high final R value is mainly due to the disorder of the polymethylene chain.

The authors thank the CNRS for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1021). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Baxter, L. A. M., Blake, A. J., Gould, R. O., Heath, G. A. & Stephenson, T. A. (1993). *Acta Cryst.* C**49**, 1311–1315.

Diantouba, B.-A., Guiguemde, I., Tayeb, A., Goetz-Grandmont, G. J. & Brunette, J. P. (1994). *Solvent Extr. Ion Exch.* **12**, 325–347.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Lakkis, M., Lakkis, Z., Goetz-Grandmont, G. J. & Brunette, J.-P. (1991). *Monatsh. Chem.* **122**, 9–15.

Li, X.-J. & Yang, R.-D. (1992). *Polyhedron*, **11**, 1545–1550.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Maslen, H. S. & Waters, T. N. (1975). *Coord. Chem. Rev.* **17**, 137–175.

Mehrotra, R. C., Bohra, R. & Gaur, D. P. (1978). *Metal β-Diketonates and Allied Derivatives.* London: Academic Press.

Miao, F.-M., Liu, X.-L. & Li, Y.-Q. (1991). *Wuji Huaxue Xuebao*, **7**(2), 129–132; *Chem. Abstr.* **116**, 245603r.

Miyazaki, S., Mukai, H., Umetani, S., Kihara, S. & Matsui, M. (1989). *Inorg. Chem.* **28**, 3014–3017.

Tobon-Cervantes, A., Toscano, R. A., Rosales, M. J., Fernandez-G., J. M. & Bernal-Uruchurtu, M. I. (1988). *Acta Cryst.* C**44**, 621–623.

Zolotov, Yu. A. & Kuz'min, N. M. (1977). *The Extraction of Metals by Acylpyrazolones.* Moscow: Nauka. (In Russian.)

Acta Cryst. (1995). C**51**, 57–60

Triruthenium Alkylidyne Cluster Complexes $[H_2Ru_3(CO)_9(\mu_3\text{-}CX)]$ (X = Pyridine, 4-Ethylpyridine)

WING-TAK WONG* AND WAI-YEUNG WONG

Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

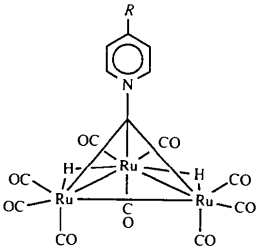
(*Received* 27 *September* 1993; *accepted* 19 *May* 1994)

Abstract

Crystal structure analyses of nonacarbonyl-1κ^3C,2κ^3C,3κ^3C-di-μ-hydrido-1:2κ^2H;2:3κ^2H-μ_3-(pyrid-1-ylmethylidyne)-*triangulo*-triruthenium, $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_5N)(CO)_9]$, (I), and nonacarbonyl-1κ^3C,2κ^3C,3κ^3C-μ_3-[(4-ethylpyrid-1-yl)methylidyne]-di-μ-hydrido-1:2κ^2H;2:3κ^2H-*triangulo*-triruthenium, $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}C_8H_9N)(CO)_9]$, (II), reveal that both compounds consist of a triruthenium alkylidyne core with the nucleophiles [pyridine in (I) and 4-ethylpyridine in (II)] bonded to the μ_3-bridging alkylidyne C atom.

Comment

This work is part of our structural and reactivity studies of triruthenium and triosmium alkylidyne carbonyl clusters. Several triosmium alkylidynes with the formula $[H_2Os_3(CO)_9(\mu_3\text{-}CY)]$ (Y = pyridine, quinoline or trimethyl phosphite) have been synthesized and fully characterized (Johnson, Lahoz, Lewis, Prior, Raithby & Wong, 1992). The title compounds, (I) and (II), have been prepared by a similar route.



