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An Inorganic Complex of Silver (III): $K_5Ag(IO_5OH)_2 \cdot 8H_2O$

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The chemical preparation and crystal structure of the trivalent silver salt $K_5Ag(IO_5OH)_2 \cdot 8H_2O$ are described (monoclinic, space group *Cc*; $a = 21.79(4)$, $b = 6.320(3)$, $c = 15.16(3)$ Å, $\beta = 96.14(4)$; four formula units per unit cell). The structure is refined until $R = 0.033$ for 2718 reflections. Isolated $Ag(IO_5OH)_2^{5-}$ units occur, which contain trivalent silver ions surrounded by four oxygen atoms from two IO_6 octahedra in rectangular configuration. The differences in the I–O bond lengths, as well as the small deviations of the crystal structure from centrosymmetry, are in agreement with an antiperiplanar position of the OH groups in both octahedra.

Introduction

Silver is a well-studied element which presents various oxidation states: "< 1+" occurs in Ag_2F (*1*) or $Ag_6Ge_{10}P_{12}$ (*2*); "1+" is the usual and most stable state; "2+" is found in some ternary silver fluorides and compounds with organic ligands containing N donors (*3*); "3+" is encountered in ternary silver fluorides (a), compounds with organic ligands (b), and periodates (c). The knowledge about crystallographic details is rather poor.

(a) By fluorination of $AgNO_3$ together with alkali chlorides Klemm (*4*) and Hoppe (*5, 6*) prepared $CsAgF_4$, $KAgF_4$, Cs_2KAgF_6. As their structural characterizations were based on powder data, only differences of the geometries of the AgF_4^- ion (planar) and the AgF_6^{-3} ion (octahedral) could be stated, but no accurate Ag–F distances were calculated.

(b) Organic compounds with ethylene bis-biguanidine ligands around the Ag^{3+} ion exist. They were prepared for the first time by Rây and Chakravarty (*7*). Three structures were solved by Kunchur (*8*), Simms *et al.* (*9*), and Coghi and Pelizzi (*10*) with a good precision for the values of Ag–N distances.

(c) Alkali silver periodate complexes of Ag^{3+} were prepared first by Malaprade (*11*) and Malatesta (*12*); Jensovsky and Skála (*13*) used anodic oxidation reactions for the preparation of these complexes. A general review of the compounds is given by McMillan (*14*). Cohen and Atkinson (*15*) arrived at a geometrical model for the $Ag(IO_6)_2^{7-}$ anions via vibrational spectroscopy.

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Using the approach of Jensovsky we prepared the new compound $K_5Ag(IO_5OH)_2 \cdot 8H_2O$ and investigated its crystal structure.

Materials and Methods

Chemical Preparation

The salt $K_5Ag(IO_5OH)_2 \cdot 8H_2O$ was obtained in two ways: (a) Direct oxidation of $AgNO_3$ by $K_2S_2O_8$ in KIO_4/KOH solution (*11*, *12*): 50 ml of $AgNO_3$ solution (0.1–0.3 *M*) is added to 100 ml of KIO_4 (1 *M*)/KOH (3 *M*) solution. The precipitated Ag_2O is reacted by the slow addition of an excess of $K_2S_2O_8$ (5–10 g) at 50°C. After 20 min the red-brown solution is separated from unreacted Ag_2O by filtration and slowly concentrated above KOH in a desiccator at room temperature. Then crystals of K_2SO_4 separate. They are removed repeatedly, until the first platelets of $K_5Ag(IO_5OH)_2 \cdot 8H_2O$ appear.

(b) Anodic oxidation of Ag in the presence of a KIO_4/KOH electrolyte (*13*): A solution of KIO_4 (1 *M*) and KOH (3 *M*) is electrolyzed with a strip of pure silver serving as anode. At 5 to 7 V cell voltage (anodic current density 0 · 5 A/cm^2) an orange-brown solution forms besides Ag_2O in the anodic compartment enclosed in a porous clay cylinder. After filtration and evaporation as described under (a) orange platelets of $K_5Ag(IO_5OH)_2 \cdot 8H_2O$ separate from the solution.

