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CRYSTAL STRUCTURES OF SILVER(I) BENZOATE AND p-HYDROXYBENZOATE

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An x-ray structural study of the complexes $[Ag_2(C_6H_5COO)_2]$ (I) and $[Ag_2(HO-C_6H_4COO)_2]\cdot H_2O$ (II) has been carried out (λMoK_α, Syntex $P2_1$ automatic diffractometer, heavy atom method, refinement by the method of least squares in the anisotropic approximation). The crystals of complex I are orthorhombic, $a=6.297(5)$, $b=8.987(6)$, $c=23.771(15)$ Å, $\alpha=\beta=\gamma=90°$, $d_{calc}=2.26$ g/cm^3, $Z=4$, $V=1345.26$ Å^3, space group $P2_12_12_1$, $R=0.067$. The crystals of complex II are monoclinic, $a=6.193(7)$, $b=9.067(17)$, $c=14.218(20)$ Å, $\beta=103.749°$, $d_{calc}=1.58$ g/cm^3, $Z=2$, $V=775.58$ Å^3, space group $P2_1/a$, $R=0.068$. The crystal structures of complexes I and II consist of isolated dinuclear molecules. The Ag–Ag distances are 2.92 and 2.90 Å respectively. The carboxylate groups act as bidentate bridging ligands, forming eight-membered rings. The average Ag–O distance is 2.21 Å. The crystal structures of complexes I and II differ in that in the case of complex II, hydrogen bonds (O...O 2.699 Å) are formed between the water molecule and the OH group of the para-hydroxybenzoate ligand.

The study of the structure of complexes of monovalent silver with metabolites is of considerable interest for bioinorganic chemistry [1] and is obviously also required for the development of the stereochemistry of Ag(I) compounds.

A large number of structural studies have established that the formation of eight-membered rings with the participation of two Ag(I) atoms is typical of this oxidation state of the complex-forming metal [2-8].

In [6], on the basis of a structural study of nitrato(1-methylcytosine)silver(I), the authors tried to relate this characteristic feature of Ag(I) to its possible interaction with DNA. It was also established that rings involving silver are also formed in complexes with p-aminobenzoic acid [8]; here, the amino-group of the ligand also enters the coordination sphere.

In a systematic study of the complexes of derivatives of benzoic acid with metals, it was possible to obtain single crystals of the complexes of Ag(I) with benzoic and p-hydroxybenzoic acids, the structural study of which promised to be of interest for the determination of the influence of substituents in the para-position on the characteristic stereochemical features of eight-membered rings with Ag atoms. The present paper gives the results of the determination of the structures of two of these complexes.

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TABLE 1. Crystallographic Data for Complexes I and II

Crystallographic data	I	II
Molecular weight	457,76	527,76
Cell parameters: a, Å	6,297(5)	6,193(7)
b, Å	8,987(6)	9,067(17)
c, Å	23,771(15)	14,218(20)
β, deg	90	103,74(9)
V, Å^3	1345,35	775,6
Space group	$P2_12_12_1$	$P2_1/a$
Z	4	2
d_{calc}, g/cm^3	2,62	1,58
Crystal dimensions, mm	0,14×0,22×0,17	0,16×0,24×0,18

TABLE 2. Coordinates of the Atoms (× 10^4 for Ag, × 10^3 for the other atoms)

Atom	x	y	z	Atom	x	y	z
	Complex I						
Ag(1)	1864(3)	500(2)	2223(1)	H(7)	911	25	13
Ag(2)	3305(3)	3236(2)	2747(1)	H(8)	983	180	30
O(1)	−74(3)	86(1)	285(1)	H(9)	991	338	100
O(2)	1(3)	325(2)	308(1)	H(10)	961	322	180
O(3)	599(2)	298(2)	215(1)				
O(4)	510(3)	66(2)	186(1)		Complex II		
C(1)	−103(3)	200(3)	311(1)	Ag	−500(2)	3629(1)	440(1)
C(2)	−287(4)	202(3)	354(1)	O(1)	313(1)	372(1)	105(1)
C(3)	−461(3)	97(3)	344(1)	O(2)	370(2)	603(1)	63(1)
C(4)	−624(5)	102(4)	386(2)	O(3)	1255(2)	507(1)	390(1)
C(5)	−620(6)	190(5)	431(1)	O(4)	1339(3)	325(2)	544(1)
C(6)	−452(6)	287(4)	440(1)	C(1)	431(2)	489(1)	110(1)
C(7)	−281(4)	294(3)	400(1)	C(2)	649(2)	491(1)	182(1)
C(8)	620(4)	177(3)	183(1)	C(3)	824(2)	585(1)	174(1)
C(9)	789(4)	181(3)	139(1)	C(4)	1021(2)	592(2)	242(1)
C(10)	783(4)	92(3)	95(1)	C(5)	1056(2)	497(2)	322(1)
C(11)	925(6)	94(3)	52(2)	C(6)	886(2)	405(2)	334(1)
C(12)	1097(6)	174(4)	58(1)	C(7)	688(2)	395(1)	263(1)
C(13)	1126(4)	270(4)	99(2)	H(1)	793	662	111
C(14)	980(6)	269(3)	142(1)	H(2)	893	662	241
H(1)	−464	33	306	H(3)	563	309	264
H(2)	−633	13	373	H(4)	863	339	391
H(3)	−643	190	460	H(5)	1290	445	446
H(4)	−454	361	479	H(6)	1343	249	496
H(5)	−293	380	407	H(7)	1476	319	578
H(6)	651	22	100				

EXPERIMENTAL

The crystals of $[Ag_2(C_6H_5COO)_2]$ (I) and $[Ag_2(HO-C_6H_4COO)_2] \cdot H_2O$ (II) were obtained by the slow addition of an aqueous solution of sodium benzoate and p-hydroxybenzoate respectively to $AgNO_3$ solution. The crystals of compounds I and II are transparent and stable, but decompose in light. The crystallographic data for compounds I and II are given in Table 1.

