

Cubique
 $Fd\bar{3}m$
 $a = 10,873$ (5) Å
 $b = 10,873$ (5) Å
 $c = 10,873$ (5) Å
 $\beta = 90,^\circ$
 $V = 1285$ (2) Å³
 $Z = 8$
 $D_x = 5,29$ (2) Mg m⁻³
 $D_m = 5,4$ (1) Mg m⁻³
 D_m mesurée par pycnométrie

Collection des données

Diffractomètre quatre cercles
 Synthex
 Balayage ω -2 θ
 Correction d'absorption:
 Méthode analytique (de Meulenaer & Tompa, 1965)
 $T_{\min} = 0,129$, $T_{\max} = 0,259$
 97 réflexions mesurées
 97 réflexions indépendantes

Affinement

Affinement basé sur les F
 (ORXFLS; Busing, 1971)
 $R = 0,047$
 $wR = 0,051$
 $S = 1,81$
 68 réflexions
 10 paramètres par cycle
 $w = 1,0$
 $(\Delta/\sigma)_{\max} = 0,0007$
 $\Delta\rho_{\max} = 1,39$ e Å⁻³
 $\Delta\rho_{\min} = -1,40$ e Å⁻³

Paramètres de la maille à l'aide de 15 réflexions
 $\theta = 6,23$ – $10,65^\circ$
 $\mu = 26,1$ mm⁻¹
 $T = 293$ K
 Plaquette triangulaire
 $0,3 \times 0,24 \times 0,04$ mm
 Noire

68 réflexions observées
 $[I > 2\sigma(I)]$
 $\theta_{\max} = 31,54^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 11$
 $l = 0 \rightarrow 16$
 3 réflexions de référence mesurées tout les 50 réflexions
 variation d'intensité: 0,0022%

Correction d'extinction: Becker & Coppens (1975) type I
 Coefficient d'extinction: $0,66 \times 10^2$
 Facteurs de diffusion de *International Tables for X-ray Crystallography* (1974, Tome IV, Tableaux 2,2A et 2,3,1)

affinements ont conduit à considérer le site spinelle 16(c) occupé uniquement par de l'ytterbium et le site 16(d), par l'indium et l'ytterbium en désordre statistique. Détermination des facteurs d'occupation de chacun des sites métalliques par variation dans des cycles séparés. La proportion d'indium et d'ytterbium sur le site 16(d) tient compte du nombre d'électrons présents sur ce site et de l'équilibre des charges (somme des coefficients d'occupation contrainte à 1,833). En raison des fortes corrélations existantes, les paramètres variables sont affinés simultanément mais avec un facteur de variation limité à 0,2.

Les listes des facteurs de structure et des facteurs d'agitation thermique anisotrope ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 55934: 2 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: DU1005]

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Structure of Hexaaquacobalt(II) Perbromate

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Abstract

The structure of [Co(H₂O)₆](BrO₄)₂ consists of stacks of water-oxygen octahedra, alternate ones of which contain a central Co^{II} ion, each surrounded by six stacks of perbromate ions. The water O atoms form a virtually regular octahedron about Co, while the perbromate geometry is nearly regular tetrahedral. The structure is compared with those of [Hg(H₂O)₆](ClO₄)₂, [Cd(H₂O)₆](ClO₄)₂ and [Ni(H₂O)₆](BrO₄)₂. Although the structures of the perchlorates cited

Tableau 1. *Coordonnées atomiques, taux d'occupation, facteurs d'agitation thermique isotrope équivalents (Å²) avec écarts-type entre parenthèses*

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Site	$x = y = z$	Multiplicateur	U_{eq}
Site 8(a)(In)	0,125	0,5	0,017 (3)
Site 16(c)(Yb)	0	0,333	0,022 (1)
Site 16(d)(Yb)	0,5	1,0	0,0213 (4)
Site 16(d)(In)	0,5	0,833	0,0213 (4)
Site 32(e)(S)	0,2559 (7)	4,0	0,0215 (3)

Tableau 2. *Distances interatomiques exprimées (Å) avec écarts-type entre parenthèses*

Site 8(a)	In—S	2,465 (5)
Site 16(c)	Yb—S	2,784 (5)
Site 16(d)	Yb/In—S	2,656 (5)

La résolution de cette structure a été simplifiée par le fait que les atomes lourds ne peuvent occuper, de par leur nombre que les positions particulières du groupe. L'indium est seul susceptible d'occuper les sites tétraédriques [8(a)], les sites octaédriques [16(c) et 16(d)] peuvent accepter indifféremment l'ytterbium et l'indium. Les atomes de soufre remplissent le site 32(e). Les

above are broadly similar to that of the title salt, and although all three structures have been assigned in space group $P\bar{3}m1$, the perchlorates and the title salt are not isostructural. Location and isotropic refinement of the single type of H atom permitted detailed analysis of the hydrogen bonding. From the point of view of the water molecules, the hydrogen bonding is remarkably similar, even in quantitative detail, to that of the water molecules in $[\text{Co}(\text{H}_2\text{O})_6] \cdot (\text{BrO}_3)_2$.