Remarks

The crystals of $K_5Ag(IO_5OH)_2 \cdot 8H_2O$ and their solution are only stable at pH > 9. Needless to say, reducing solvents like alcohols or acetone destroy the complex. Crystals decompose slowly in air, but can be handled without cautions for a short time; they are safe in closed glass tubes under argon. The composition of the compound is based on the results of the crystal structure analysis.

Crystal Structure

A crystal of prismatic shape and approximate dimensions 0.11 × 0.16 × 0.16 mm^3 was sealed together with some of its saturated solution in a glass capillary.

Crystal data. According to precession photographs (Mo$K\alpha$) and diffractometer data (*vide infra*) the crystal is monoclinic, $a = 21.79(4)$, $b = 6.320(3)$, $c = 15.16(3)$ Å, and $\beta = 96.14(4)$; possible space groups are *C2/c* or *Cc*; $Z = 4$.

Structure determination. 3124 independent reflections were collected in the $\omega/2\theta$ mode with an automatic four-circle diffractometer, Philips PW1100, using Ag$K\bar{\alpha}$ radiation (0.5608 Å). The θ range was 3–25°, the scan speed 0.02°/sec, and the scan width 1.20°. The background was measuring during 10 sec at the starting and final position of each scan. No absorption correction was made ($\mu K\alpha$Ag = 25.7 cm^{-1}).

The crystal structure was solved and refined using the program system SDP (Version RSX11M, September 1977; ENraf-Nonius). A three-dimensional Patterson function revealed the atomic positions of Ag and I. A Fourier synthesis and difference Fourier synthesis showed the location of all potassium and oxygen atoms. The structure was first solved in the centrosymmetric space group *C2/c*. But the refinement in this space group converged to only $R = 0.08$ and undefined electron density occurred near the positions of all heavy atoms, amounting to up to 10% of the densities of the atomic peaks. The space group *Cc* permitted the refinement to 0.033 $\left(R = \frac{\Sigma|F_0 - |F_c||}{\Sigma F_0}\right)$. The unweighted value $R = 0.033$ was reached with 2718 independent reflections satisfying the condition $F_0^2 > 4\sigma(F_0^2)$, $\sigma(F_0^2)$ = counting statistics. For all observed reflections (= 3124) the residual is $R = 0.039$. The final difference Fourier map is uniform to $\pm 0.6\ e \cdot$ Å^{-3} but does not reveal the hydrogen atoms.

The positional and thermal parameters are summarized in Table I. Interatomic distances and angles of significance are given in Table II.

A list of observed and calculated structure factors will be sent on request (R.M.).

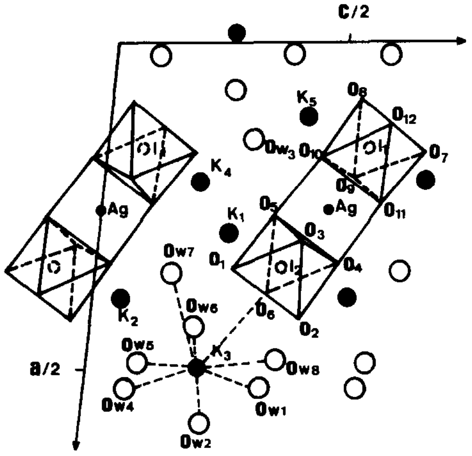

FIG. 1. Projection of the atomic positions (except hydrogen) along [010] of the monoclinic unit cell of $K_5Ag(IO_5OH)_2 \cdot 8H_2O$.

