5–7.

LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A30, 580–584.

MOTHERWELL, W. D. S. (1976). *PLUTO*. A program for plotting molecular and crystal structures. Univ. Chemical Laboratory, Cambridge, England.

NARDELLI, M. (1983). *Comput. Chem.* 7, 95–98.

SHELDRICK, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. Chemical Laboratory, Cambridge, England.

SHELDRICK, G. M. (1984). *SHELX*84. Eighth European Crystallographic Meeting, Liège, Abstracts, p. 272.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A39, 158–166.

XRAY system (1976). Editor J. M. STEWART. Computer Science Centre, Univ. of Maryland, College Park, Maryland, USA.

ZOBETZ, E. (1982). *Z. Kristallogr.* 160, 81–92.

Structures of Nearly 1:1:1 Phases in M–Cu–Al (M=Ca, Sr, Ba) Systems

BY M. L. FORNASINI AND F. MERLO

Istituto di Chimica Fisica, Università di Genova, Corso Europa 26, 16132 Genova, Italy

Abstract. $Ca_{30}Cu_{29.5}Al_{33.7}$, $M_r = 3986.1$, hexagonal, $hP93.2$, $P6/mmm$, $a = 15.256$ (2), $c = 9.252$ (1) Å, $V = 1864.9$ (4) Å^3, $Z = 1$, $D_x = 3.55$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 10.9$ mm^{-1}, $F(000) = 1894$, room temperature, $R = 0.038$ for 723 reflections with $F_o > 3\sigma(F_o)$. $Sr_6Cu_{6.6}Al_{7.4}$ ($Ba_6Cu_{6.8}Al_{7.2}$), $M_r = 1144.7$ (1450.4), tetragonal, $tI80$, $I4/mcm$, $a = 8.427$ (2), $c = 25.995$ (7) [$a = 8.533$ (1), $c = 27.249$ (4)] Å, $V = 1846.0$ (8) [1984.1 (4)] Å^3, $Z = 4$, $D_x = 4.12$ (4.86) Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 26.0$ (19.7) mm^{-1}, $F(000) = 2062$ (2507), room temperature, $R = 0.055$ (0.051) for 481 (658) reflections with $F_o > 3\sigma(F_o)$. The CaCuAl structure presents in part features of a Frank–Kasper layer structure and is closely related to the cubic $Mg_{32}(Zn,Al)_{49}$ phase. Several atomic sites have occupational disorder, especially those occupied by small atoms. All Cu and/or Al atoms but one are icosahedrally coordinated. $Sr_6Cu_7Al_7$ and $Ba_6Cu_7Al_7$ are isotypic, with a slight difference in the mixed filling of a site by Cu and Al atoms. Their structure is a site-occupation variant of the $La_6Co_{11}Ga_3$ structure. All small atoms are surrounded by icosahedra, save an Al atom coordinated with ten alkaline earths in the form of a bicapped square antiprism.