Comment

In a previous study, the structure of $[\text{Ni}(\text{H}_2\text{O})_6] \cdot (\text{BrO}_4)_2$ at room temperature was assigned in space group $P\bar{3}$ (Gallucci, Gerkin & Reppart, 1990); the corresponding perchlorate structure and that of $[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ had been assigned in $Pmn2_1$ (West, 1935). These results stimulated further interest in the comparison of metal hexahydrate perchlorate and perbromate structures. Here the structure of $[\text{Co}(\text{H}_2\text{O})_6](\text{BrO}_4)_2$ is presented. The present structure, assigned in $P\bar{3}m1$, is similar to those of $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and $[\text{Cd}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, also assigned in $P\bar{3}m1$ (Johansson & Sandström, 1978, 1987), and to that of $[\text{Ni}(\text{H}_2\text{O})_6](\text{BrO}_4)_2$ cited above.

Final atomic coordinates and isotropic and equivalent isotropic displacement parameters and their e.s.d.'s are given in Table 1. Selected interatomic distances and angles in the coordination polyhedron about Co, in the perbromate ion and in the water molecule are given in Table 2, together with their e.s.d.'s. In the title salt the single type of Co coordination polyhedron has, by symmetry (the site symmetry at Co is $\bar{3}m$), a single Co—O(3) distance and is very nearly a regular octahedron, the nominal 90° angles differing by only $0.6(2)^\circ$ from that value. The observed Co—O(3) distance [$2.084(4) \text{ \AA}$] is in reasonably close agreement with the corresponding single Co—O distance reported for $[\text{Co}(\text{H}_2\text{O})_6](\text{BrO}_3)_2$ [$2.095(2) \text{ \AA}$]; Blackburn, Gallucci & Gerkin, 1990].

The site symmetry at Br is $3m$ and for the single type of perbromate ion two Br—O distances are allowed by symmetry, Br—O(1) [axial, observed value $1.600(6) \text{ \AA}$] and Br—O(2) [trigonal, observed value $1.609(3) \text{ \AA}$]; the corresponding values observed in the room-temperature $[\text{Ni}(\text{H}_2\text{O})_6](\text{BrO}_4)_2$ structure are Br—O(axial) $1.602(3)$ and Br—O(trigonal) $1.609(2) \text{ \AA}$ (Gallucci, Gerkin & Reppart, 1990). The observed O—Br—O perbromate-ion angles differ by only $\sim 0.2(1)^\circ$ from the value for a regular tetrahedron.

For the water molecule, the observed angle [$115(7)^\circ$] may be compared with the average water angle as determined by neutron diffraction for hydrates of class *J* (to which this water belongs)

Table 1. Fractional positional parameters and isotropic or equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{iso}} \text{ for H; for other atoms } B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	$B_{\text{iso}}/B_{\text{eq}}$
Co	0	0	0	1.98 (4)
Br	1/3	2/3	0.67783 (15)	2.01 (2)
O(1)	1/3	2/3	0.3953 (10)	3.5 (2)
O(2)	0.4442 (2)	0.8883	0.7737 (6)	3.8 (2)
O(3)	0.1251 (3)	-0.1251	0.2104 (7)	3.62 (5)
H	0.069 (7)	-0.247 (5)	0.210 (6)	7.3 (13)

Table 2. Selected bond distances (\AA) and angles ($^\circ$)

Co—O ₆ polyhedron			
Co—O(3)	2.084 (4)	O(3)—Co—O(3 ⁱ)	90.6 (2)
		O(3)—Co—O(3 ⁱⁱ)	180
		O(3)—Co—O(3 ⁱⁱⁱ)	89.4 (2)
Perbromate ion			
Br—O(1)	1.600 (6)	O(1)—Br—O(2)	109.7 (1)
Br—O(2)	1.609 (3)	O(2)—Br—O(2 ^v)	109.2 (1)
Water molecule			
O(3)—H	0.83 (4)	H—O(3)—H ^v	115 (7)
Symmetry code: (i) $-y, -y + x, z$; (ii) $-x, -y, -z$; (iii) $y, y - x, -z$; (iv) $-x + y, 1 - x, z$; (v) $-y, -x, z$.			