(I) R = H
(II) R = Et

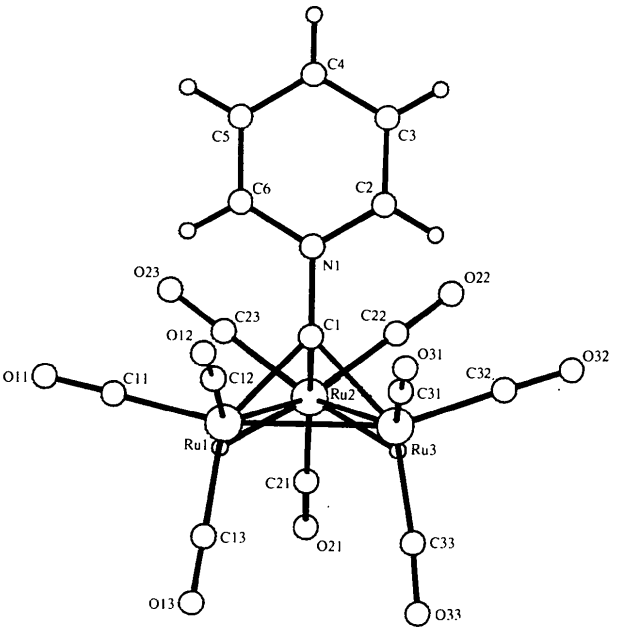


Fig. 1. The molecular structure of $[H_2Ru_3(CO)_9(\mu_3\text{-}Cpy)]$ (I).

The structures of (I) and (II), as shown by X-ray analyses, each consist of a triruthenium alkylidyne core with the nucleophile substituted at the apical C atom. Both molecules have approximate C_s symmetry. The hydride atoms of (I) and (II), evident from their ^{1}H NMR spectra, could not be located by X-ray analysis. However, potential-energy calculations (Orpen, 1980) suggested that one bridges the Ru1—Ru2 edge and the other the Ru2—Ru3 edge in both (I) and (II). These two edges [averages 2.844 Å for (I), 2.835 Å for (II)] are significantly longer than the unbridged Ru1—Ru3 bonds [2.739 (1) for (I), 2.729 (1) Å for (II)]. This is consistent with the general observation that M—M distances are increased when bridged by a hydride atom (Humphries & Kaesz, 1979). The N—C(alkylidyne) bond lengths in both (I) [1.46 (1) Å] and (II) [1.458 (9) Å] are comparable to those of the triosmium alkylidynes with other N-donors substituted on the apical C atom.

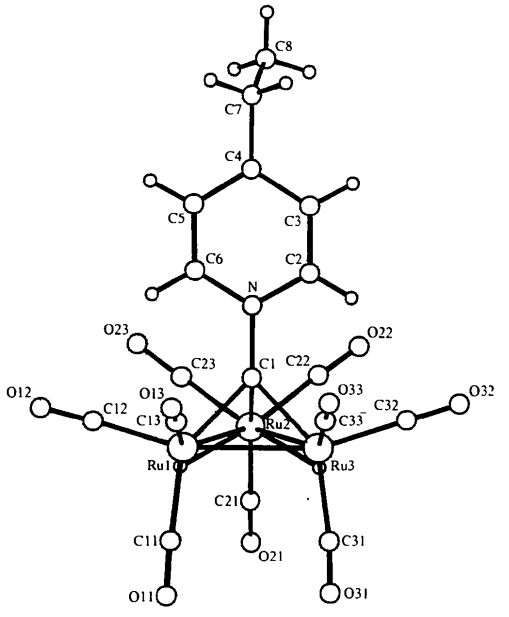


Fig. 2. The molecular structure of [$H_2Ru_3(CO)_9(\mu_3$-C{4-Etpy})] (II).

