JOURNAL OF SOLID STATE CHEMISTRY **113**, 393–397 (1994)

Tetrasilvermesoperiodate, $Ag_4H_2I_2O_{10}$: Structure and Color Phenomenon

Andreas Trnoska, Edgar Nachbaur,[1] and Ferdinand Belaj

Institut für Anorganische Chemie, Universität Graz, Schubertstrasse 1, A-8010 Graz, Austria

Received November 23, 1993; in revised form March 8, 1994; accepted March 15, 1994

A single-crystal X-ray structural analysis of the material previously known as "Ag_2HIO_5" has shown it to be $Ag_4H_2I_2O_{10}$, M_r = 847.29, monoclinic, $P2_1/n$, a = 6.243(3), b = 7.247(3), c = 10.196(4) Å, β = 98.00(3)°, V = 456.8(3) Å^3, Z = 2, D_x = 6.160 g cm^{-3}, $\lambda(MoK_\alpha)$ = 0.71069 Å, μ = 151.1 cm^{-1}, $F(000)$ = 744, T = 90K, R = 0.0570, wR = 0.0547, S = 1.85 for 898 unique observed reflections and 73 parameters. The dark-red crystal is composed of centrosymmetric $H_2I_2O_{10}^{4-}$ ions built up of two edge-sharing $IO_5(OH)$ units. The Ag^+ ions equally surrounding the anion display the coordination numbers 5 and 7. The shortest Ag–Ag distance is 3.321(2) Å, revealing the absence of any attractive Ag–Ag interaction. The geometrical parameters obtained for the $H_2I_2O_{10}^{4-}$ ion are in close accordance with those reported for the same anion in the colorless alkaline metal salts. The color-induction phenomenon is due to considerable covalent Ag–O interaction causing a red shift of electronic transitions in the "cation–anion complex". © 1994 Academic Press, Inc.

INTRODUCTION

Our interest in colored silver salts (1, 2) recently led us to a study of slightly soluble silver (1) periodates precipitated under various conditions in the system $AgNO_3$–H_5IO_6–H_2O (3).

We expected that $Ag_4H_2I_2O_{10}$ might be a new candidate for investigations dealing with the color-induction phenomenon in heavy B metal salts (4–7). In order to obtain more information about the validity and the scope of known models providing an explanation for this phenomenon, the structural features of the red-colored title compound and those reported for the related colorless alkaline metal periodates are compared.

We have performed a single-crystal structure analysis of the ruby-red material previously known as "Ag_2HIO_5" to elucidate the correct empirical formula for the compound, which remained questionable from earlier studies (8, 9).

EXPERIMENTAL

Ruby-red crystals were obtained by dissolving 2.00 g $NaIO_4$ (Fluka) in 200 ml H_2O at 70°C and slowly adding 2.20 g $AgNO_3$ (Fluka) dissolved in 40 ml H_2O (optimum pH value: 4.0 to 4.5).

Data were collected from a single crystal (0.10 × 0.12 × 0.20 mm) at 90 K with a modified Stoe 4-circle diffractometer using graphite-monochromatized MoK_α radiation with Nonius low-temperature equipement. Cell parameters were obtained from a least-squares fitting of 58 well-refined reflections, 3045 reflections measured using ω-scans (scan range 3.5°) for 2Θ from 3° to 60° (h −8 to 8, k 0 to 10, l 0 to 14), 1797 reflections with $I > 3\sigma(I)$, 906 unique reflections, internal consistency factor R_{int} = 0.073 due to the moderate crystal quality and to the high absorption, with LP correction, empirical absorption correction with DIFABS (10), omission of 8 low-order reflections probably suffering from extinction. A structural solution was obtained by direct methods using SHELXS-86 (11) with no localization of the hydrogen atom.

