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Silver Oxalate, $2Ag^+.C_2O_4^{2-}$

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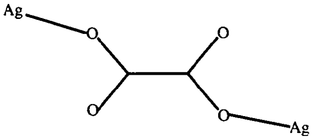
Abstract

The early data of Griffith [*J. Chem. Phys.* (1943), pp. 499–505] and of Kolesnikov & Baumer [*Vestn. Khar'k. Univ. Ser. Khim.* (1975), **127**, 38–41] on the structure of silver oxalate, $2Ag^+.C_2O_4^{2-}$, are revised and refined. In the structure, the oxalate anions form a framework with channels extended along [100] and Ag^+ cations are located in these channels, forming dimers with an Ag—Ag bond distance of 2.945 (1) Å (close to that in metallic Ag). A noticeable elongation of C—C bond is observed.

Comment

Metal oxalates have been used in studies of the various aspects of solid-state reactivity since the early 1940's and are still attracting attention today (Brown, Dollimore & Galwey, 1980). The first structural studies of oxalates were reported 60 years ago (Hendricks, 1935); however, crystal structures of many metal oxalates remain unknown, mainly because of the experimental difficulties in obtaining single crystals.

Early structural studies of $2Ag^+.C_2O_4^{2-}$ were reported by Griffith (1943) and by Kolesnikov & Baumer (1975), but there were discrepancies between the data sets reported. Besides, since photographic methods were used, both studies were not very precise. The value of R_f was not reported by Griffith (1943) but can be calculated from his published F_o and F_c values as 0.299 for 84 F_{hkl}. The value of R_f in the study of Kolesnikov & Baumer (1975) was 0.133 for 735 F_{hkl}. Since the precise data on the structure of $2Ag^+.C_2O_4^{2-}$, (I), are very important for understanding the mechanism of the photochemical and thermal decomposition of this salt (Boldyrev, 1993), we have undertaken a new structural study.



(I)

According to our data, the anion in the structure of silver oxalate is practically flat (deviations of C and O atoms from the common plane do not exceed 0.006 Å). The site symmetry is $\bar{1}$, but the geometry of the oxalate anion is very close to being idealized, with point symmetry *mmm*. The value of the C—C bond length (Table 2) somewhat exceeds the statistically averaged value [1.56 (2) Å] reported by Allen *et al.* (1987) for oxalate groups in various structures. The elongation of the C—C bond may be essential for the decomposition of silver oxalate, since, according to the model suggested, the primary step of the reaction is the cleaving of this bond (Boldyrev, 1993).

Each oxalate anion in the structure is coordinated to six Ag^+ cations. Two different types of Ag—O bonds are observed (Table 2). Oxalate anions form a framework with the layers in the (200) planes and the channels extended along [100]. Ag—Ag dimers are located in these channels; the Ag—Ag distance of 2.945 (1) Å is close to that in metallic silver (2.889 Å; Guinier, 1956). Each Ag atom is coordinated to four O atoms of three oxalate anions (forming a flattened tetrahedron) and another Ag atom (Fig. 1). Ag atoms in the structure form strips of a 'stair type' extended along [100] at $y = \frac{1}{2}$ and $y = 0$ (corresponding values of z are ±0.15 and $\frac{1}{2} \pm 0.15$). The width of a stair step is determined by the short Ag—Ag distance; the height of a step is equal to the translation along x.

The results of our study allow revision of the data of Griffith (1943) and refinement of that of Kolesnikov & Baumer (1975). The values of the lattice parameters and the structure of the silver sub-lattice obtained in our study are in reasonable agreement with the data reported by Kolesnikov & Baumer (1975). They can be correlated also with the model of Griffith (1943) if one assumes that the value of the β angle is 104° (and not 76°, as stated in the text of the Griffith's paper). The structure of the oxalate sub-lattice in our model is also similar to that proposed by Kolesnikov & Baumer (1975), but differs noticeably from the model of Griffith (1943). It should be noted that one can correlate the two models if the oxalate sub-lattice in Griffith's model is shifted with respect to the cation sub-lattice by a $\frac{1}{2}$ lattice translation along the *a* axis. The data on the internal geometry of the oxalate anion obtained in our study differ from those of Griffith (1943), but are in good agreement with the results of Kolesnikov & Baumer (1975), and are more precise than the latter.

