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Structure of Pentasilver(I) Dicopper(II) Mononitrate Tetraselenite(IV)

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Abstract. Ag₅Cu₂(NO₃)(SeO₃)₄, $M_r = 1236.26$, triclinic, $P\bar{1}$, $a = 5.148$ (2), $b = 7.050$ (2), $c = 10.540$ (3) Å, $\alpha = 73.09$ (1), $\beta = 89.08$ (1), $\gamma = 88.50$ (1)°, $V = 365.85$ Å³, $Z = 1$, $D_x = 5.61$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 18.6$ mm⁻¹, $F(000) = 556$, room temperature, $R(F) = 0.045$ for 3026 independent reflections with $F_o > 3\sigma(F_o)$ and 143 variables. Elongated tetragonal dipyramids Cu^{[4+2]O₆} and SeO₃ groups are corner connected to form layers in (010). Irregularly coordinated Ag atoms with Ag—O ≥ 2.202 Å join them to form a three-dimensional network. The orientation of the nitrate group is disordered with the N atom formally on $\bar{1}$.

Introduction. Syntheses within the system Ag₂O—CuO—SeO₂ and nitric solvents produced the new compound Ag₅Cu₂(NO₃)(SeO₃)₄. Copper(II)-nitrate-selenite(IV) salts are known from the two compounds PbCu₃(OH)(NO₃)(SeO₃)₃·½H₂O and Pb₂Cu₃O₂(NO₃)₂(SeO₃)₂ (Effenberger, 1986). In connection with systematic studies of the stereochemistry of Cu^{II} with O atoms the crystal structure of the title compound was determined.

Experimental. For synthesis 2 g of an equimolar mixture of Cu(OH)₂, SeO₂ and AgNO₃ were heated under hydrothermal conditions in a Teflon-lined autoclave (~6 ml capacity, $T = 503$ K, 80% degree of filling, reaction time 2 d). The ratio of primary products can be varied over a wide range yielding the same reaction products but in different amounts. The

title compound forms emerald green, multifaceted crystals, typically 0.1 to 0.5 mm in diameter, which were easily separated from the accompanying reaction products (Ag₂SeO₃ and CuSeO₃·2H₂O) by hand picking.

Single-crystal X-ray Weissenberg photographs showed a metrically triclinic cell. Data collection from a 0.16 × 0.23 × 0.39 mm single crystal, crystallographic forms {010}, {011}, {01 $\bar{1}$ }, {001}, {210}, {211} and {021}; Stoe-AED2 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from 75 reflections with $44.3 \leq 2\theta \leq 55.0^\circ$; $2\theta/\omega$ -scan mode, step width of 1.44° increased for α_1 - α_2 dispersion, 0.24° on each side for background correction, scan speed 1.2 to 3.6° per min; three standard reflections, intensity drop 14% during data collection; 7021 reflections in the range $4.0 \leq 2\theta \leq 70.0^\circ$ ($h: -8 \rightarrow 8$, $k: -11 \rightarrow 11$, $l: -17 \rightarrow 17$), 3221 reflections in unique data set [$R_{\text{int}}(F^2) = 0.060$], 3026 reflections with $F_o > 3\sigma(F_o)$ were used for structure refinement, absorption correction according to crystal shape (Gaussian integration: transmission factors from 0.021 to 0.162), corrections for Lorentz and polarization effects. Complex neutral atomic scattering functions (*International Tables for X-ray Crystallography*, 1974, Vol. IV). All calculations were performed with the program system STRUCSY on an ECLIPSE S140 (Data General). Some of the atomic coordinates of the Ag, Cu and Se atoms were located by direct methods, the others by subsequent Fourier and difference Fourier summations. The nitrate group shows an

orientational disorder with the N atom formally on a centrosymmetric position according to the average space group $P\bar{1}$. The appearance of superstructure reflections on long-time exposure Weissenberg film photographs was not observed, nor could ordering due to a lower space group symmetry be verified within the accuracy of the structure refinement. Several cycles of least-squares refinement on F with anisotropic displacement parameters for all atoms and a split model for the nitrate group gave $R = 0.045$ and $wR = 0.047$, $w = [\sigma(F_o)]^{-2}$ (143 variables). $\Delta/\sigma < 10^{-3}$; maximum and minimum heights in the final difference Fourier summation are 3.4 and $-3.1 \text{ e } \text{Å}^{-3}$, highest maxima near the Ag atoms. Extinction correction gave $g = 1.89 (7) \times 10^{-5}$ (Zachariassen, 1967). The final atomic coordinates are compiled in Table 1,* Table 2 gives some important interatomic distances and angles.