Results and Discussion

The crystal structure of $K_5Ag(IO_5OH)_2 \cdot 8H_2O$ is projected along [010] in Fig. 1 (H atoms omitted). Our interest will be focused on the anion $Ag(IO_5OH)_2^{5-}$, the structure of which is shown in more detail in Fig. 2. The configuration of the periodate complex of Ag^{3+} as it is predicted from spectroscopic analysis (*15*) of solutions and polycrystalline specimens is confirmed by the present X-ray analysis. The silver atom is surrounded by four oxygen atoms in a rectangular configuration. The closest plane to the atoms Ag, 04, 05, 010,

TABLE I

ATOMIC, ISOTROPIC, AND ANISOTROPIC[a] THERMAL PARAMETERS OF $K_5Ag(IO_5OH)_2 \cdot 8H_2O$

Atom	x	y	z	B_{iso} (Å²)	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
I1	0.16423(3)	0.0482(1)	0.08187(5)	1.20	0.00056(1)	0.0081(1)	0.00138(2)	0.00034(7)	0.00022(2)	−0.0009(1)
I2	0.84144(3)	0.9785(1)	0.91440(5)	1.17	0.00064(1)	0.0076(1)	0.00126(2)	0.00048(7)	0.00023(2)	−0.0004(1)
Ag	0.2500(0)	0.7490(2)	0.0000(0)	1.23	0.00062(1)	0.0086(1)	0.00132(2)	0.00071(6)	0.00010(2)	−0.00132(9)
K1	0.2902(1)	0.0281(4)	0.2862(2)	1.78	0.00150(5)	0.0089(5)	0.00238(9)	0.0007(3)	−0.0013(1)	−0.0003(4)
K2	0.3836(1)	−0.0006(5)	0.0626(2)	2.38	0.00143(5)	0.0146(6)	0.00307(11)	−0.0008(3)	−0.0003(1)	0.0018(5)
K3	0.4878(3)	0.2390(7)	0.2525(4)	5.60	0.00534(20)	0.0304(11)	0.00343(14)	−0.0081(8)	−0.0014(3)	0.0005(10)
K4	0.7134(1)	0.9696(4)	0.7140(2)	2.50	0.00168(6)	0.0116(5)	0.00229(9)	0.0000(3)	−0.0003(1)	−0.0014(4)
K5	0.6129(1)	−0.0003(5)	0.9364(2)	2.90	0.00146(5)	0.0152(6)	0.00359(12)	−0.0014(3)	−0.0010(1)	0.0022(5)
O1	0.3371(4)	0.630(1)	0.3038(6)	1.81	0.0016(2)	0.007(2)	0.0024(3)	0.0008(9)	0.0014(4)	0.001(1)
O2	0.4135(3)	0.650(1)	0.4621(5)	1.75	0.0005(1)	0.014(2)	0.0021(3)	0.0008(8)	0.0003(3)	−0.003(1)