(106.9° ; Chiari & Ferraris, 1982; Ferraris & Franchini-Angela, 1972).

As illustrated in Fig. 1, this structure consists of stacks of face-sharing water-oxygen octahedra along the *z* direction, alternate ones of which are occupied centrally by a Co ion; each oxygen polyhedron stack is surrounded by six perbromate ion stacks which alternate in having their axial Br—O bonds all oriented in one (or the other) sense along the *z* direction ('up' or 'down'). {This arrangement has been discussed previously for $[\text{Ni}(\text{H}_2\text{O})_6](\text{BrO}_4)_2$ (Gallucci, Gerkin & Reppart, 1988).} Given this arrangement, two cases may arise which we arbitrarily designate as *A* and *B*: case *A* is characterized by the metal-ion *z* coordinate being the same as the mean *z* coordinate of the axial O atoms of the anion, while case *B* is characterized by the metal-ion *z* coordinate being the same as the mean *z* coordinate of the trigonal O atoms of the anion. As indicated in Table 4, $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and $[\text{Cd}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ exhibit case *A* behavior and $[\text{Ni}(\text{H}_2\text{O})_6](\text{BrO}_4)_2$ and $[\text{Co}(\text{H}_2\text{O})_6](\text{BrO}_4)_2$ case *B*.* It is noteworthy that in spite of the general similarities of the Hg, Cd and Co structures under discussion and their assignments in $P\bar{3}m1$, the Co structure is not isostructural with the other two.

The hydrogen bonds in the title salt form a richly developed three-dimensional network (Fig. 2 and Table 3). Each H atom participates in three hydrogen bonds: a strong bond to a trigonal perbromate O

* It should be noted that Fig. 1 of Johansson & Sandström (1987) is not drawn consistently with their atomic coordinates for 'ordered' perchlorate ions, but rather for 'disordered' (inverted) perchlorate ions. Otherwise, this is a very helpful figure.

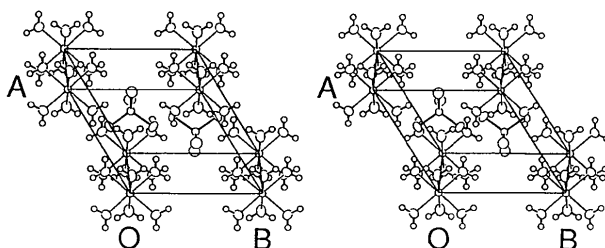


Fig. 1. Stereoview of a unit cell of the hexaaquacobalt(II) perbromate structure drawn using *ORTEP* (Johnson, 1976). Ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. Hydrogen bonds have been omitted for clarity.

atom, a bifurcated bond to an axial perbromate O atom in an adjacent perbromate stack and a weak bond to a water O atom in the same cation polyhedron. Each water O atom is involved in two weak hydrogen bonds with H atoms of two other water molecules in the same cation polyhedron. Each axial perbromate O atom is involved in three bifurcated hydrogen bonds containing H atoms from water molecules in three coordination complexes, while each trigonal perbromate O atom is involved in two strong hydrogen bonds with H atoms from water molecules in two coordination complexes. The

Table 3. *Hydrogen-bond parameters* (\AA , $^\circ$)

O(3)—H...O	O(3)...O	H—O	H—O*	O(3)—H...O
O(3)—H...O(2 ⁱ)	2.950 (3)	2.13 (4)	1.99	171 (4)
O(3)—H ⁱⁱⁱ ...O(2 ⁱⁱ)	2.950 (3)	2.13 (4)	1.99	171 (4)
O(3)—H...O(1 ^{iv})	3.032 (4)	2.71 (4)	2.68	105 (4)
O(3)—H ⁱⁱⁱ ...O(1 ^{iv})	3.032 (4)	2.71 (4)	2.68	105 (4)
O(3)—H...O(3 ^v)	2.933 (7)	2.82 (4)	2.83	89 (3)
O(3)—H ⁱⁱⁱ ...O(3 ^{vi})	2.933 (7)	2.82 (4)	2.83	89 (3)

Symmetry code: (i) $y - 1, y - x - 1, 1 - z$; (ii) $y - 1, x - 1, -z + 1$; (iii) $-y, -x, z$; (iv) $x, y - 1, z$; (v) $y, y - x, -z$; (vi) $x - y, x, -z$.