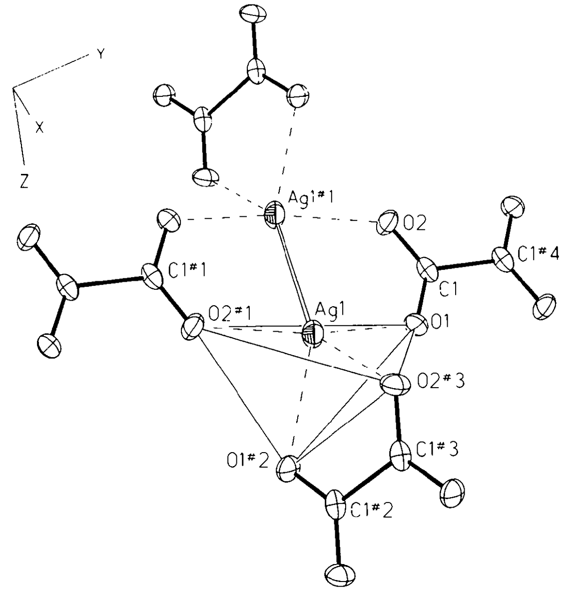


Fig. 1. The coordination of silver dimers by O atoms in the crystal structure of $2Ag^+.C_2O_4^{2-}$. Displacement ellipsoids are plotted at the 50% probability level.

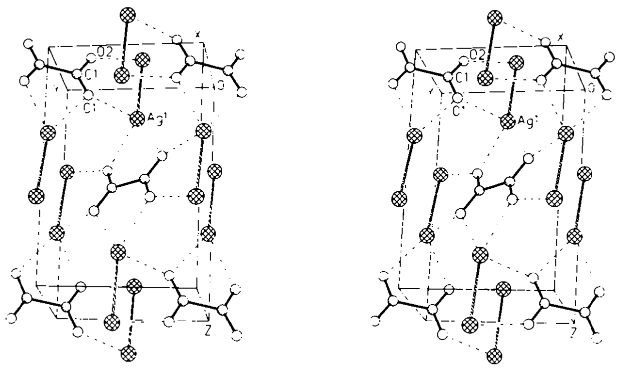


Fig. 2. Stereoplot of the crystal structure of $2Ag^+.C_2O_4^{2-}$ viewed along [100].

Experimental

Colourless crystals of $2Ag^+.C_2O_4^{2-}$ were grown using the technique described by Boldyrev (1963). Aqueous solutions of $Na_2C_2O_4$ (0.1 *M*) and $AgNO_3$ (0.2 *M*) were allowed to diffuse slowly into a reaction vessel filled with an aqueous solution of $NaNO_3$ (0.1 *M*). Crystal growth, crystal manipulations, and diffraction experiments were carried out under red light to prevent photochemical decomposition.

Crystal data

$2Ag^+.C_2O_4^{2-}$
$M_r = 303.76$
Monoclinic
$P2_1/c$
$a = 3.4603$ (5) Å
$b = 6.1972$ (9) Å
$c = 9.548$ (2) Å
$\beta = 103.47$ (1)°
$V = 199.12$ (6) Å^3
$Z = 2$
$D_x = 5.066$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 22 reflections
$\theta = 13$–27°
$\mu = 78.141$ mm^{-1}
$T = 300$ (2) K
Prism
0.17 × 0.08 × 0.06 mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{min} = 0.011$, $T_{max} = 0.121$
548 measured reflections
274 independent reflections
234 observed reflections $[I > 2\sigma(I)]$

$R_{int} = 0.0464$
$\theta_{max} = 57.17°$
$h = -3 \rightarrow 3$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 10$
3 standard reflections monitored every 47 reflections intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0259$
$wR(F^2) = 0.0519$
$S = 1.188$
274 reflections
38 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0206P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.580$ e Å^{-3}
$\Delta\rho_{min} = -0.647$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0058 (5)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ag1	0.1416 (2)	0.49443 (7)	0.15782 (6)	0.0257 (4)
O1	0.507 (2)	0.7859 (8)	0.1183 (6)	0.026 (1)
O2	0.175 (2)	0.8228 (7)	−0.1097 (6)	0.024 (1)
C1	0.403 (2)	0.884 (1)	0.0037 (9)	0.018 (2)

