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A Copper (III) Periodate Peroxo Complex: $K_4H_4Cu(IO_6)_2O_2 \cdot 6H_2O$

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The chemical preparation and crystal structure of the trivalent copper salt $K_4H_4Cu(IO_6)_2O_2 \cdot 6H_2O$ are described. Crystals are monoclinic (space group $P2_1/n$; $a = 12.650(2)$, $b = 9.780(2)$, $c = 7.710(2)$ Å, $\beta = 95.2°(1)$, $Z = 2$). The structure is refined until $R = 0.038$ for 2223 reflections. Isolated $Cu(IO_6)_2^{7-}$ units and O_2^- superoxide groups occur. In the $Cu(IO_6)_2^{7-}$ unit, the trivalent copper ion is surrounded by four oxygen atoms in a rectangular configuration.

Introduction

The difficulty of obtaining and stabilizing the copper (III) oxidation state explains the lack of structural information on this subject in the literature.

Copper (III) fluorides K_3CuF_6 and Cs_2KCuF_6 were prepared by Klemm and Huss (*1*) and their structural data based on X-ray powder diffractograms (*2*). Only the octahedral geometry of the CuF_6^{3-} ion could be stated but no accurate Cu–F distances were calculated. A recent investigation of the structural and physical properties of the lithium copper (III) oxide, Li_3CuO_3 (*3*), reveals a square planar oxygen coordination of Cu^{3+}. The chemical reactions involving the formation of the alkali copper (III) periodate and tellurate complexes are described in Gmelin (*4*). The alkali solutions of copper (III) periodate were handled for the first time by Malaprade (*5*) and Malatesta (*6*) and crystals were likely obtained from these solutions. Ralek and Jensovsky (*7*) have prepared potassium copper (III) periodate solutions using chemical or anodic oxidations. An attempt at structural determination of a sodium potassium copper (III) periodate salt was undertaken by Hadinec *et al.* (*8*), but no accurate crystallographic data were published.

Using the chemical approach of Malaprade (*5*) we have succeeded in the preparation of a potassium copper periodate salt $K_4H_4Cu(IO_6)_2O_2 \cdot 6H_2O$ and investigated its crystal structure.

Chemical Preparation

A direct oxidation of $CuSO_4$ by potassium persulfate, $K_2S_2O_8$, in KIO_4/KOH solutions provides potassium copper (III) periodate solutions with a red-brown color. One hundred milliliters of $CuSO_4$ solution (0.1 *M*) is added to 200 ml of KIO_4 (1 *M*)/KOH (5 *M*) solution. The precipitated mixture ($Cu(OH)_2 \cdot KOH \cdot H_2O$) contains Cu^{2+} ions. The solution and precipitate are reacted by the addition of a large excess of $K_2S_2O_8$ (10 to 20 g) at 50°C. The solution be-

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comes red brown. A filtration removes the excess of precipitate. The explanation of the previous chemical reactions may be the following: there is formation of IO_6^{5-} or $(IO_5OH)^{4-}$ anions in KIO_4/KOH solution. First Cu^{2+} is oxidized to Cu^{3+},

$$S_2O_8^{2-} + 2Cu^{2+} \rightarrow 2Cu^{3+} + 2SO_4^{2-},$$

then IO_6^{5-} anions chelate the Cu^{3+} with the formation of $Cu(IO_6)_2^{7-}$ complex. Crystals of K_2SO_4 are removed from solution by repeated crystallizations in ice. The final solution is concentrated in a dessicator above KOH. Repeated crystallizations from fresh solutions do not produce crystals of good quality for an X-ray study. After aging solutions, red-brown crystals of prismatic habit are separated. Their composition $K_4H_4Cu(IO_6)_2O_2 \cdot 6H_2O$ is based on the results of the crystal structure analysis. The solutions of this complex are stable with pH 10 to 14. Crystals decompose slowly in air and instantaneously with contact of weak reducing agents but they are stable in closed glass tubes under argon.

Crystal Structure

A crystal of irregular prismatic shape and approximate dimensions: 0.24 × 0.24 × 0.24 mm^3 was sealed with some of its saturated solution in a glass capillary.

(*a*) *Crystal data.* According to the diffractometer data, the cell parameters are refined using 20 collected θ reflections ($10° < \theta < 13°$, Ag*K*α radiation). The crystal is monoclinic, $P2_1/n$, $Z = 2$, $a = 12.650(2)$, $b = 9.780(2)$, $c = 7.710(2)$ Å, $\beta = 95.2°(1)$, $d_x = 2.83$ g/cm^3.