O3	0.2988(4)	0.777(1)	0.4512(6)	2.27	0.0014(2)	0.010(2)	0.0023(3)	0.0026(9)	0.0009(4)	0.002(1)
O4	0.3281(4)	0.410(1)	0.5321(4)	1.51	0.0009(1)	0.017(2)	0.0005(2)	−0.0022(8)	−0.0008(3)	0.001(1)
O5	0.2585(4)	0.394(1)	0.3853(5)	1.34	0.0010(1)	0.007(1)	0.0018(3)	−0.0022(8)	0.0008(3)	−0.001(1)
O6	0.3768(4)	0.273(1)	0.3835(6)	1.96	0.0011(2)	0.011(2)	0.0040(4)	0.0006(9)	0.0019(4)	−0.004(1)
O7	0.6686(4)	0.366(1)	0.6993(5)	1.52	0.0010(1)	0.013(2)	0.0009(2)	0.0002(9)	0.0001(3)	0.003(1)
O8	0.5864(3)	0.364(1)	0.5422(5)	1.68	0.0006(1)	0.013(2)	0.0021(3)	−0.0030(8)	0.0000(3)	0.000(1)
O9	0.7031(3)	0.213(1)	0.5472(5)	1.29	0.0007(1)	0.008(2)	0.0024(3)	0.0001(7)	0.0009(3)	−0.002(1)
O10	0.6716(4)	0.601(1)	0.4693(6)	1.62	0.0008(1)	0.008(1)	0.0028(3)	−0.0015(8)	0.0005(3)	0.004(1)
O11	0.7420(3)	0.602(1)	0.6126(5)	1.74	0.0004(1)	0.015(2)	0.0016(3)	−0.0018(8)	−0.0008(3)	0.002(1)
O12	0.6281(4)	0.728(1)	0.6165(6)	2.28	0.0014(2)	0.014(2)	0.0024(3)	0.0023(10)	−0.0007(4)	−0.005(1)
OW1	0.5195(5)	0.444(2)	0.8878(9)	4.91	0.0019(2)	0.028(3)	0.0065(6)	−0.0047(16)	0.0021(6)	−0.010(3)
OW2	0.5725(4)	0.162(1)	0.7680(7)	2.86	0.0009(1)	0.015(2)	0.0042(4)	−0.0021(10)	0.0011(4)	0.003(2)
OW3	0.6495(6)	0.682(2)	0.8209(6)	3.97	0.0032(3)	0.019(3)	0.0019(4)	0.0012(17)	0.0002(6)	0.002(2)
OW4	0.5180(5)	0.956(2)	0.5946(8)	3.87	0.0013(2)	0.024(3)	0.0059(6)	0.0022(14)	0.0011(6)	0.000(2)
OW5	0.4797(4)	0.546(2)	0.1149(5)	2.13	0.0008(1)	0.023(3)	0.0018(3)	−0.0013(11)	0.0004(3)	−0.001(2)
OW6	0.4260(5)	0.838(2)	0.2314(7)	2.88	0.0018(2)	0.017(2)	0.0042(5)	−0.0010(13)	0.0004(5)	0.004(2)
OW7	0.3498(6)	0.319(2)	0.1747(7)	2.58	0.0029(3)	0.014(2)	0.0031(4)	−0.0012(15)	−0.0001(6)	−0.002(2)
OW8	0.4761(5)	0.043(2)	0.4223(7)	3.28	0.0014(2)	0.017(2)	0.0047(5)	0.0017(12)	0.0000(5)	−0.005(2)