Refinement with anisotropic thermal parameters for all atoms until no parameter shifts occurred gave R = 0.0570, wR = 0.0547 [$w = 1/\sigma^2(F)$, 898 reflections, 73 parameters]. The strongest peaks in the final difference-Fourier map of up to 2.89 eÅ^{-3} lay near (0.73–0.99 Å) the iodine and silver atoms. Scattering factors and anomalous dispersion corrections were from "The International Tables for X-ray Crystallography" (12). Analysis was performed on a VAX6000 computer with SHELX-76 (13), PLATON (14), and ORTEP (15).

UV-VIS diffuse reflectance data were collected on a Varian CARY 05E UV–VIS–NIR spectrophotometer using a praying mantis accessory (Harrick Scientific Corp., New York) (16, 17).

RESULTS AND DISCUSSION

Single-crystal X-ray diffraction. The final atomic positions and thermal parameters are listed in Table 1, and

---

[1] To whom correspondence should be addressed.

0022-4596/94 $6.00

TABLE 1

Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters (in Å^2, $\times 10^4$) with Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag(1)	9169(2)	3500(2)	3588(2)	177(7)	208(7)	161(7)	33(5)	8(5)	−15(5)
Ag(2)	508(2)	8834(2)	3394(1)	165(6)	242(7)	155(7)	8(5)	15(5)	12(6)
I(1)	5790(2)	6920(2)	4541(1)	144(5)	116(5)	119(5)	3(4)	25(4)	10(4)
O(1)	4681(19)	7782(16)	6142(13)	205(57)	45(49)	215(67)	−10(45)	15(51)	17(47)
O(2)	4259(18)	8670(19)	3554(13)	110(53)	263(66)	150(63)	65(49)	42(48)	9(52)
O(3)	8312(17)	8130(18)	5045(13)	67(49)	238(65)	206(66)	−83(48)	−18(46)	106(57)
O(4)	6748(19)	5932(17)	3075(13)	202(57)	103(51)	182(65)	26(50)	15(50)	−23(50)
O(5)	6818(19)	4752(15)	5640(13)	183(57)	36(47)	194(64)	−52(43)	−38(48)	24(47)

Note. The form of the temperature factor used is $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$.

the bond lengths and angles are given in Table 2. The thermal ellipsoid plot of an anion, together with the surrounding Ag^+ cations and the atom numbering, is shown in Fig. 1. The packing of the compound in the unit cell is shown in Fig. 2.

The structure contains binuclear $H_2I_2O_{10}^{-4}$ anions lying around centers of symmetry. Each anion is built up of two octahedral edge-sharing $IO_5(OH)$ units as was observed in $K_4H_2I_2O_{10} \cdot 8\ H_2O$ (18–20) and in $Na_4H_2I_2O_{10} \cdot NaOH \cdot 14\ H_2O$ (21). As shown by Tobias and Jansen (21), the three structure determinations of $K_4H_2I_2O_{10} \cdot 8\ H_2O$ are inconsistent. The geometrical parameters and length and bond angles) of the anion in $Na_4H_2I_2O_{10} \cdot NaOH \cdot H_2O$ as well as of the anion in $K_4H_2I_2O_{10} \cdot 8\ H_2O$ (18) reveal no significant difference from those in $Ag_4H_2I_2O_{10}$.

The positions of the hydrogen atoms could not be determined, but the substantially longer I(1)–O(1) distance

TABLE 2

Bond Distances (Å) and Bond Angles (°) in the Periodate Anion and in the Coordination Polyhedra of the Silver Atoms

$H_2I_2O_{10}^{-4}$-Anion

I(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(5′)
O(1)	1.96(1)	2.69(2)	2.68(2)	—	2.66(2)	2.66(2)
O(2)	91.1(5)	1.81(1)	2.79(2)	2.61(2)	—	2.73(2)
O(3)	90.2(5)	100.9(6)	1.81(1)	2.64(2)	2.72(2)	—
O(4)	175.4(5)	91.5(6)	92.9(6)	1.83(1)	2.75(2)	2.78(2)
O(5)	84.6(5)	167.0(5)	91.4(5)	92.0(5)	2.02(1)	2.48(2)
O(5′)	83.9(5)	90.7(5)	167.1(6)	92.4(5)	76.7(5)	1.98(1)

