

Discussion. Atomic coordinates of non-H atoms are in Table 1.* The atomic arrangement around Y is shown in Fig. 1. The atomic distances and angles are listed in Table 2.

The Y atom has nine oxygen neighbours, six from three bidentate nitrate groups and three from water molecules. The coordination polyhedron around Y can be described as a distorted pentagonal pyramid with three additional atoms from the other side of the base of the pyramid. The basal plane of the pyramid is defined by O11, O12, OW2, O31 and OW3. The distances of the atoms from the least-squares basal plane are 0.158 (3), 0.195 (3), 0.163 (4), 0.076 (3) and 0.034 (3) Å respectively. The apex of the pyramid is occupied by OW1 at a distance of 1.922 (4) Å from the basal plane. Y is displaced out of the basal plane by 0.404 (1) Å. Three additional atoms from the other side of the base are O21, O22 and O32 at distances of 2.461 (3), 2.393 (3) and 2.006 (3) Å from the basal

plane. All Y—O(water) distances [ave. 2.325 (4) Å] are shorter than Y—O(nitrate) distances [ave. 2.432 (4) Å]. In each nitrate group the non-coordinated O atom is closer to N than the other two, and the metal-bound O—N—O angles are significantly smaller than the other O—N—O angles, which is a common property of all bidentate nitrate groups. The Y atom lies in the plane of each nitrate group [max. dev. 0.028 (1) Å]. Dihedral angles formed by (NO₃)1 and (NO₃)2, (NO₃)1 and (NO₃)3, (NO₃)2 and (NO₃)3 are 73.4 (2), 82.4 (2) and 81.7 (2)° respectively. Water oxygen distances from the O atoms of neighbouring coordination polyhedra listed in Table 3 indicate possible hydrogen bonds which hold the coordination polyhedra in a three-dimensional network (Fig. 2.).

This study was sponsored by the Research Foundation of the Socialist Autonomous Province Vojvodina (Yugoslavia).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44588 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Enraf-Nonius (1983). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
 RADIVOJEVIĆ, P., MILINSKI, N., RIBÁR, B. & LAZAR, D. (1984). *Croat. Chem. Acta*, **57**, 451–455.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1988). **C44**, 597–599

Structure of a Copper(III) Periodate Complex

BY VOLRATH ADELSKÖLD, LARS ERIKSSON, PEI-LING WANG* AND PER-ERIK WERNER

Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

(Received 16 June 1986; accepted 12 November 1987)

Abstract. Tetrasodium potassium bis(periodato)cuprate dodecahydrate, $\text{KNa}_4[\text{Cu}(\text{HIO}_6)_2] \cdot 12\text{H}_2\text{O}$, $M_r = 858.60$, monoclinic, $P2_1/c$, $a = 6.119$ (3), $b = 25.118$ (8), $c = 14.741$ (5) Å, $\beta = 97.87$ (4)°, $V = 2244.15$ Å³, $D_x = 2.560$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 38.37$ cm⁻¹, $F(000) = 1664$, $Z = 4$, room temperature, $R = 0.068$ for 2991 independent reflections. The complex anion consists of two IO₅(OH) octahedra, each sharing an edge with a square-planar coordination around a Cu atom so as to form a planar O₂—I—O₂—Cu—O₂—I—O₂ network. The octahedra around the I atoms are distorted, and hydrogen bonds between anions are formed by the hydroxy groups located perpendicular to the network. Water

molecules are situated axial to the square-planar-coordinated copper at 2.708 (10) and 3.576 (10) Å.

Introduction. Copper(III) (d^8) complexes of general formula $M_x\text{H}_{7-x}[\text{Cu}(\text{IO}_6)_2] \cdot n\text{H}_2\text{O}$ ($M = \text{K}, \text{Na}$) were first reported by Malaprade (1937). Malatesta (1941*a,b*) prepared a number of crystallizable compounds of this type by complexing copper with periodic acid, and it was evident that these compounds were much more stable than the trivalent copper compounds obtained previously. From chemical analysis, IR spectra and conductimetric measurements Balikungeri, Pelletier & Monnier (1977) showed that the anion of bis(periodato)cuprate(III) is $[\text{Cu}(\text{HIO}_6)_2]^{5-}$. The trivalent state of Cu was confirmed from magnetic measurements by Malatesta (1941*a*), and the diamagnetic character has also been confirmed by the present

* On leave from Shanghai Institute of Ceramics, Academia Sinica, 865 Chang-Ning Road, Shanghai, China.

authors. The discovery by Bednorz & Müller (1986) of a new class of copper-containing ceramics which exhibit superconductivity to temperatures as high as