Discussion. The coordinations of the three crystallographically different Ag atoms exhibit distinct coordination figures, symmetry is $\bar{1}$ for atom Ag(1) and 1 for atoms Ag(2) and Ag(3). The nearest-neighbour environments of atoms Ag(1) and Ag(2) are well defined: ligands are exclusively O atoms of the ordered selenite groups whereas some of the O atom ligands of the Ag(3) atom belong to nitrate groups which show orientational disorder.

The linear [2] coordination of the Ag(1) atom in $\text{Ag}_5\text{Cu}_2(\text{NO}_3)(\text{SeO}_3)_4$ with Ag—O bond distances of 2.384 Å is worth mentioning, although it is known from a few Ag^I oxides. The Ag^[2]—O bond lengths are always shorter than in the title compound: in Ag₂O, Ag—O is 2.051 Å (Swanson, Morris, Stinchfield & Evans, 1962) in monoclinic and tetragonal Ag^IAg^{III}O₂ the two Ag^I—O bond lengths are 2.161 (5) and 2.183 (3) Å, respectively (Jansen & Fischer, 1988; Yvon, Bezingé, Tissot & Fischer, 1986); and in rhombohedral and hexagonal Ag^IFe^{III}O₂ the Ag—O bond distances are 2.067 (8) and 2.07 (1) Å, respectively (Prewitt, Shannon & Rogers, 1971; Okamoto, Okamoto & Ito, 1972). Peculiar are the high anisotropic displacement parameters of the Ag(1) atom: the r.m.s. amplitudes are 0.307, 0.224 and 0.148 Å. In addition, the sum of bond valences calculated according to Brown & Altermatt (1985) amounts to 0.74 v.u. which seems to be definitely too small for monovalent silver. Therefore, the obvious supposition is that the disorder concerns not only the nitrate group but also the Ag(1) atom. The delocalization of the Ag(1)

Table 1. Atomic fractional coordinates and equivalent isotropic displacement factors (Å^2) with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ag(1)	0	$\frac{1}{2}$	0	0.0606 (5)
Ag(2)	0.49712 (9)	0.28547 (6)	0.14190 (3)	0.0319 (2)
Ag(3)	0.95412 (9)	0.42839 (7)	0.31704 (5)	0.0409 (2)
Cu(1)	0	0	0	0.0148 (3)
Cu(2)	$\frac{1}{2}$	0	$\frac{1}{2}$	0.0164 (3)
Se(1)	0.00564 (7)	-0.03145 (6)	0.32410 (3)	0.0148 (2)
O(11)	0.1943 (6)	0.1057 (5)	0.3923 (2)	0.019 (1)
O(12)	0.0748 (6)	0.0835 (5)	0.1612 (3)	0.022 (1)
O(13)	-0.2881 (6)	0.0780 (6)	0.3368 (3)	0.022 (1)
Se(2)	0.47566 (8)	0.75135 (6)	0.16446 (3)	0.0162 (2)
O(21)	0.3145 (6)	0.8277 (5)	0.0161 (3)	0.023 (1)
O(22)	0.3620 (8)	0.5206 (5)	0.2280 (3)	0.029 (2)
O(23)	0.7769 (6)	0.7012 (6)	0.1153 (3)	0.026 (2)
N	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.026 (3)
O(1)	0.7364 (19)	0.5609 (18)	0.4584 (8)	0.048 (5)
O(2)	0.3559 (18)	0.6443 (14)	0.5044 (8)	0.039 (4)
O(3)	0.5396 (17)	0.6609 (11)	0.4573 (6)	0.030 (4)

Table 2. Selected interatomic distances (Å) and bond angles (°)

Bond distances Ag—O and Ag—Ag < 3.50 and Cu—O < 3.00 Å are listed. Indices indicate the distinct orientation of the nitrate group (simultaneous occurrence of interatomic distances indexed *a* and *b* or *c* and *d*, respectively, is impossible).