I(1) ··· I(1′) 3.138(2)

$Ag(1)O_7$-Polyhedron

Ag(1)	O(3)	O(4*a*)	O(2)	O(4)	O(1)	O(5)	O(5)
O(3)	2.28(1)	—	—	—	—	—	—
O(4*a*)	154.0(5)	2.33(1)	—	—	—	—	—
O(2)	103.7(5)	95.0(5)	2.52(1)	—	—	—	—
O(4)	95.8(5)	109.1(5)	62.2(5)	2.53(1)	—	—	—
O(1)	108.4(5)	73.6(5)	125.5(5)	71.6(5)	2.63(1)	—	—
O(5)	63.4(5)	104.2(5)	77.4(5)	128.9(5)	156.9(5)	2.82(1)	—
O(5*a*)	95.6(5)	62.8(5)	156.7(5)	129.1(5)	57.8(5)	100.3(5)	2.86(1)

$Ag(2)O_5$-Polyhedron

Ag(2)	O(2)	O(3)	O(4)	O(1)	O(3*a*)
O(2)	2.33(1)	—	—	—	—
O(3)	128.0(5)	2.37(1)	—	—	—
O(4)	124.3(5)	103.2(5)	2.44(1)	—	—
O(1)	96.6(5)	118.3(5)	73.0(5)	2.57(1)	—
O(3*a*)	79.3(5)	84.0(5)	86.7(5)	152.4(5)	2.75(1)

Ag(1) ··· Ag(2^{VII}) 3.321(2)

Note. The symmetry codes are given in Fig. 1.

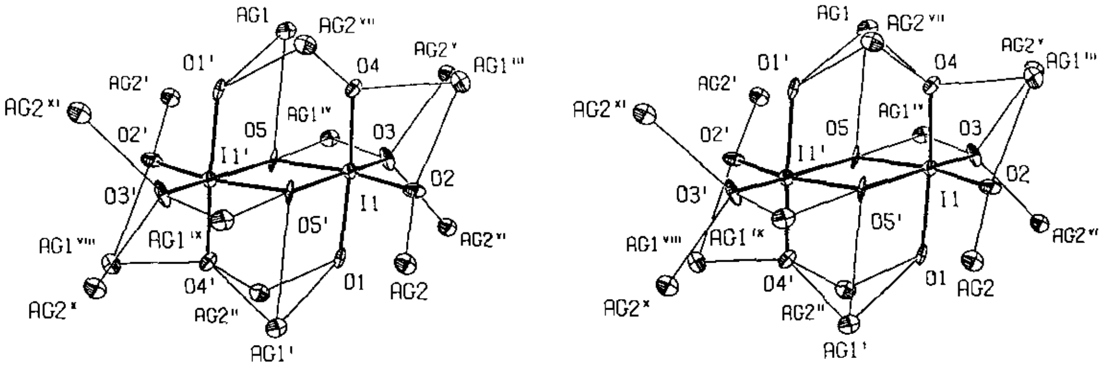

FIG. 1. Plot of the $H_2I_2O_{10}^{4-}$ anion together with its nearest Ag^+ cations. The thermal ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $\frac{1}{2}+x, 1\frac{1}{2}-y, \frac{1}{2}+z$; (iii) $1\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $2-x, 1-y, 1-z$; (v) $1+x, y, z$; (vi) $1-x, 2-y, 1-z$; (vii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$: (viii) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (ix) $x-1, y, z$; (x) $-x, 1-y, 1-z$; (xi) $x, y-1, z$.

[1.962(13) Å] compared with the distances between I(1) and O(2)/O(3)/O(4) [1.808(13)–1.832(13) Å] has led us to suggest that the hydrogen atoms are attached to O(1). The only short intermolecular O ··· O distance below 3.00 Å [O(1) ··· $O(2^{vi})$: 2.66(2) Å] therefore implies the existence of a strong hydrogen bond.