[a] $T = \exp - (H^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})$. Standard deviations in parentheses.

TABLE II

Interatomic Distances in $K_5Ag(IO_5OH)_2 \cdot 8H_2O$ (O–O Distances up to 3.0 Å; Selected Angles (o))

Ag-03		= 3.291(7)	K2	02	2.807(09)	K5	08	2.898(09)
Ag-04		= 1.993(7)	K2	03	2.758(10)	K5	09	2.789(09)
Ag-05		= 1.985(8)	K2	04	2.875(09)	K5	010	2.846(08)
Ag-09		= 3.197(6)	K2	06	3.205(11)	K5	012	3.214(10)
Ag-010		= 1.965(8)	K2	011	3.317(09)	K5	OW1	3.499(14)
Ag-011		= 1.973(8)	K2	OW4	2.930(11)	K5	OW2	2.806(12)
I1-07		= 1.853(8)	K2	OW6	2.818(12)	K5	OW3	2.836(11)
I1-08		= 1.823(8)	K2	OW7	2.788(11)	K5	OW4	3.343(11)
I1-09		= 1.837(6)	K2	OW8	3.095(11)	K5	OW8	2.978(10)
I1-010		= 1.973(8)	K3	06	3.296(10)	01	02	2.774(15)
I1-011		= 1.955(7)	K3	OW1	2.899(16)	01	03	2.635(12)
I1-012		= 2.009(7)	K3	OW2	3.129(09)	01	05	2.674(11)
I2-01		= 1.806(9)	K3	OW4	2.831(13)	01	06	2.665(12)
I2-02		= 1.844(9)	K3	OW5	2.840(11)	02	03	2.613(12)
I2-03		= 1.971(7)	K3	OW6	2.873(11)	02	04	2.700(11)
I2-04		= 1.967(7)	K3	OW7	3.151(14)	02	06	2.745(11)
I2-05		= 1.985(8)	K3	OW8	2.894(13)	03	04	2.665(11)
I2-06		= 1.835(7)	K4	01	2.954(10)	03	05	2.727(11)
K1	01	2.715(07)	K4	05	2.814(10)	03	09	2.697(06)
K1	03	2.953(09)	K4	07	2.693(07)	04	05	2.558(11)
K1	05	2.881(08)	K4	09	2.947(09)	04	06	2.734(12)
K1	06	2.744(10)	K4	011	2.889(09)	05	05	2.693(12)
K1	07	2.908(08)	K4	012	2.717(09)	07	08	2.822(13)
K1	011	2.850(09)	K4	OW2	3.482(10)	07	09	2.684(12)
K1	OW3	3.432(13)	K4	OW3	2.892(11)	07	011	2.638(11)
K1	OW6	3.379(11)	K4	OW7	3.369(13)	07	012	2.710(11)
K1	OW7	2.898(11)	K5	05	3.412(09)	08	09	2.712(11)
08	010	2.712(10)	07-I1-012		= 89.0			
08	012	2.676(11)	08-I1-09		= 95.6			
09	010	2.780(10)	08-I1-010		= 91.1			
09	011	2.753(10)	08-I1-011		= 167.9			
010	011	2.522(12)	08-I1-012		= 88.4			
010	012	2.642(12)	09-I1-010		= 93.6			
011	012	2.613(11)	09-I1-011		= 93.1			
OW1	02	2.740(15)	09-I1-012		= 174.9			
OW1	08	2.890(16)	010-I1-011		= 79.9			
OW1	OW2	2.873(16)	010-I1-012		= 83.1			
OW2	07	2.758(11)	011-I1-012		= 82.5			
OW2	OW1	2.873(16)	01-I2-02		= 98.9(4)			
OW3	07	2.777(13)	01-I2-03		= 88.4			
OW3	010	2.875(14)	01-I2-04		= 168.5			
OW4	012	2.787(13)	01-I2-05		= 89.6			
OW4	OW8	2.730(11)	01-I2-06		= 94.1			
OW5	02	2.873(13)	02-I2-03		= 86.4			
OW5	08	2.736(12)	02-I2-04		= 90.1			
OW5	OW6	2.890(15)	02-I2-05		= 169.1			
OW6	01	2.670(13)	02-I2-06		= 96.5			
OW7	01	2.811(13)	03-I2-04		= 85.2			
OW7	04	2.758(14)	03-I2-05		= 87.1			
OW8	02	2.927(12)	03-I2-06		= 175.9			
OW8	06	2.620(13)	04-I2-05		= 80.6			

TABLE II—*Continued*

04-Ag-05 = 80.0(3)
05-Ag-010 = 99.8(3)
010-Ag-011 = 79.7(3)
04-Ag-011 = 100.5(3)
07-I1-08 = 100.3(4)
07-I1-09 = 93.3
07-I1-010 = 166.0
07-I1-011 = 87.6

04-I2-06 = 91.9
05-I2-06 = 89.5

and 011 is defined by the equation $0.547x + 0.780y - 0.360z = 0$. The Ag atom lies in the plane; 04 and 010 deviate by −0.027 Å and 05 and 011 by +0.026 Å. The plane therefore is twisted very slightly. The distances d_{Ag-O} range from 1.97 to 1.99 Å. Within their standard deviations these distances are identical to d_{Ag-N} in the ethylene-bis-biguanidine silver (III) cation $Ag(C_2H_7N_5)_2^{3+}$ (*10*). Yet the rectangular distortion of the square planar environment of the silver atoms which might be considered as a hybrid valence bond of dsp^2 type is more pronounced in the case of the periodate complex as reflected in the difference of the O–Ag–O angles, 80 and 100°, respectively. This distortion is easily explained by assuming an electrostatic repulsion between the positively charged silver and iodine atoms as indicated by a relative shortening of the distances d_{I-O} involving the peripheral 0 atoms (*vide infra*).