Ag(1)—O(23)	2.384 (3)	2 ×	Ag(3)—O(1)	2.248 (10) ^r
Ag(1)—O(21)	2.902 (3)	2 ×	Ag(3)—O(22)	2.316 (3)
Ag(1)—O(12)	2.953 (3)	2 ×	Ag(3)—O(2)	2.395 (8) ^r
Ag(1)—O(22)	3.103 (3)	2 ×	Ag(3)—O(11)	2.483 (3)
Ag(2)—O(22)	2.202 (3)		Ag(3)—O(23)	2.587 (3)
Ag(2)—O(21)	2.243 (3)		Ag(3)—O(13)	2.748 (3)
Ag(2)—O(13)	2.413 (3)		Ag(3)—O(1)	2.894 (9) ^r
Ag(2)—O(12)	2.603 (3)		Ag(3)—O(22)	3.198 (3)
Ag(2)—O(11)	3.004 (2)		Ag(3)—O(3)	3.248 (7) ^r
Ag(2)—O(23)	3.052 (3)		Ag(3)—O(12)	3.348 (3)
Ag(2)—O(23)	3.236 (3)		Ag(3)—O(3)	3.396 (7) ^r
Ag(2)—O(12)	3.247 (3)		Ag(3)—O(3)	3.477 (7) ^r
Ag(1)—Ag(2)	3.111 (1)	2 ×	Ag(1)—Ag(3)	3.237 (1)
Ag(1)—Ag(2)	3.161 (1)	2 ×	Ag(2)—Ag(3)	3.362 (1)
O(22)—Ag(2)—O(21)	153.8 (3)		O(1)—Ag(3)—O(11)	122.4 (4)
O(22)—Ag(2)—O(13)	97.1 (1)		O(22)—Ag(3)—O(2)	152.5 (5)
O(21)—Ag(2)—O(13)	100.7 (1)		O(22)—Ag(3)—O(11)	79.5 (1)
O(1)—Ag(3)—O(22)	125.4 (3)		O(2)—Ag(3)—O(11)	95.6 (2)
Cu(1)—O(21)	1.978 (3)	2 ×	Cu(2)—O(11)	1.956 (2)
Cu(1)—O(12)	1.999 (3)	2 ×	Cu(2)—O(13)	1.968 (2)
Cu(1)—O(23)	2.414 (3)	2 ×	Cu(2)—O(3)	*2.560 (7)
			Cu(2)—O(2)	*2.621 (9)
Se(1)	O(11)	O(12)	O(13)	
O(11)	1.694 (3)	2.571 (4)	2.586 (4)	
O(12)	98.2 (2)	1.708 (2)	2.602 (4)	
O(13)	99.2 (2)	99.5 (2)	1.701 (3)	
Se(2)	O(21)	O(22)	O(23)	
O(21)	1.718 (2)	2.629 (5)	2.642 (5)	
O(22)	101.2 (2)	1.685 (3)	2.603 (5)	
O(23)	101.7 (2)	101.0 (2)	1.688 (3)	
N	O(1)	O(2)	O(3)	
O(1)	1.33 (1)	2.12 (1)	2.13 (1)	
O(2)	110.4 (7)	1.26 (1)	2.13 (2)	
O(3)	120.9 (8)	127.6 (8)	1.12 (1)	

* Only two of these four additional Cu—O bond distances occur in one $\text{Cu}^{4+2}\text{O}_6$ polyhedron.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54341 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atoms off the $\bar{1}$ position (either statistically or dynamically) towards the additional ligands might increase the coordination number of Ag(1) according to a decrease of the Ag—O distances.

The irregular coordination figures found for the atoms Ag(2) and Ag(3) agree well with crystal chemical experience. The sum of bond valences is 1.18 v.u. for the Ag(2) atom and varies from 0.98 to 1.13 v.u. for Ag(3) depending on the distinct orientation of the nitrate group (coordination numbers [5] or [6]). Consequently the Ag(2) atom has the lowest r.m.s. amplitudes of the three Ag atoms in the title compound (0.214, 0.170 and 0.130 Å), whereas the Ag(3) atom has r.m.s. amplitudes of 0.265, 0.166 and 0.156 Å.