(*b*) *Structure determination.* Independent reflections (3057) were collected in ω mode with a Philips PW 1100 automatic four circle diffractometer using Ag*K*α radiation (0.56087 Å). The θ range was 3–30°, the scan width 1.40°, and the scan speed 0.03°/sec. The reference reflections were 163 and $\overline{1}6\overline{3}$. The background was measured for 10 sec at the starting and final position of each scan. No absorption correction was made (μAg*K*α = 27.9 cm^{-1}). The crystal structure was solved and refined using the program system SDP (version RSX 11M, 1977, Enraf–Nonius). A three-dimensional Patterson function revealed the atomic positions of I and Cu. Successive difference Fourier synthesis showed all the oxygen and potassium atomic positions. The unweighted final value $R = 0.039$ was reached with 2223 reflections satisfying the condition: $F_o^2 > 8\sigma F_o^2$, σF_o^2 = counting statistics. For the 3057 observed reflections the reliability factor is $R = 0.045$. The residual difference Fourier peaks are less than 1.4 e $Å^{-3}$ with 3 e $Å^{-3}$ around the second site of potassium K2. Table I contains all the positional and thermal parameters and Table II the interatomic distances and angles. A list of observed and calculated structure factors will be sent on request to the authors.

(*c*) *Structure description.* The crystal structure represented in Fig. 1 is a projection along the [010] direction. The framework is built with $Cu(IO_6)_2^{7-} \cdot O_2^-$ anions and water molecules: potassium atoms alternate between $Cu(IO_6)_2^{7-}$ anions. The interest of this X-ray structural determination is to show without ambiguity the conformation of the $Cu(IO_6)_2^{7-}$ anion. IO_6 octahedra chelate the copper (III) ion in a rectangular oxygen atom configuration which may be considered to be a distortion of an ideal square planar configuration described by a hybrid valence bond of dsp^2 type. The $Cu(IO_6)_2^{7-}$ anion has the same conformation as the $Ag(IO_6H)_2^{5-}$ anion, found in the $K_5Ag(IO_6H)_2 \cdot 8H_2O$ salt (*9*).

Unfortunately, the present structure analysis does not yield a direct localization of the hydrogen atoms: their positions would be useful in completing the understanding of the structure. The two oxygen atoms in the independent O_2 units are separated by 1.214(8) Å. This distance is near to $d_{O-O} = 1.207$ Å in O_2 molecule (*10*). The

TABLE I

ATOMIC, ISOTROPIC,[a] AND ANISOTROPIC[b] THERMAL PARAMETERS OF $K_4H_4Cu(IO_6)_2O_2 \cdot 6H_2O$

Atom	x	y	z	B_{iso} (Å^2)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	0.01689(3)	0.26716(4)	0.14655(6)	1.343(5)	0.00235(1)	0.00297(2)	0.00596(4)	0.00003(6)	0.00079(4)	−0.00060(9)
Cu	0.000	0.000	0.000	1.57(2)	0.00240(6)	0.00321(0)	0.0081(2)	0.0003(1)	−0.0003(2)	−0.0009(2)
O1	0.9755(5)	0.1922(6)	0.3477(8)	3.1(1)	0.0064(4)	0.0089(6)	0.0091(8)	0.003(1)	0.0066(9)	0.006(1)
O2	0.9190(4)	0.4039(5)	0.1429(7)	2.10(9)	0.0033(3)	0.0036(4)	0.0120(9)	0.0014(6)	0.0021(8)	−0.001(1)
O3	0.1036(4)	0.1091(5)	0.1054(7)	1.78(8)	0.0025(2)	0.0032(4)	0.0104(8)	0.0004(5)	−0.0013(8)	−0.0015(9)
O4	0.4177(4)	0.3491(5)	0.5083(7)	1.95(9)	0.0022(2)	0.0037(4)	0.0123(9)	−0.0004(5)	−0.0019(8)	0.003(1)
O5	0.1305(5)	0.3573(6)	0.2513(8)	3.1(1)	0.0039(3)	0.0077(6)	0.016(1)	−0.0017(8)	−0.003(1)	−0.009(1)
O6	0.5592(5)	0.1702(6)	0.4201(7)	2.6(1)	0.0063(4)	0.0047(5)	0.0092(8)	−0.0004(7)	0.0081(8)	−0.001(1)
O	0.4964(4)	0.0497(6)	0.0463(6)	3.07(9)	0.0012(2)	0.0137(6)	0.0131(7)	−0.0033(6)	−0.0023(6)	0.0263(8)
OW1	0.6168(6)	0.4421(8)	0.096(1)	4.1(2)	0.0057(4)	0.0109(8)	0.018(1)	0.004(1)	−0.006(1)	−0.002(2)
OW2	0.7153(5)	0.0984(7)	0.0775(9)	3.2(1)	0.0042(4)	0.0103(7)	0.013(1)	−0.0011(9)	0.002(1)	0.001(2)
OW3	0.376(1)	0.233(2)	0.146(1)	17.1(4)	0.044(2)	0.035(2)	0.031(2)	−0.051(3)	−0.059(2)	0.032(4)
K1	0.7451(1)	0.3083(2)	0.3401(2)	2.64(3)	0.00370(9)	0.0088(2)	0.0093(2)	−0.0010(2)	0.0006(3)	−0.0004(4)
K2	0.2694(2)	0.0823(4)	0.3564(3)	7.76(7)	0.0081(2)	0.0390(6)	0.0125(4)	0.0234(4)	−0.0055(4)	−0.0145(8)