Experimental

Compound (I)

Crystal data

[$Ru_3H_2(C_6H_5N)(CO)_9$]
M_r = 648.43
Monoclinic
Cc
a = 18.585 (3) Å
b = 9.562 (1) Å
c = 15.012 (4) Å
β = 131.83 (3)°
V = 1987.8 (12) Å^3
Z = 4
D_x = 2.163 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–12°
μ = 2.25 mm^{-1}
T = 293 K
Block
0.22 × 0.16 × 0.14 mm
Orange
Crystal source: recrystallized from CH_2Cl_2/n-hexane

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
T_{min} = 0.901, T_{max} = 0.999
1456 measured reflections
1395 independent reflections
1295 observed reflections [$F_o > 3\sigma(F_o)$]
R_{int} = 0.022
θ_{max} = 22.5°
h = −20 — 20
k = 0 — 10
l = 0 — 16
3 standard reflections
frequency: 120 min
intensity variation: <2%

Refinement

Refinement on F
R = 0.037
wR = 0.050
S = 1.876
1295 reflections
126 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max}$ = 0.04
$\Delta\rho_{max}$ = 0.98 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (II)

Crystal data

[$Ru_3H_2(C_8H_9N)(CO)_9$]
M_r = 676.49
Orthorhombic
$P2_12_12_1$
a = 10.971 (2) Å
b = 11.034 (2) Å
c = 18.100 (5) Å
V = 2191.0 (14) Å^3
Z = 4
D_x = 2.051 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11–13°
μ = 2.05 mm^{-1}
T = 293 K
Block
0.32 × 0.22 × 0.20 mm
Orange
Crystal source: recrystallized from CH_2Cl_2/n-hexane

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
T_{min} = 0.895, T_{max} = 0.999
2221 measured reflections
2221 independent reflections
2046 observed reflections [$F_o > 3\sigma(F_o)$]
θ_{max} = 25°
h = 0 — 13
k = 0 — 13
l = 0 — 21
3 standard reflections
frequency: 120 min
intensity variation: <3%

Refinement

Refinement on F
R = 0.028
wR = 0.040
$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}

$S = 1.394$
2046 reflections
271 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
Extinction correction: none
Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for Ru atoms in (I) and all non-H atoms in (II); B_{iso} for all others.