Both Cu atoms (site symmetry $\bar{1}$) are tetragonal bipyramidally [4 + 2] coordinated by O atoms; this distortion from a regular octahedron is well known for divalent Cu atoms due to their electron configuration d^9 (Jahn–Teller effect). The average \langle Cu—O \rangle bond lengths of the four equatorial O atoms differ significantly for the two Cu atoms (1.989 and

1.962 Å). The nearest-neighbour environment is an approximate square; the O—Cu—O angles deviate by ± 4.6 (1)° and ± 1.7 (1)° from 90°, corresponding O—O edges vary from 2.697 (4) to 2.922 (5) Å. The deviation from a regular coordination is somewhat larger for the apices: the distortion of the angles O_{equatorial}—Cu—O_{apical} is up to ± 11.9 (2)°, the edges O_{equatorial}—O_{apical} vary from 2.934 (10) to 3.588 (10) Å. The six ligands of the Cu(1) atoms and the four nearest neighbours of the Cu(2) atom are exclusively formed by O atoms of selenite groups; the apical ligands of the Cu(2) atom belong to the nitrate group; this seems to be the reason for the somewhat higher temperature factor of the Cu(2) atom as compared to the Cu(1) atom.

The average \langle Se—O \rangle bonds of the two selenite groups are equal to each other within limits of error. In contrast, the \langle O—Se—O \rangle angle at the Se(1) atom (99.0°) is significantly smaller than at the Se(2) atom (101.3°), in accordance the average \langle O—O \rangle edges are 2.586 and 2.625 Å, respectively. It is to be expected that these differences result from the particular connection of the selenite groups with the other coordination polyhedra: each of the three O atoms of the Se(1)O₃ group participates in a short Cu—O bond, only one O atom of the Se(2)O₃ group takes part in the formation of a short Cu—O bond and another one in a long Cu—O bond; the third O atom of the Se(2)O₃ group is not involved in the coordination of the Cu atoms. On the contrary the shortest Ag—O bonds are formed with O atoms of the Se(2)O₃ group.

As mentioned above the nitrate group shows an orientational disorder restricted by an inversion centre which causes inaccurate atomic coordinates of O(1), O(2) and O(3). N—O(1) seems to be too long, N—O(3) too short; nevertheless the sequence of individual N—O bond lengths coincides with the distinct coordination of each of the three atoms O(1), O(2) and O(3).

The crystal structure of Ag₅Cu₂(NO₃)(SeO₃)₄ consists of sheets in (010) formed by a corner connection of CuO₄ squares and Se(1)O₃ groups. Se(2)O₃ groups are branched to these sheets *via* the atoms O(21) and O(23) (Fig. 1). Connection is achieved by the complex coordination polyhedra of the Ag atoms. The nitrate group is bound to the Cu(2) atom (additional ligands) and to the Ag(3) atom. The linkage of the coordination polyhedra in the title compound is in accordance with a good cleavage parallel to (010).

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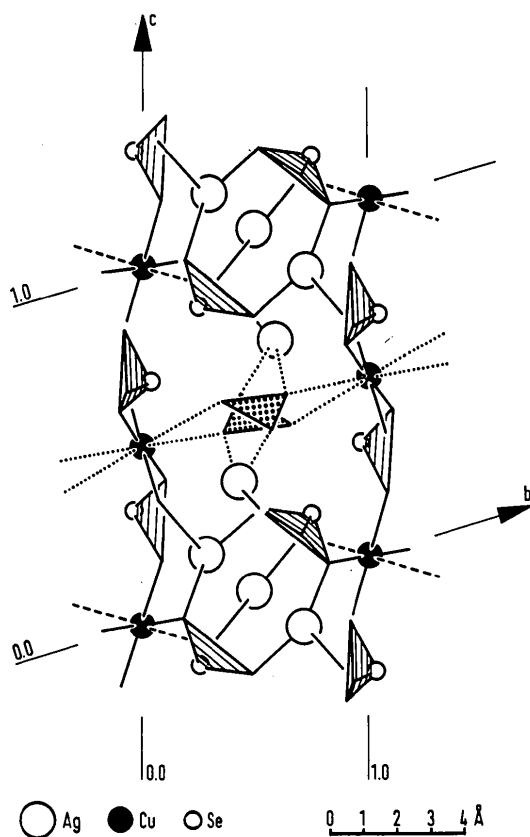


Fig. 1. The crystal structure of Ag₅Cu₂(NO₃)(SeO₃)₄ projected on (100). The selenite groups are hatched, the nitrate groups are dotted. Both orientations of the nitrate group are indicated; Ag—O and Cu—O bonds to the half occupied O-atom positions are dotted, additional Cu(1)—O bonds are drawn by a broken line.