* Neutron-adjusted distance.

Table 4. *Geometrical parameters* (\AA , $^\circ$) of stacked water-oxygen octahedra in $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, $[\text{Cd}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, $[\text{Ni}(\text{H}_2\text{O})_6](\text{BrO}_4)_2$ and $[\text{Co}(\text{H}_2\text{O})_6](\text{BrO}_4)_2$

In each of these salts, the site symmetry at the metal is $\bar{3}$ or $\bar{3}m$; thus in each salt there is a single O(water)—M distance and the degree of distortion of the O_6 octahedra can be characterized by the departure of the appropriate O—M—O angles from 90° , the value for a regular octahedron. In the stacks of oxygen octahedra in each salt, alternate octahedra are unoccupied but their centers are also $\bar{3}$ or $\bar{3}m$ sites and the appropriate O—X—O angles (where X is a hypothetical central atom) can be used to characterize distortion of these unoccupied octahedra in the same manner as for the occupied octahedra.

	$[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2^a$	$[\text{Cd}(\text{H}_2\text{O})_6](\text{ClO}_4)_2^b$	$[\text{Ni}(\text{H}_2\text{O})_6](\text{BrO}_4)_2^c$	$[\text{Co}(\text{H}_2\text{O})_6](\text{BrO}_4)_2^d$
Occupied octahedra				
O—O	3.188 (6)	3.155 (1)	2.863 (3)	2.962 (7)
	3.430 (9)	3.285 (3)	2.939 (3)	2.933 (7)
Smallest $\angle \text{O—M—O}$	85.8 (2)	87.7 (1)	88.5 (1)	89.4 (2)
Height along z	2.898	2.733	2.431	2.383
Arrangement along z	A	A	B	B
Unoccupied octahedra				
O—O	3.188 (6)	3.155 (3)	2.863 (3)	2.962 (7)
	3.059 (9)	3.169 (4)	3.015 (4)	3.699 (8)
Smallest $\angle \text{O—M—O}$	87.7 (2)	89.7 (1)	85.1 (1)	77.4 (2)
Height along z	2.446	2.593	2.992	3.280

Notes: (a) Johansson & Sandström (1978); (b) Johansson & Sandström (1987); (c) Gallucci, Gerkin & Reppart (1990); (d) this paper.

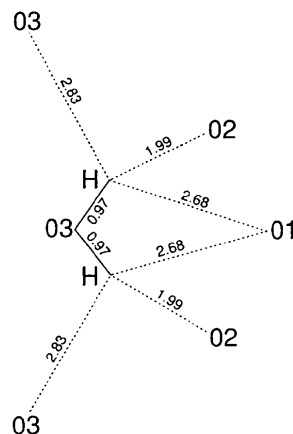


Fig. 2. Schematic drawing of the six hydrogen bonds (dashed lines) involving the H atoms of a given water molecule in the hexaaquacobalt(II) perbromate structure. This type of hydrogen bonding has been designated as three-center/bifurcated hydrogen bonding (Jeffrey & Maluszynska, 1986). Bond lengths are given in \AA and are neutron adjusted (see text).

hydrogen-bonding interactions of a single water molecule thus involve O atoms in three adjacent perbromate stacks.

From the point of view of the water molecules, there is a remarkable similarity between the hydrogen-bonding geometry in the present salt and in $[\text{Co}(\text{H}_2\text{O})_6](\text{BrO}_3)_2$, even when numerical details are considered, especially taking into account the fact that the O atoms involved as acceptors in the two cases are quite different. This type of interaction has been described as three-center/bifurcated hydrogen bonding (Jeffrey & Maluszynska, 1986). [The situation in the bromate salt is illustrated in Fig. 2 of Blackburn, Gallucci & Gerkin (1990).]

It is now possible to extend a conclusion reached previously (Gallucci, Gerkin & Reppart, 1988) when

comparing the Hg (perchlorate) and Ni (perbromate) structures: whereas in the Hg and Cd hexahydrated perchlorates the occupied O octahedra are more distorted than the unoccupied ones, the occupied O octahedra in the Ni and Co hexahydrated perbromates are less distorted than the unoccupied ones, the effect being most pronounced for the title salt (Table 4).