Table 2. *Selected geometric parameters* (Å, °)

Ag1—Ag1^{i}	2.945 (1)	Ag1—O2^{iii}	2.471 (6)
Ag1—O1	2.286 (5)	O1—C1	1.23 (1)
Ag1—O1^{ii}	2.551 (6)	O2—C1	1.24 (1)
Ag1—O2^{i}	2.245 (5)	C1—C1^{iv}	1.60 (1)

O1—Ag1—O1^{ii}	111.4 (1)	O2^{iii}—Ag1—Ag1^{i}	147.5 (1)
O1—Ag1—O2^{iii}	82.8 (2)	Ag1—O1—C1	118.6 (6)
O2^{i}—Ag1—O1	157.0 (2)	Ag1—O1^{ii}—C1^{ii}	118.6 (5)
O2^{i}—Ag1—O1^{ii}	81.0 (2)	Ag1—O2^{i}—C1^{i}	128.8 (5)
O2^{iii}—Ag1—O1^{ii}	64.3 (2)	Ag1—O2^{iii}—C1^{iii}	122.1 (4)
O2^{i}—Ag1—O2^{iii}	120.3 (1)	O1—C1—O2	128.4 (7)
O1—Ag1—Ag1^{i}	83.0 (2)	O1—C1—C1^{iv}	117 (1)
O1^{ii}—Ag1—Ag1^{i}	148.2 (1)	O2—C1—C1^{iv}	115.1 (9)
O2^{i}—Ag1—Ag1^{i}	77.3 (2)		

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (iv) $1-x, 2-y, -z$.

Data were collected using $\theta/2\theta$ scans with a variable scan rate of 1.98–14.5° min^{-1} and employing background counts for 0.25 of the total scan time on each side. The scan width was $[1.9 + 2\theta(\alpha_2) - 2\theta(\alpha_1)]$. Refinement was by full-matrix least-squares method on F^2 using all reflections with $I_{hkl} > 0$.

Data collection: *Recentering θ/2θ Collection Program* in *XTL* (Syntex, 1973). Cell refinement: $P2_1$ in *XTL*. Data reduction: *TAPER* in *XTL*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIFTAB* (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: VS1014). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diazidobis(2,2′-bipyridine)nickel(II) Monohydrate

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Abstract

The compound $[Ni(N_3)_2(bipy)_2].H_2O$ (I) (bipy = 2,2′-bipyridine) has been synthesized and its structure determined at room temperature. The coordination polyhedron of the Ni atom shows an octahedral topology with the two bipy and the two azido ligands in a *cis* arrangement. Two monomeric units form an outer-sphere dimer through hydrogen bonding with the water molecule to give the overall formula $[Ni(bipy)_2(N_3)_2]_2.2H_2O$.

Comment

Polynuclear nickel(II)–azido systems have been a focus of investigation in recent years (Arriortua, Cortés, Lezama, Rojo, Solans & Font-Bardia, 1990; Cortés, Urtiaga, Larramendi, Lezama, Arriortua & Rojo, 1992; Vicente, Escuer, Ribas, Salah El Fallah, Solans & Font-Bardia, 1994; Escuer, Vicente, Ribas, Salah El Fallah & Solans, 1994). Both dinuclear and chain structures have been obtained. The azide ion was chosen for its versatility of coordination; this includes both end-to-end and end-on bridging modes which lead to antiferromagnetic (Pierpoint, Hendrickson, Duggan, Wagner & Barefield, 1975) and ferromagnetic type interactions (Arriortua, Cortés, Lezama, Rojo, Solans & Font-Bardia, 1990), respectively, between the metallic centres.

The ligands selected to block the metal have been shown to play an important role in determining the final structure. The use of tridentate aromatic amine ligands, which favour *cis* coordination of the azido bridges, has led to dinuclear nickel(II) systems with end-on azido bridges, while the use of bidentate or tetradentate aliphatic amines, which favour *trans* coordination of the azido bridges, has led to nickel(II)–*trans*-azido chains. To our knowledge, no nickel(II)–*cis*-azido chains have been structurally characterized to date. The preparation of an appropriate precursor containing the azido ligands in the desired configuration may be useful in the synthesis of such *cis*-azido chain compounds. We decided,

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