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Structure of $[\text{Et}_4\text{N}][\text{In}\{\text{Co}(\text{CO})_4\}_3]$

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Abstract. Tetraethylammonium iodotris(tetracarbonylcobaltio)indate(1⁻), $\text{C}_8\text{H}_{20}\text{N}^+\text{C}_{12}\text{Co}_3\text{IInO}_{12}$, $M_r = 884.9$, monoclinic, $P2_1/c$, $a = 11.341$ (1), $b = 16.551$ (1), $c = 16.429$ (1) Å, $\beta = 92.110$ (6)°, $V = 3081.7$ (4) Å³, $Z = 4$, $D_x = 1.91$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 33.6$ cm⁻¹, $F(000) = 1704$, $T = 298$ K, $R = 0.039$ for 3647 unique observed reflections. The anion contains an indium atom coordinated to an iodine and three cobalt atoms in a slightly distorted tetrahedral environment.

Introduction. There are several examples of cobalt carbonyl complexes containing indium (Clarkson, McCrudden, Norman & Farrugia, 1990) and herein we report the structure of $[\text{Et}_4\text{N}][\text{In}\{\text{Co}(\text{CO})_4\}_3]$ (1). Compound (1) completes a series of the general formula $[\text{In}X_n\{\text{Co}(\text{CO})_4\}_{4-n}]^-$ (A), where X is a halide. Previous examples are $[\text{PPN}][\text{InBr}_3\{\text{Co}(\text{CO})_4\}_2]$ (2) (PPN = $\text{Ph}_3\text{PNPPH}_3^+$) (Burlitch, Leonowicz, Petersen & Hughes, 1979), $[\text{Et}_4\text{N}][\text{InBr}_2\{\text{Co}(\text{CO})_4\}_2]$ (3) (Cradwick, 1971), $[\text{Q}][\text{InCl}_2\{\text{Co}(\text{CO})_4\}_2]$ [$\text{Q} = \text{PPN}$ (4); $\text{Q} = \text{Co}(\text{CO})_3(\text{PPh}_3)_2$ (5)] (Clarkson *et al.*, 1990) and $[\text{Ph}_4\text{As}][\text{In}\{\text{Co}(\text{CO})_4\}_4]$ (6) (Robinson & Schussler, 1971). Compounds (3)–(5) have been structurally characterized. A crystal of (1) was obtained from the reaction between $\text{K}[\text{Co}(\text{CO})_4]$ and $[\text{In}\{\text{Co}(\text{CO})_4\}_3]$ followed by addition of $[\text{Et}_4\text{N}]\text{I}$ and crystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$ mixtures, although this pro-

cedure afforded $[\text{Et}_4\text{N}][\text{In}\{\text{Co}(\text{CO})_4\}_4]$ as the main product. With regard to the formation of (1), we note that the reaction between $[\text{In}\{\text{Co}(\text{CO})_4\}_3]$ and $[\text{Ph}_4\text{As}]\text{Cl}$ was reported (Robinson & Schussler, 1971) to give a compound $[\text{Cl}(\text{In}\{\text{Co}(\text{CO})_4\}_3)_2]^-$, with no evidence for a 1:1 indium-halide species. Compound (1) is therefore the first of type A with $n = 1$.

Experimental. Yellow prisms from dichloromethane/hexane solution: crystal dimensions ca $0.4 \times 0.4 \times 0.5$ mm; systematic absences: $k = 2n + 1$ in $0k0$; $l = 2n + 1$ in $h0l$; Enraf-Nonius CAD-4F diffractometer; graphite monochromator; $\theta/2\theta$ scan mode; cell parameters refined by least-squares methods from setting angles of 25 independent reflections with $11 < \theta < 13^\circ$; intensities measured to $\theta = 25.0^\circ$ over hkl range 0 to 13, 0 to 19, -19 to 19; $\bar{2}77$, $\bar{1}$, $11,0$ and $\bar{3},10,\bar{1}$ measured every 2 h with a 5% decay over 49.5 h data collection; 5398 data measured, 5423 independent data with 3647 having $I > 3.0\sigma(I)$ considered observed and used in structure determination and refinement; R_{int} 0.134 before and 0.036 after absorption correction; corrected for decomposition, L_p and absorption (DIFABS; Walker & Stuart, 1983), max., min. values of applied absorption correction 1.27, 0.73. Solved by direct methods (MITHRIL; Gilmore, 1984) and subsequent full-matrix least squares; anisotropic thermal parameters for all non-H atoms, fixed isotropic thermal parameters ($U = 0.08$ Å²) for H atoms; H atoms included at calculated positions ($\text{C}-\text{H} = 1.0$ Å); $\sum w(|F_o| -$

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