Experimental

Crystal data

[Co(H ₂ O) ₆](BrO ₄) ₂	Mo K α radiation
$M_r = 454.83$	$\lambda = 0.71073 \text{ \AA}$
Trigonal	Cell parameters from 25 reflections
$P\bar{3}m1$	$\theta = 12.5\text{--}15.0^\circ$
$a = 7.8906 (3) \text{ \AA}$	$\mu = 7.95 \text{ mm}^{-1}$
$c = 5.6628 (4) \text{ \AA}$	$T = 296 \text{ K}$
$V = 305.34 (3) \text{ \AA}^3$	Section of clear plate
$Z = 1$	$0.23 \times 0.19 \times 0.19 \text{ mm}$
$D_x = 2.473 \text{ Mg m}^{-3}$	Orange-red

Data collection

Rigaku AFC-5S diffractometer	264 observed reflections
ω - 2θ scans	$[I > 0.01\sigma(I)]$
Absorption correction:	$R_{\text{int}} = 0.032$
North, Phillips & Mathews (1968), six ψ scans averaged	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.774$, $T_{\text{max}} = 1.000$	$h = -10 \rightarrow 10$ (Parts I, II)
2798 measured reflections	$k = 0 \rightarrow 10$ (Part I)
290 independent reflections	$k = -10 \rightarrow -1$ (Part II)
	$l = -9 \rightarrow 9$ (Parts I, II)
	6 standard reflections monitored every 150 reflections
	intensity variation: $\pm 1.9\%$

Refinement

Refinement on F	$\Delta\rho_{\text{max}} = 0.91 \text{ e \AA}^{-3}$
Final $R = 0.036$	(0.38 \AA from Br)
$wR = 0.033$	$\Delta\rho_{\text{min}} = -0.77 \text{ e \AA}^{-3}$
$S = 1.33$	(0.06 \AA from Co)
264 reflections	Extinction correction:
26 parameters	Zachariasen (1963, 1968)
All H-atom parameters refined	Extinction coefficient:
$w = (2FLp)^2 / [\sigma_{\text{cs}}^2(I) + (0.03I)^2]$	$44 (8) \times 10^{-7}$
$(\Delta/\sigma)_{\text{max}} < 0.01$	Atomic scattering factors from Cromer & Waber (1974) (Co, Br, O), Stewart, Davidson & Simpson (1965) (H)

BaO was reacted with a slight excess of $\sim 0.7 \text{ M}$ HBrO₄ to form aqueous Ba(BrO₄)₂ which was then reacted with aqueous CoSO₄. The solid BaSO₄ was removed by filtration and the filtrate placed in a desiccator over concentrated H₂SO₄. The desiccator was kept at $\sim 283 \text{ K}$ for crystal growth because saturated solutions of [Co(H₂O)₆](BrO₄)₂ tend to decompose at room temperature; the crystals are sufficiently stable for diffraction studies at room temperature. The experimental sample was coated with Apiezon L grease to retard the loss or gain of water.

The unit-cell parameters were obtained from a symmetry-constrained least-squares fit. Reflection intensities were consistent with two non-centrosymmetric ($P321$, $P3m1$) and one centrosymmetric ($P\bar{3}m1$) space group. The centrosymmetric choice ($P\bar{3}m1$, No. 164) was given initial preference on the basis of intensity statistics, and since refinement proceeded well, it was adopted.

Scan widths were $(1.60 + 0.35\tan\theta)^\circ$ in ω and the ratio of background to scan time was 0.5. No corrections were made for decay but the data were corrected for Lorentz-polarization and absorption effects. The secondary extinction coefficient (Zachariasen, 1963, 1968) was least-squares refined; the largest effect was 6.7% of F_o for $\bar{1}11$.

The TEXSAN (Molecular Structure Corporation, 1989) structure analysis package provided a Patterson map from which the initial position of the Br atom was assigned. Difference Fourier methods were then used to locate the remaining atoms. The non-H atoms were refined anisotropically and the H atom isotropically using full-matrix least-squares techniques.

Neither the Co-O₆ polyhedron nor the perbromate ion conformed to rigid-body behavior when analyzed using THMA11 (Trueblood, 1986).

For analysis of the hydrogen bonding, the position of the isotropically refined H atom was adjusted along the direction of the O(3)—H bond (as determined from the X-ray data) until the O(3)—H distance became 0.973 \AA , which is the average O(water)—H bond length for waters of hydrate class *J* as determined by neutron diffraction (Chiari & Ferraris, 1982; Ferraris & Franchini-Angela, 1972). This hydrate-class assignment was made on the basis that the ray from Co to O(3) lies almost along an oxygen lone-pair orbital. The neutron-adjusted H—O(acceptor) distances are taken to be the hydrogen-bond lengths.