Note. Standard deviations are given in parentheses.

[a] $B_{iso} = \frac{4}{3} \Sigma_i \Sigma_j \beta_{ij} a_i \cdot a_j$.

[b] $T = \exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})$.

O–O bond lengths found in hydrogen peroxide (1.47 Å) and peroxo organic and inorganic salts (1.33 to 1.55 Å) are quite different (*11*). In this ionic structure, the existence of O_2 isolated molecules is difficult to imagine. In addition, the origin of O_2 units is the primitive solution containing peroxo groups, O_2^{2-} and O_2^-, coming from

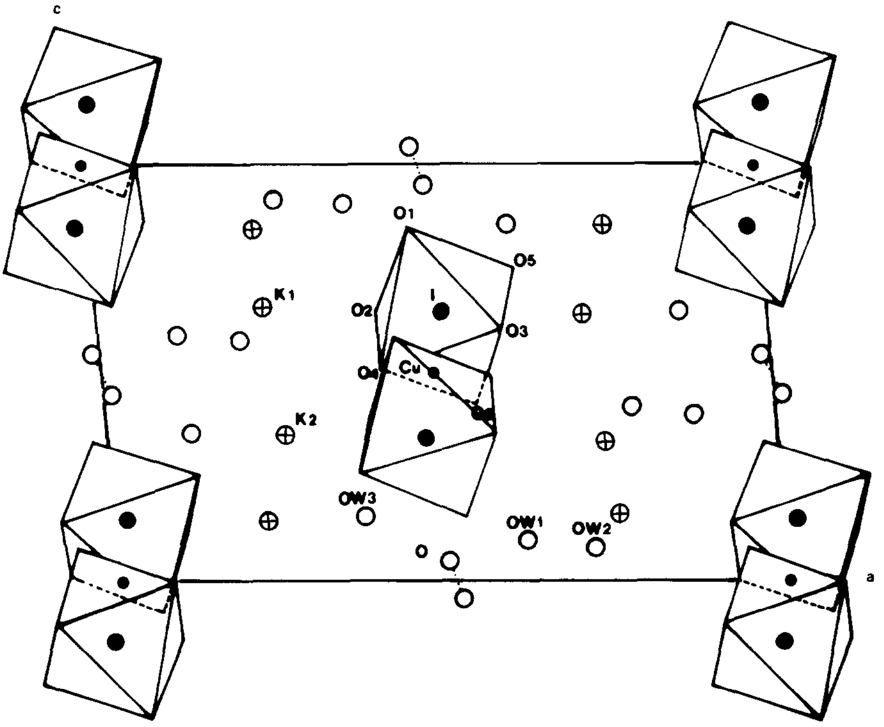

FIG. 1. The (a,c) projection of the $K_4H_4Cu(IO_6)_2O_2 \cdot 6H_2O$ structure.

TABLE II

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN $K_4H_4Cu(IO_6)_2O_2 \cdot 6H_2O$