In the main plane of the anion [I(1), O(2), O(3), O(5), O(5′); maximum deviation: I(1) 0.06(3) Å] the O(5)–I(1)–O(5′) angle is less than 90° [76.7(5)°] whereas the opposite angle O(2)–I(1)–O(3) [100.9(6)°] is considerably larger than the 90° value in the regular octahedron.

The Ag^+ ions are situated equally around the anions with Ag–O distances ranging from 2.281(12) to 2.865(12) Å [next distance 3.135(12) Å]. The two crystallographically independent Ag^+ ions have the coordination numbers 7 (distorted pentagonal bipyramid: $O_2^{short}O_3^{medium}O_2^{long}$) and 5 (distorted trigonal bipyramid: $O_2^{short}O_3^{medium}$).

The shortest Ag–Ag distance [3.321(2) Å] comes close to the sum of two van der Waals contact radii for Ag [3.40 Å] (22). Consequently, no attractive Ag–Ag interaction has to be accounted for.

Each O atom in $Ag_4H_2I_2O_{10}$ displays the coordination number 4 [distorted tetrahedron; O(1) and O(2): Ag_2HI; O(3) and O(4): Ag_3I; O(5) Ag_2I_2] (see Fig. 1).

Color phenomenon. In order to discuss the color-induction phenomenon of the ruby-red $Ag_4H_2I_2O_{10}$ consideration has to be given to the following facts:

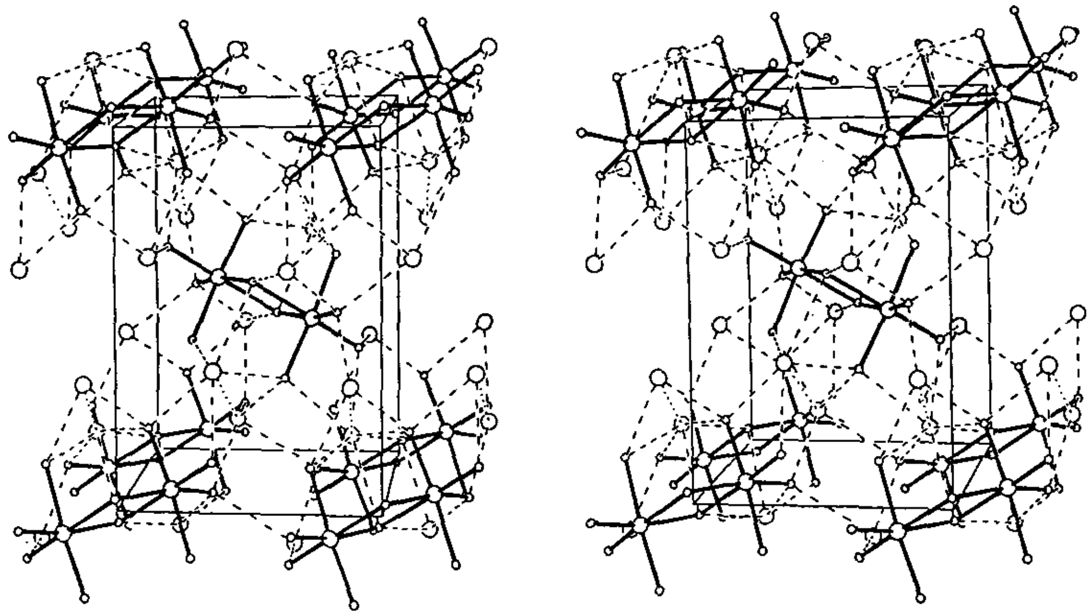

FIG. 2. ORTEP plot showing the packing of the ions in the unit cell. The atoms are drawn with arbitrary radii. The Ag ··· O distances below 3.1 Å are drawn with dashed lines; the shortest Ag ··· Ag contacts of 3.321(2) Å are drawn with dotted lines.