Table 1. Positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 100$) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{Cu}
I(1)	5664 (1)	603 (0)	2856 (1)	1.03 (2)
I(2)	4171 (2)	2594 (0)	4699 (1)	1.24 (3)
Cu	4810 (3)	1602 (1)	3786 (1)	1.36 (5)
K	7322 (6)	2389 (1)	2110 (2)	3.1 (1)
Na(1)	1982 (10)	1560 (2)	1596 (4)	2.3 (2)
Na(2)	9462 (9)	688 (2)	9702 (4)	2.6 (2)
Na(3)	9878 (9)	1295 (2)	7096 (4)	2.5 (2)
Na(4)	8738 (10)	613 (2)	4988 (3)	2.7 (2)
O(1)	6011 (15)	551 (3)	1637 (6)	1.5 (3)
O(2)	5231 (16)	-65 (3)	3141 (7)	2.2 (4)
O(3)	4852 (16)	876 (3)	4030 (6)	1.6 (3)
O(4)	5567 (15)	1406 (3)	2677 (5)	1.4 (3)
O(5)	8589 (16)	647 (4)	3320 (6)	2.3 (4)
O(6)	2461 (15)	675 (4)	2379 (6)	1.6 (3)
O(7)	5057 (17)	2308 (3)	3570 (6)	2.0 (3)
O(8)	4002 (15)	1829 (3)	4882 (6)	1.7 (3)
O(9)	3702 (16)	2727 (3)	5868 (6)	1.8 (3)
O(10)	4883 (16)	3265 (3)	4373 (6)	2.0 (3)
O(11)	7379 (16)	2491 (3)	5223 (6)	2.0 (4)
O(12)	1260 (17)	2615 (4)	4192 (6)	2.4 (4)
On(1)	527 (17)	1721 (4)	3061 (6)	2.6 (4)
On(2)	2974 (17)	972 (3)	327 (6)	2.2 (4)
On(3)	8369 (16)	1378 (4)	900 (6)	2.4 (4)
On(4)	5819 (18)	4616 (4)	4223 (7)	3.6 (4)
On(5)	8928 (17)	422 (4)	6612 (7)	2.7 (4)
On(6)	1387 (17)	2806 (4)	2084 (7)	3.0 (4)
On(7)	8983 (18)	3532 (4)	3642 (6)	3.0 (4)
On(8)	2434 (18)	311 (4)	5183 (6)	3.0 (4)
On(9)	3489 (20)	1033 (4)	7667 (7)	4.4 (5)
On(10)	6212 (18)	3413 (5)	1631 (7)	4.0 (4)
On(11)	9822 (16)	1492 (4)	5337 (7)	3.1 (3)
On(12)	9666 (16)	70 (3)	1083 (6)	2.4 (4)

92 K has caused a renewed interest in Cu—O coordinations.

Although a number of diamagnetic copper(III) complexes with the general formula given above have been reported, no complete structure determination has been pursued. In a short communication by Linek, Syneček, Jenšovský & Hadinec (1963), the space group and unit-cell dimensions for the compound Na₃-KH₃[Cu(IO₆)₂].14H₂O were given. They briefly described the copper coordination but no coordinates were given. As the unit-cell dimensions within error limits are the same as those found in the present study, however, it can be concluded that the correct stoichiometry and formula of the compound is KNa₄[Cu(HIO₆)₂].12H₂O.

Experimental. Dark-brown crystals were obtained according to the procedure described by Balikungeri *et al.* (1977). Crystal selected for data collection 0.05 × 0.02 × 0.015 mm. Systematic absences $h0l$: l odd and $0k0$: k odd indicated space group $P2_1/c$; unit cell: least-squares refinement of θ values of 15 selected reflections. Siemens Stoe/AED2 diffractometer, graphite monochromator, Mo $K\alpha$ radiation; intensity measurements up to $2\theta = 50^\circ$, $\theta-2\theta$ scan technique, scan speed $0.02^\circ \text{ s}^{-1}(2\theta)$; 4060 reflections measured, 2991 intensities with $|F_o| \geq 3\sigma(|F_o|)$ considered as observed and used for the structure determination; corrections for Lorentz and polarization, but absorption ignored. Patterson and $\Delta\rho$ methods, refinement by full-matrix least squares on F . H positions from $\Delta\rho$ maps but not refined. Hydrogen isotropic

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) (with e.s.d.'s in parentheses)