We acknowledge, with pleasure, the many contributions of Dr J. C. Gallucci to this research. We thank Dr Trueblood for providing a copy of the program THMA11. Partial support of the research through the purchase of the diffractometer system by an NIH grant is also gratefully acknowledged.

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55992 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1038]

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Acta Cryst. (1993). **C49**, 1275–1277

Structure du Monophosphate Synthétique de Cuivre et de Sodium

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Abstract

The structure of copper sodium monophosphate is built from two kinds of Cu atoms occupying the centres of symmetry of a dsp^2 square plane of O atoms, with two additional O atoms; these two Cu–O octahedra are linked by edge sharing to form chains parallel to the a axis. The PO_4 tetrahedra and Na–O polyhedra connect these Cu–O chains. The structure is another polymorph of α - $NaCuPO_4$. The former was synthesized at 2000 kg cm^{-2} ($\cong 2 \times 10^5 \text{ kPa}$ pressure) and 773 K, resulting in a structure of high density ($d_x = 3.96 \text{ Mg m}^{-3}$), while the latter corresponds to the structure synthesized with low-pressure conditions ($d_x = 3.61 \text{ Mg m}^{-3}$, 10^2 kPa , 1023 K); this may explain the fact that the PO_4 tetrahedra of the former are more distorted than those of the latter.

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Commentaire

Cette étude a été commencée dans le cadre de la systématization des structures des monophosphates alcalins de cuivre. Kolsi, Quarton & Freundlich (1981) ont décrit les résultats des études par les rayons X d'une série des composés de $NaBPO_4$ ($B = \text{Cu, Pb, Ba}$). Quarton & Oumba (1983) ont aussi montré les données cristallographiques de $NaCuPO_4\text{-}\alpha$ et $AgCuPO_4\text{-}\beta$. Au cours de la synthèse des composés des phosphates, les auteurs présents ont réussi à obtenir une série de composés nouveaux au moyen de la synthèse hydrothermale. L'article présent donne le résultat de la détermination de la structure cristalline de l'une de ces phases nouvelles.

Le composé est obtenu après le chauffage à 773 K et sous une pression d'eau de 2000 kg cm^{-2} pendant trois jours avec le mélange stœchiométrique de $CuSO_4 \cdot 5H_2O$ et de $Na_3PO_4 \cdot 12H_2O$. Les mélanges ont été pressés dans les tubes en argent avec de l'eau distillée. Les tubes ont tous un diamètre de 3 mm. Le four a été refroidi après le traitement hydrothermal avec une vitesse d'1 K par 30 min. Les cristaux obtenus ont été lavés avec de l'eau pure. La composition chimique a été déterminée comme $NaCuPO_4$ à l'aide de la microsonde électronique de JEOL JXA. Les clichés de Weissenberg de cette phase ont montré que les données cristallographiques ne correspondaient pas à ceux des phases connues jusqu'à présent. Il est alors considéré comme s'agissant d'un autre polymorphe de $NaCuPO_4\text{-}\alpha$ décrit par Quarton & Kolsi (1983). Nous donnons à ce composé le nom de $NaCuPO_4\text{-}\beta$.

La densité calculée de ce composé est $3,96 \text{ Mg m}^{-3}$, tandis que celle de la phase- α est $3,61 \text{ Mg m}^{-3}$ reflétant la condition de la synthèse à haute pression de la phase- β . L'image stéréographique est donnée dans la Fig. 1. Deux atomes de cuivre se trouvent aux centres de l'inversion, en prenant la configuration anionique de l'orbitale hybride de dsp^2 , ajoutée par deux atomes d'oxygène, dont les distances du cuivre sont plus longues. Les deux octaédres de cuivre-oxygène sont liés les uns aux autres en mettant en commun leurs arêtes pour former les chaînes suivant l'axe a . Ces chaînes sont liées par les tétraédres de PO_4 et les polyèdres de NaO_8 . La Fig. 2 ne montre qu'une partie de la différence structurale entre la phase- α et β . La situation structurale de PO_4 autour des axes hélicoïdaux est presque la même entre les deux composés, mais ces tétraédres sont retournés par des atomes de cuivre situés aux centres d'inversion dans le cas de a phase- β (en haut), tandis que dans la phase- α , ces tétraédres sont arrangés par l'intervention des polyèdres de sodium autour des axes hélicoïdaux binaire (en bas).

Les distances moyennes de quatre Cu–O de deux carrés sont 1,935 et 1,982 Å, tandis que dans le cas