TABLE 3
Ag–O Distances and O–Ag–O Angles in Varicolored Silver–Oxygen Compounds with Twice-Coordinated Ag Atoms

Compound	Color	Ag–O Distance (Å)	O–Ag–O angle (°)	Reference
$KAgCO_3$	Colorless	2 × 2.09	170.0	(26)
Na_3AgO_2	Colorless	2 × 2.08	180.0	(27)
KAgO	Slight-yellow	2 × 2.058(8)	179.5	(28)
NaAgO	Slight-yellow	2 × 2.066(3)	178.2	(28)
$AgAlO_2$	Yellow	2 × 2.101(5)	180.0	(29)
$AgInO_2$	Yellow	2 × 2.076(8)	180.0	(30)
Ag_2PbO_2	Yellow	2 × 2.096(4) 2 × 2.111(4)	180.0 180.0	(31)
$AgFeO_2$	Red	2 × 2.067(8)	180.0	(32)
$LiAg_3O_2$	Red	2 × 2.15 2 × 2.17	180.0 180.0	(33)
$NaAg_3O_2$	Red	2 × 2.10 2 × 2.12	180.0 180.0	(34)
Ag_2O	Black	2 × 2.051	180.0	(35)

(i) Several studies dealing with the color-induction phenomenon of heavy B-metal salts have been reported recently (4–7). In one of those studies (4) this phenomenon has been related to a cation-induced geometrical distortion of the anion. In contrast to the obviously cation-induced electronic perturbation of the $H_2I_2O_{10}^{-4}$ anion, any geometrical distortion induced by the Ag^+ cation has to be discounted on the basis of our results and those observed in the related alkaline-metal salts.

(ii) Due to the long Ag–Ag distances observed in the crystal there is no evidence of a special type of Ag–Ag bonding in the title compound. This means that the formation of cluster-like silver aggregates within the crystal structure that might be responsible for the color enhancement phenomenon (6, 7) is not observed, either.

(iii) A correlation between the color of silver salts of oxyacids and the observed Ag–O distances has been postulated by several groups (23–25). However, the comparison between relevant data (Ag–O distances and colors) for known Ag–O compounds, such as those with bicoordinate Ag atoms, provides no support for this hypothesis (see Table 3).

TABLE 4
UV–VIS Data Obtained by Diffuse Reflectance Spectroscopy

Compound	Midpoint of absorbtion edge (nm)	Relative shift of absorbtion edge (kJ/Mol)
$K_4H_2I_2O_{10} \cdot 8\ H_2O$	348	0
$Na_4H_2I_2O_{10} \cdot NaOH \cdot 14\ H_2O$	373	−19
$Ag_4H_2I_2O_{10}$	646	−159

In conclusion, it is felt that the color-induction phenomenon in $Ag_4H_2I_2O_{10}$ can only be the result of considerable covalent parts in the Ag–O interactions with a concomitant red shift of electronic transitions in the "cation–anion complex" (see Table 4). This view is consistent with the results of XANES (X-ray absorption near edge structure) studies on oxidic Ag(I) compounds, by which the covalent part of the Ag–O bond is revealed by the intensity of the AgL_3 edge feature signalling unoccupied 4*d* states (36).

Furthermore, theoretical calculations on the *ab initio* pseudopotential level of the electronic structures, excitation energies, and oscillator strength in the molecular model systems $NaIO_4$ and $AgIO_4$ reveal a significant red shift of the vertical electronic excitation energies in accordance with experimental results (37).

ACKNOWLEDGMENT

The authors are greatly indebted to Associate Professor Doctor Ch. Kratky, Institute of Physical Chemistry, University of Graz, Austria, for providing the diffractometer.

REFERENCES

1. F. Belaj, Ch. Kratky, E. Nachbaur, and A. Popitsch, *Monatsh. Chem.* **118,** 947 (1987).
2. Ch. Kratky, E. Nachbaur, and A. Popitsch, *Monatsh. Chem.* **112,** 529 (1981).
3. A. Trnoska, Diplomawork, Univ. Graz, Austria (1992); A. Trnoska and E. Nachbaur, to be published.
4. S. P. McGlynn, T. Azumi, and D. Kumar, *Chem. Rev.* **81,** 475 (1981).
5. A. Yamashita and T. Azumi, *J. Phys. Chem.* **88,** 4622 (1984).
6. M. Jansen, *Angew. Chem.* **99,** 1136 (1987); *Angew. Chem. Int. Ed. Engl.* **26,** 1098 (1987).