Cu—O(3)	1.858 (8)	On(1)—Cu—O(3)	99.8 (4)
Cu—O(4)	1.827 (8)	On(1)—Cu—O(4)	91.5 (4)
Cu—O(7)	1.811 (8)	On(1)—Cu—O(7)	85.6 (4)
Cu—O(8)	1.843 (9)	On(1)—Cu—O(8)	87.2 (4)
Cu—On(11)	2.708 (10)	On(11)—Cu—O(3)	79.2 (4)
Cu—On(11)	3.576 (10)	On(11)—Cu—O(4)	104.5 (4)
		On(11)—Cu—O(7)	96.0 (4)
O(3)—Cu—O(4)	84.8 (4)	On(11)—Cu—O(8)	76.9 (4)
O(4)—Cu—O(7)	94.0 (4)	O(3)—Cu—O(7)	174.5 (5)
O(7)—Cu—O(8)	83.7 (4)	O(4)—Cu—O(8)	177.5 (4)
O(8)—Cu—O(3)	97.6 (4)	On(1)—Cu—On(11)	163.7 (3)
I(1)—O(1)	1.850 (8)	O(5)—I(1)—O(1)	97.4 (4)
I(1)—O(2)	1.832 (8)	O(5)—I(1)—O(2)	95.6 (4)
I(1)—O(3)	1.962 (8)	O(5)—I(1)—O(3)	91.0 (4)
I(1)—O(4)	1.958 (8)	O(5)—I(1)—O(4)	92.4 (4)
I(1)—O(5)	1.826 (10)	O(6)—I(1)—O(1)	84.3 (4)
I(1)—O(6)	1.993 (9)	O(6)—I(1)—O(2)	88.0 (4)
		O(6)—I(1)—O(3)	86.5 (4)
O(1)—I(1)—O(2)	98.9 (4)	O(6)—I(1)—O(4)	83.7 (4)
O(2)—I(1)—O(3)	91.9 (4)	O(11)—I(1)—O(3)	165.6 (4)
O(3)—I(1)—O(4)	78.7 (4)	O(2)—I(1)—O(4)	167.8 (4)
O(4)—I(1)—O(1)	89.2 (4)	O(5)—I(1)—O(6)	175.7 (4)
I(2)—O(7)	1.956 (8)	O(11)—I(2)—O(7)	84.8 (4)
I(2)—O(8)	1.944 (8)	O(11)—I(2)—O(8)	83.6 (4)
I(2)—O(9)	1.816 (9)	O(11)—I(2)—O(9)	86.1 (4)
I(2)—O(10)	1.821 (8)	O(11)—I(2)—O(10)	88.0 (4)
I(2)—O(11)	2.025 (10)	O(12)—I(2)—O(7)	91.8 (4)
I(2)—O(12)	1.835 (10)	O(12)—I(2)—O(8)	91.0 (4)
		O(12)—I(2)—O(9)	96.3 (4)
O(7)—I(2)—O(8)	77.4 (4)	O(12)—I(2)—O(10)	96.9 (4)
O(8)—I(2)—O(9)	91.8 (4)	O(7)—I(2)—O(9)	166.7 (4)
O(9)—I(2)—O(10)	98.9 (4)	O(8)—I(2)—O(10)	165.9 (4)
O(10)—I(2)—O(7)	90.6 (4)	O(11)—I(2)—O(12)	174.1 (4)

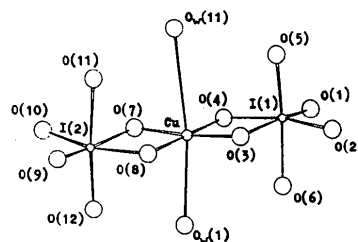


Fig. 1. The Cu^{III} complex anion network in the title molecule.

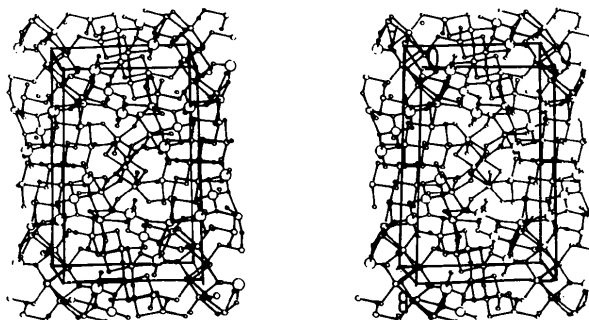


Fig. 2. A stereoview of the crystal structure. The circles denote, in decreasing size, I, Cu, K, Na and O.

temperature factors (0.020–0.042 Å²) equal to those of their parent atoms. Anisotropic temperature factors assigned to all non-H atoms in final cycles of refinement. Final $R = 0.068$ and $wR = 0.050$ using 2991 'observed' reflections for 289 refined parameters. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/\sigma^2(F_o)$ where $\sigma^2(F_o) = \sigma_c^2 + 0.000054 |F_o|^2$ with σ_c from counting statistics. $(\Delta/\sigma)_{\max} = 0.01$. A final difference map showed residual fluctuations of -1.7 to $1.6 \text{ e } \text{Å}^{-3}$ (especially close to the I atoms). Scattering factors from *International Tables for X-ray Crystallography* (1974). *SHELX* (Sheldrick, 1976) used for structure determination and refinement, *PLUTO* (Motherwell & Clegg, 1976) for figures.