	x	y	z	B_{iso}/B_{eq}
(I)				
Ru1	0.646†	0.06082 (9)	0.107†	2.58 (2)
Ru2	0.44197 (5)	0.05228 (9)	−0.08242 (6)	2.50 (2)
Ru3	0.56793 (6)	−0.12780 (8)	−0.07440 (8)	2.76 (2)
O11	0.6638 (6)	0.328 (1)	0.2320 (7)	5.1 (2)
O12	0.8308 (8)	0.109 (2)	0.1591 (9)	7.3 (3)
O13	0.7431 (8)	−0.147 (2)	0.316 (1)	8.1 (4)
O21	0.3069 (7)	−0.054 (1)	−0.0450 (8)	5.9 (3)
O22	0.2944 (7)	0.052 (1)	−0.3519 (8)	5.6 (2)
O23	0.4194 (6)	0.359 (1)	−0.0558 (7)	5.0 (2)
O31	0.7477 (7)	−0.130 (1)	−0.0419 (9)	6.4 (3)
O32	0.4451 (8)	−0.237 (2)	−0.3263 (9)	7.5 (3)
O33	0.6159 (7)	−0.396 (2)	0.0713 (9)	6.4 (3)
N1	0.5553 (5)	0.193 (1)	−0.1453 (6)	2.6 (2)
C1	0.5564 (5)	0.086 (1)	−0.0753 (7)	1.9 (2)
C2	0.5185 (7)	0.168 (2)	−0.2559 (9)	3.8 (2)
C3	0.5112 (8)	0.271 (2)	−0.328 (1)	4.6 (3)
C4	0.5407 (7)	0.404 (1)	−0.2841 (9)	3.3 (2)
C5	0.5813 (8)	0.429 (1)	−0.170 (1)	3.9 (2)
C6	0.5875 (6)	0.325 (1)	−0.1021 (8)	3.0 (2)
C11	0.6582 (6)	0.226 (1)	0.1844 (8)	3.3 (2)
C12	0.7584 (8)	0.090 (2)	0.1354 (9)	4.2 (3)
C13	0.7039 (8)	−0.069 (2)	0.237 (1)	4.2 (3)
C21	0.3601 (7)	−0.017 (1)	−0.0550 (8)	3.3 (2)
C22	0.3470 (7)	0.055 (1)	−0.2497 (8)	3.3 (2)
C23	0.4258 (6)	0.243 (1)	−0.0664 (8)	3.1 (2)
C31	0.6789 (7)	−0.129 (1)	−0.0529 (9)	3.3 (2)
C32	0.4919 (7)	−0.194 (1)	−0.2314 (8)	3.8 (2)
C33	0.5953 (8)	−0.298 (2)	0.012 (1)	4.9 (3)
HA‡	0.5329	0.0736	0.0749	5
HB‡	0.4519	−0.1223	−0.1133	5
(II)				
Ru1	0.46060 (5)	0.10649 (4)	0.01346 (3)	2.873 (9)
Ru2	0.51780 (5)	−0.14357 (4)	0.01192 (3)	3.15 (1)
Ru3	0.35897 (5)	−0.03952 (5)	0.11844 (3)	3.47 (1)
O11	0.2242 (5)	0.1436 (5)	−0.0758 (4)	5.9 (1)
O12	0.6472 (5)	0.2137 (5)	−0.0903 (3)	5.5 (1)
O13	0.4423 (6)	0.3338 (5)	0.1077 (3)	6.4 (1)
O21	0.3920 (7)	−0.2921 (5)	−0.1087 (3)	6.4 (2)
O22	0.6052 (9)	−0.3539 (5)	0.1065 (3)	8.4 (2)
O23	0.7658 (6)	−0.0990 (6)	−0.0580 (4)	6.7 (2)
O31	0.0981 (5)	−0.0095 (6)	0.0612 (4)	6.8 (2)
O32	0.3460 (9)	−0.2397 (6)	0.2361 (4)	8.3 (2)
O33	0.3354 (8)	0.1612 (6)	0.2315 (3)	7.8 (2)
N1	0.6455 (5)	0.0084 (5)	0.1384 (3)	3.0 (1)
C1	0.5378 (7)	−0.0062 (5)	0.0921 (3)	3.2 (1)
C2	0.6499 (7)	−0.0434 (7)	0.2050 (4)	4.4 (2)
C3	0.753 (1)	−0.0316 (7)	0.2479 (4)	5.6 (2)
C4	0.8542 (8)	0.0341 (7)	0.2241 (4)	4.5 (2)
C5	0.8469 (7)	0.0842 (7)	0.1547 (4)	4.3 (2)
C6	0.7427 (7)	0.0729 (6)	0.1142 (4)	3.7 (1)
C7	0.964 (1)	0.050 (1)	0.2727 (5)	8.5 (3)
C8	1.049 (1)	−0.056 (2)	0.2694 (6)	12.7 (5)
C11	0.3127 (7)	0.1336 (6)	−0.0435 (4)	4.0 (1)
C12	0.5825 (7)	0.1724 (6)	−0.0517 (4)	3.4 (1)
C13	0.4503 (7)	0.2484 (7)	0.0738 (4)	4.1 (1)
C21	0.4404 (7)	−0.2409 (6)	−0.0665 (4)	4.0 (1)
C22	0.5750 (9)	−0.2752 (6)	0.0718 (4)	5.0 (2)
C23	0.6713 (7)	−0.1211 (6)	−0.0332 (4)	3.9 (1)
C31	0.1897 (7)	−0.0263 (7)	0.0835 (5)	4.7 (2)
C32	0.3525 (9)	−0.1655 (8)	0.1920 (5)	5.5 (2)
C33	0.3433 (8)	0.0856 (8)	0.1890 (4)	4.8 (2)
HA‡	0.4864	−0.0214	−0.0477	5
HB‡	0.3811	−0.1720	0.0592	5

† Coordinate fixed to define origin.
‡ These atoms were not located in the analyses. Their positions were deduced from potential-energy calculations (Orpen, 1980).