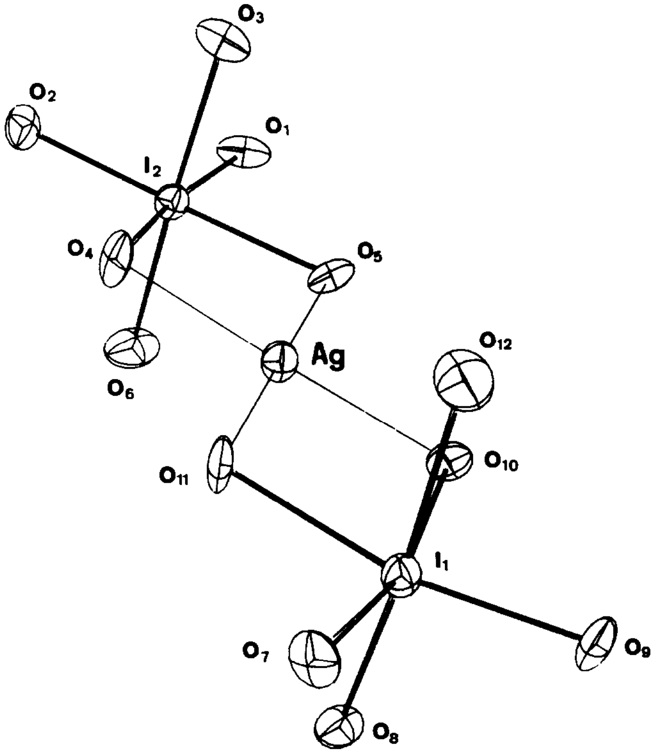

FIG. 2. Complex anion in the compound $K_5Ag(IO_5OH)_2 \cdot 8H_2O$ (H atoms omitted).

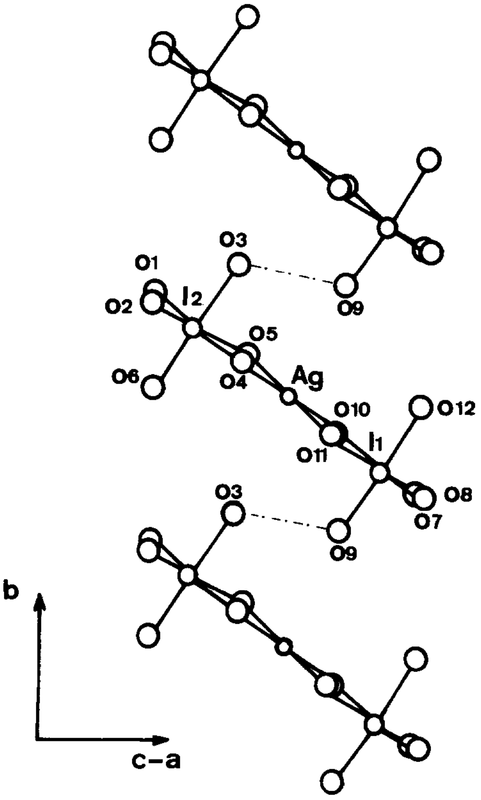

FIG. 3. Arrangement of the anions in the structure of $K_5Ag(IO_5OH)_2 \cdot 8H_2O$. The proposed hydrogen positions are indicated.

The present structure analysis does not yield a direct localization of the hydrogen atoms. But the positions of the OH groups in the $Ag(IO_5OH)_2^{5-}$ anions can be deduced unambiguously from a close inspection of the crystal structure. First conclusions can be drawn from the fact that the structure of $K_5Ag(IO_5OH)_2 \cdot 8H_2O$ is nearly but not exactly centrosymmetric. One might argue that the anion lacks a center of inversion because of the positions of the hydrogen atoms. This idea is proved by an inspection of the O–O and O–I distances in the anion. The IO_6 octahedra are distorted (Fig. 2). The main component of this distortion can be traced back to a repulsion between Ag and I ($d_{Ag-I} = 3.02$ Å). It is reflected in the distances $d_{04-05} = 2.56$ and $d_{010-011} = 2.52$ Å, which are the shortest O–O distances in the structure in contrast to $d_{01-02} = 2.77$ and $d_{07-08} = 2.82$ Å. The same holds for the I–O distances, where $d_{I1-07} = 1.85$, $d_{I1-08} = 1.82$ Å and $d_{I2-01} = 1.81$, $d_{I2-02} = 1.84$ Å belong to the short category in contrast to $d_{I2-04} = 1.97$, $d_{I2-05} = 1.99$ Å. From this point of view one would expect d_{I1-012} (= 2.01 Å) to be shorter than d_{I1-09} (= 1.84 Å) and d_{I2-06} (= 1.84 Å) to be shorter than d_{I2-03} (= 1.97 Å), which definitely is not true in the case of d_{I1-012}/d_{I1-09}. This additional component of distortion must have chemical reasons; 012 is most probably an OH group. Around the atom I2 the three distances to 01, 02, and 06 are short (and lie within a narrow range). Only 03 is a possible candidate to represent the OH group. Thus an antiperiplanar configuration of the anion with respect to the OH groups is very probable. The geometry of the anion also gives evidence for a correct compound formulation, as alternative formulations like $Ag(IO_4(OH)_2)_2^{3-}$, where the lack of negative charges is compensated by the replacement of H_2O molecules by OH^- ions, are excluded quite safely.