Discussion. Final atom parameters are listed in Table 1, distances and angles in Table 2.* The structure is built up from $[\text{Cu}(\text{HIO}_6)_2]^{5-}$, K^+ , Na^+ and crystal water. Two distorted $\text{IO}_5(\text{OH})$ octahedra are joined to a central CuO_4 square by edge sharing (see Fig. 1), forming a planar $\text{O}_2\text{—I—O}_2\text{—Cu—O}_2\text{—I—O}_2$ network. According to Hathaway & Hodgson (1973) a normal short Cu—O distance is about 2.00 Å but Cu—O distances of 1.90 Å are frequent in square-coplanar Cu complexes. In the present structure containing trivalent copper the average Cu—O distance is as short as 1.84 (2) Å. Inspection of the difference map indicated that the anion contains hydrogen bonds to O(5) and O(11) although the I(1)—O(5) bond, 1.826 (10) Å, is significantly shorter than the I(1)—O(6) bond, 1.993 (9) Å, in the opposite direction. Chains of anions

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a list of interatomic distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44529 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1988). C44, 599–601

Refinement of the Crystal Structure of $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$

BY Y. ELERMAN

Department of Physical Engineering, Faculty of Science, University of Ankara, Beseyler-Ankara, Turkey

(Received 17 October 1984; accepted 10 December 1987)

Abstract. Cobalt(II) sulfate hexahydrate, $M_r = 263.08$, monoclinic, $C2/c$, $Z = 8$, $a = 10.022$ (3), $b = 7.217$ (2), $c = 24.224$ (3) Å, $\beta = 98.42$ (2)°, $V = 1733.2$ Å³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $D_x = 2.02 \text{ Mg m}^{-3}$, $\mu(\text{Mo } K\alpha) = 2.3 \text{ mm}^{-1}$, 629 independent single-crystal diffractometer data up to $(\sin\theta)/\lambda = 0.55 \text{ Å}^{-1}$, $F(000) = 1080$, $T = 297$ (1) K, $R = 0.032$,

0108-2701/88/040599-03\$03.00

are linked together by hydrogen bonds O(5)—H...O(6) and O(11)—H...O(12) in the direction of the a axis. The position of the H in the O(5)...O(6) bond may be considered, however, as somewhat uncertain from the above discussion. All 26 H atoms are involved in hydrogen bonding. The observed H-atom positions confirm this conclusion although in some cases alternative hydrogen bonds may be proposed. Furthermore, all 12 crystal waters and seven of the 12 oxygen atoms in the anion are coordinated to alkali ions. The four Na^+ ions are coordinated by six oxygens, and the K^+ ion is coordinated by seven oxygens. The crystal packing, as viewed down a , is shown in Fig. 2.

The stability, shape, hydrogen-bonding capability and charge of the $[\text{Cu}(\text{HIO}_6)_2]^{5-}$ ion make it potentially useful for preparation of heavy-atom derivatives of protein structures.

This work has been financially supported by the Swedish Natural Science Research Council (NFR).

References

- BALIKUNGERI, A., PELLETIER, M. & MONNIER, D. (1977). *Inorg. Chim. Acta*, **22**, 7–14.
 BEDNORZ, J. G. & MÜLLER, K. A. (1986). *Z. Phys. B*, **53**, 189–193.
 HATHAWAY, B. J. & HODGSON, P. G. (1973). *J. Inorg. Nucl. Chem.* **35**, 4071–4081.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 LÍNEK, A., SYNEČEK, V., JENŠOVSKÝ, L. & HADINEC, I. (1963). *Acta Cryst.* **16**, A35.
 MALAPRADE, L. (1937). *C. R. Acad. Sci.* **204**, 979–980.
 MALATESTA, L. (1941a). *Gazz. Chim. Ital.*, **71**, 467–474.
 MALATESTA, L. (1941b). *Gazz. Chim. Ital.* **71**, 580–584.
 MOTHERWELL, W. D. S. & CLEGG, W. (1976). *PLUTO*. Program for plotting crystal and molecular structures. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

$wR = 0.028$. The structure consists of alternate layers of $\text{Co}(\text{H}_2\text{O})_6$ octahedra and SO_4 tetrahedra. Each water molecule is a donor for two hydrogen bonds with O...O distances between 2.663 (4) and 2.984 Å.

Introduction. The crystal structure of $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ has been solved by Zalkin, Ruben & Templeton (1962).

© 1988 International Union of Crystallography