7. M. Jansen *in* "Unkonventionelle Wechselwirkungen in der Chemie metallischer Elemente" (B. Krebs, Ed.), p. 412. VCH Press, Weinheim, 1992.
8. R. Curti, St. Locchi, and V. Riganti, *Chimia* **15,** 557 (1961).
9. F. P. Temme, J. A. Smith, and T. C. Waddington, *J. Chem. Soc., Faraday Trans. 1* (1973).
10. N. Walker and D. Stuart, *Acta Crystallogr., Sect. A* **39,** 158 (1983).
11. G. M. Sheldrick, "SHELXS-86. A Computer Program for Crystal Structure Solution," Univ. of Göttingen, 1986.
12. J. A. Ibers and W. C. Hamilton, "International Tables for X-Ray Crystallography," Vol. IV, pp. 99, 149. Kynoch Press, Birmingham, 1974.
13. G. M. Sheldrick, "SHELX-76. A Computer Program for Crystal Structure Determination," Univ. of Cambridge, England, 1976.
14. A. L. Spek, "Computational Crystallography" (D. Sayre, Ed.), p. 528. Clarendon, London/New York, 1982.
15. C. K. Johnson, ORTEP. Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.
16. R. Hoppe, *GIT Fachz. Lab* **4,** 297 (1993).
17. N. J. Harrick, "Optical Spectroscopy: Sampling Techniques Manual," Harrick Scientific Corp., New York, 1987.
18. A. Ferrari, A. Braibanti, and A. Tiripicchio, *Acta Crystallogr.* **19,** 629 (1965).
19. H. Wedemeyer, Thesis, Bergakademie Clausthal, FRG, 1965.
20. I. Mikhail, *Mater. Res. Bull.* **12,** 489 (1977).
21. K. M. Tobias and M. Jansen, *Z. Anorg. Allg. Chem.* **538,** 159 (1986).
22. A. Bondi, *J. Chem. Phys.* **68,** 441 (1964).
23. H. Y-P. Hong, J. A. Kafalas, and J. B. Goodenough, *J. Solid State Chem.* **9,** 345 (1974).
24. J. Donohue and L. Helmholz, *J. Am. Chem. Soc.* **66,** 295 (1944).
25. W. G. Palmer, "Experimental Inorganic Chemistry," pp. 114–115. Cambridge Univ. Press, London/New York, 1965.
26. G. A. Barclay, B. F. Hoskins, *J. Chem. Soc.* 2807 (1963).
27. M. Klassen, R. Hoppe, *Z. Anorg. Allg. Chem.* **485,** 92 (1982).
28. D. Fischer, W. Carl, H. Glaum, and R. Hoppe, *Z. Anorg. Allg. Chem.* **585,** 75 (1990).
29. G. Brachtel and M. Jansen, *Cryst. Struct. Commun.* **10,** 173 (1981).
30. B. U. Köhler and M. Jansen, *J. Solid State Chem.* **71,** 566 (1987).
31. M. Jansen and M. Bortz, *Z. Anorg. Allg. Chem.* **579,** 123 (1989).
32. S. Okamoto, S. I. Okamoto, and T. Ito, *Acta Crystallogr., Sect. B* **28,** 1774 (1972).
33. M. Jansen, *Z. Naturforsch. B* **30,** 854 (1975).
34. M. Jansen, *Z. Naturforsch. B* **31,** 1544 (1976).
35. K. S. Pitzer, R. E. Gerkin, L. V. Gregor, and C. N. R. Rao, *Pure Appl. Chem.* **2,** 211 (1961).
36. P. Behrens, *Solid State Commun.* **81,** 235 (1992).
37. R. Janoschek, E. Nachbaur, and A. Trnoska, 2nd Int. Conference Inorganic Chemistry, Abstract II-2, Stuttgart, FRG, 1993.