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

	(I)	(II)
Ru1—Ru2	2.8440 (6)	2.8297 (7)
Ru1—Ru3	2.739 (1)	2.7291 (8)
Ru2—Ru3	2.843 (2)	2.8409 (8)
Ru1—C1	2.060 (8)	2.071 (6)
Ru2—C1	2.08 (1)	2.109 (7)
Ru3—C1	2.06 (2)	2.052 (7)
N1—C1	1.46 (1)	1.458 (9)
N1—C2	1.33 (2)	1.335 (9)
N1—C6	1.35 (2)	1.35 (1)
C2—C3	1.40 (2)	1.38 (1)
C3—C4	1.36 (3)	1.39 (1)
C4—C5	1.36 (2)	1.37 (2)
C5—C6	1.38 (3)	1.51 (1)
C5—C6	–	1.36 (2)
C7—C8	–	1.50 (2)
Ru1—*HA*	1.82	1.82
Ru2—*HA*	1.78	1.76
Ru2—*HB*	1.78	1.76
Ru3—*HB*	1.82	1.83
Ru2—Ru1—Ru3	61.19 (4)	61.44 (2)
Ru1—Ru2—Ru3	57.59 (3)	57.54 (2)
Ru1—Ru3—Ru2	61.22 (3)	61.02 (2)
Ru1—C1—Ru2	86.7 (5)	85.3 (2)
Ru1—C1—Ru3	83.4 (3)	82.9 (3)
Ru2—C1—Ru3	86.7 (5)	86.1 (3)
C1—N1—C2	121 (1)	120.0 (6)
C1—N1—C6	122 (1)	120.7 (5)
C2—N1—C6	118 (2)	119.3 (6)
C4—C7—C8	–	112 (2)
Ru1—*HA*—Ru2	104.5	104.2
Ru2—*HB*—Ru3	104.6	104.0

The metal-atom positions were obtained by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Each structure was refined by a full-matrix least-squares method with anisotropic displacement parameters for the Ru atoms in (I) and for all non-H atoms in (II). All calculations were performed using the *SDP* system (Enraf–Nonius, 1985) on a MicroVAX II computer. The absolute structures were assigned on the basis of the lowest R values after identical refinements.

We thank the Hong Kong Research Grants Council and the University of Hong Kong for support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: MU1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1985). *Structure Determination Package. SDP/PDP User's Guide.* Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Humphries, A. P. & Kaesz, H. D. (1979). *Prog. Inorg. Chem.* **25**, 145–222.
Johnson, B. F. G., Lahoz, F. J., Lewis, J., Prior, N. D., Raithby, P. R. & Wong, W.-T. (1992). *J. Chem. Soc. Dalton Trans.* pp. 1701–1708.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Orpen, A. G. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2509–2516.

Acta Cryst. (1995). C**51**, 60–62

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

DMITRY YU. NAUMOV

Novosibirsk State University, Pirogova Street 2, Novosibirsk 630090, Russia

ALEXANDER V. VIROVETS AND NINA V. PODBEREZSKAYA

Institute of Inorganic Chemistry SD RAS, Ak.Lavrent'eva Street 3, Novosibirsk 630090, Russia

ELENA V. BOLDYREVA

Institute of Solid State Chemistry SD RAS, Derzhavina Street 18, Novosibirsk 630090, Russia

(*Received* 6 *April* 1994; *accepted* 14 *July* 1994)

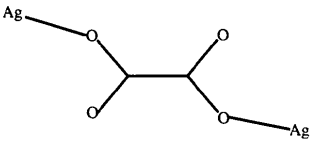
Abstract

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