Cu–O3	1.823(3) (×2)		
Cu–O4	1.811(3) (×2)		
O3–Cu–O4	84.2(1) (×2)		
O3–Cu–O4	95.8(1) (×2)		
I–O1	1.834(4)		
I–O2	1.822(3)		
I–O3	1.938(3)		
I–O4	1.939(3)		
I–O5	1.812(4)		
I–O6	1.970(3)		
O1–I–O2	93.4(2)	O2–I–O6	89.9(2)
O1–I–O3	91.6(2)	O3–I–O4	77.9(1)
O1–I–O4	90.6(2)	O3–I–O5	91.3(2)
O1–I–O5	95.3(2)	O3–I–O6	84.2(1)
O1–I–O6	174.4(2)	O4–I–O5	167.8(2)
O2–I–O3	167.8(1)	O4–I–O6	84.8(2)
O2–I–O4	91.0(9)	O5–I–O6	88.6(2)
O2–I–O5	99.3(2)		
K1–O1	3.124(4)	K2–O2	2.778(4)
K1–O2	2.937(4)	K2–O3	2.734(3)
K1–O3	2.950(4)	K2–O5	2.707(5)
K1–O6	2.828(4)	K2–O5	3.274(5)
K1–OW1	2.706(4)	K2–OW1	2.803(6)
K1–OW2	2.884(5)	K2–OW3	2.648(10)
K1–OW2	2.940(5)		
K1–OW3	2.780(6)		
O–O	1.214(8)	O–OW2	2.799(5)
O–O1	2.952(5)	O–OW3	2.52(2)
O–O2	2.907(5)	O–O5	3.000(5)

the decomposition of $K_2S_2O_8$. The value of O–O bond in O_2 units involves the existence of O_2^- superoxide ions. The O–O bond length for O_2^- in the superoxide αKO_2 is 1.28(2) Å (*12*).

Remark on the chemical formula. Three different formulas may be written after the localization of Cu, I, O, and K atoms in the unit cell with respect to the electroneutrality.

$$K_4H_3Cu(IO_6)_2 \cdot O_2 \cdot 6H_2O \text{ (I)}$$

$$K_4H_4Cu(IO_6)_2O_2 \cdot 6H_2O \text{ (II)}$$

$$K_4H_3Cu(IO_6)_2 \cdot H_2O_2 \cdot 6H_2O \text{ (III)}$$

The cell contains two formula units. Formulas (I) and (III) involve a hydrogen atom in a special position (center of symmetry) of the $P2_1/n$ space group. The steric impossibility and the dissymetry of hydrogen bonds forbid the use of this special position. Thus (II) is adopted. The short distance O–OW3 = 2.52(2) Å indicates a possible interaction between O_2^- and OW3 through a hydrogen bond. The OW3 water molecule has a large vibrational amplitude and the K2 atom is not rigidly bonded.

Conclusion

The potassium copper (III) periodate solutions, stabilized and purified by successive crystallizations, may be used for other chemical reactions:

(a) With NaOH solutions, a red-brown colored precipitate is obtained. Crystals may be prepared.

(b) Using RbOH and CsOH, rubidium and cesium may replace potassium atoms and give new complexes.

(c) Solutions of $K_4H_4Cu(IO_6)_2O_2 \cdot 6H_2O$ are source of Cu^{3+} in exchange reactions if the oxidizing state of these solutions is kept. We assume that the copper (III) periodate anion conformation is not modified in solution.

We can imagine other ligands around Cu^{3+} ion as the ethylenebis(biguanidine) (N donors) which chelate Ag^{3+} in $Ag[C_6H_{16}N_{10}]SO_4HSO_4 \cdot H_2O$ salt (*13*).

References

1. W. KLEMM AND E. HUSS, *Z. Anorg. Chem.* **258,** 221 (1949).

2. R. HOPPE AND R. HOMANN, *Naturwissenschaften* **53,** 501 (1966).

3. H. N. MIGEON, A. COURTOIS, M. ZANNE, C. GLEITZER, AND J. AUBRY, *Rev. Chim. Miner.* **12,** 203 (1975).

4. GMELIN, "Handbuch der Anorganischen Chemie," 60-Cu[B], 1027 Kaliumkupfer (III) perjodate, 1002 Natriumkupfer (III) tellurate, Verlag Berlin (1965).

5. L. MALAPRADE, *C. R. Acad. Sci.* **204,** 979 (1937).

6. L. MALATESTA, *Gazz. Chim. Ital.* **71,** 467 (1941).

7. M. RALEK, AND L. JENSOVSKY, *Collect. Trav. Chim. Tchecosl.* **24,** 3495 (1959).

8. I. Hadinec, L. Jensovsky, A. Linek, and V. Synecek, *Naturwissenschaften* **47,** 377 (1960).
9. R. Masse and A. Simon, *J. Solid State Chem.* **44,** 201 (1982).
10. H. D. Babcock and L. Herzberg, *Astrophys. J.* **108,** 167 (1948).
11. A. F. Wells, "Structural Inorganic Chemistry," 5th ed., pp. 498–506, Oxford Univ. Press (Clarendon), New York/London (1984).
12. S. C. Abrahams and J. Kalnajs, *Acta Crystallogr.* **8,** 503 (1955).
13. L. Coghi and G. Pelizzi, *Acta Crystallogr. Sect. B* **31,** 131 (1975).