As Fig. 3 shows the $Ag(IO_5OH)_2^{5-}$ anions form a file in the [010] direction. The anions are obviously linked via hydrogen bonds involving 03 and 09 ($d_{03-09} = 2.70$ Å). According to the discussion of the I–O bond lengths the hydrogen bridge between 03 and 09 is asymmetric and the H atom is essentially bonded to 03. The position of the H atom might explain the difference between the distances $d_{Ag-03} = 3.29$, $d_{Ag-09} = 3.20$ Å on one side and $d_{Ag-I1} = 3.017$ and $d_{Ag-I2} = 3.022$ Å on the other as a consequence of electrostatic repulsion between Ag and H.

Besides hydrogen bonds between adjacent anions, such bonds involving the H_2O molecules seem to be essential in the structure of $K_5Ag(IO_5OH)_2 \cdot 8H_2O$. The H_2O molecules concentrate in planes parallel to (100), and all 0 atoms find neighbors in a range of distances (2.60 to 2.90 Å) which are suitable for hydrogen bonding. Last but

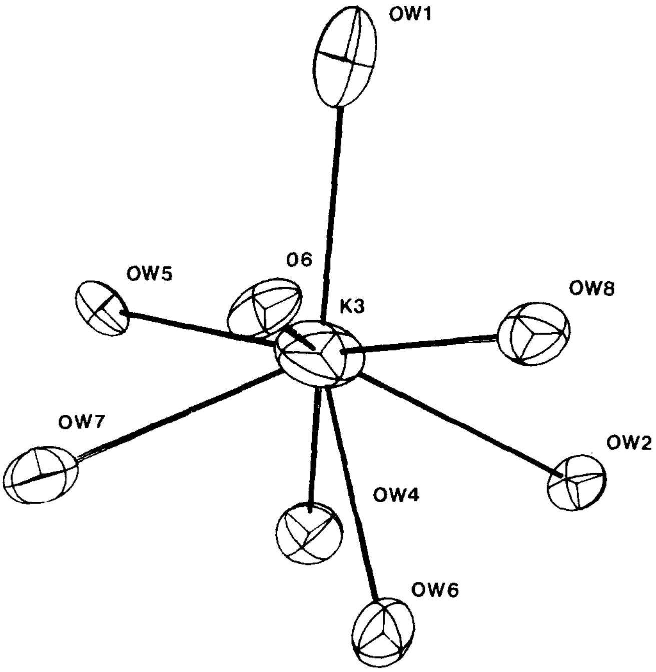

FIG. 4. Coordination sphere of oxygen atoms around K3.

not least, an interesting aspect is concerned with the potassium ions in the structure of $K_5Ag(IO_5OH)_2 \cdot 8H_2O$. Two kinds of cations exist. One kind, represented by K1, K2, K4, and K5, is concentrated in planes parallel to (101). These cations are rather rigidly bonded to the anions as can be concluded from their vibrational amplitudes. On the contrary, K3 represents a rather special situation (Fig. 4). It is surrounded only by H_2O molecules in an arrangement of a very distorted Archimedian antiprism. K3 is characterized by a temperature factor approximately twice as large as that of the other K atoms. It should be possible to replace K3 by a larger alkali metal cation and even to stabilize the structure type by this exchange.

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