The structures of compounds I and II were determined by the heavy-atom method. The determination and refinement of the structures were carried out using 759 (I) and 1523 (II) independent reflections with $I \geq 2\sigma$, measured (like the cell parameters) on a Syntex $P2_1$ automatic diffractometer (λMoK_α, $2\theta \leq 50°$). All the calculations were carried out on a BÉSM-6 computer using the programs Rentgen-75 [9]. The analysis of the three-dimensional Patterson function established the coordinates of the Ag atoms, and successive approximations of the electron density determined and refined the coordinates of all the atoms other than hydrogen. The refinement of the structures was carried out by the method of least squares, first in the isotropic and then in the anisotropic approximation as far as R = 0.067 and 0.068 for compounds I and II respectively. The coordi-

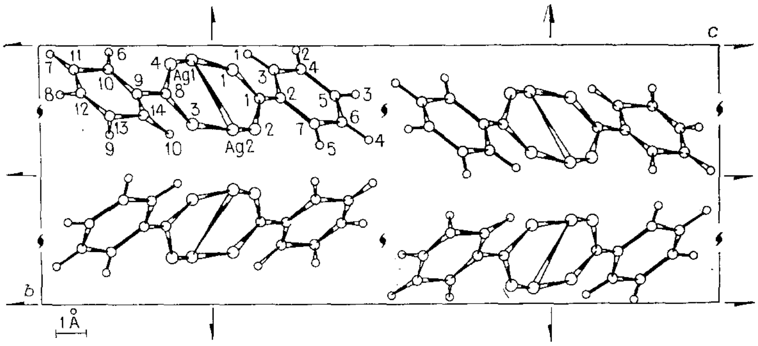

Fig. 1. Crystal structure of compound I (view along [100]).

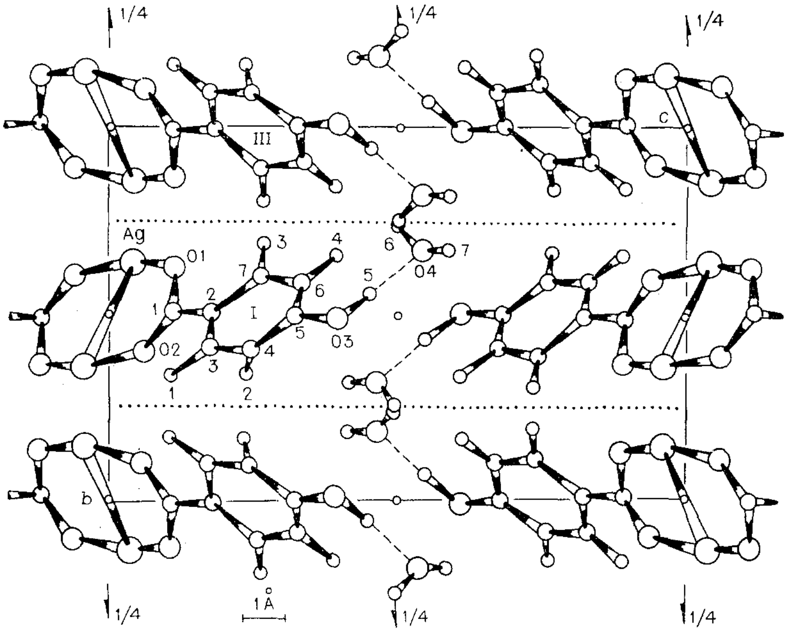

Fig. 2. Crystal structure of compound II (view along [100]).

nates of the basis atoms of compounds I and II are given in Table 2* (the positions of the hydrogen atoms were calculated from geometric considerations).

DESCRIPTION OF THE CRYSTAL STRUCTURES AND DISCUSSION OF RESULTS

The crystal structures of compounds I and II are made up of dimeric molecules (Figs. 1 and 2); the bond lengths and valence angles in the structures are given in Tables 3-5. The overall configuration and the nature of the packing of the molecules are essentially the same in the two structures.

The configuration of the dimeric molecule is determined by the formation of eight-membered rings involving two Ag atoms. In the structure of compound I, the dimeric molecule is situated in a general position, but has a noncrystallographic center of symmetry. Short interatomic distances are observed between the Ag atoms and the O atoms of two carboxyl groups. The average value of these distances (2.22 Å) coincides with the average values of the analogous distances in [$NH_2CH_2COOH \cdot AgNO_3$] [2] and [$Ag(H_2NC_6H_4COO)$] [8]. With allowance for the second Ag atom, which is situated at a distance of 2.902 Å from the first, each Ag atom can be regarded as three-coordinated.

Within the limits of accuracy, the bond lengths in the ligand coincide with the analogous distances in the structure of the acid and its other complexes [10, 11]. The plane of the phenyl ring is almost coplanar with the plane of the chelate ring AgOCOAg.

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*The values of the thermal parameters can be obtained from the authors.

TABLE 3. Bond Lengths d, Å

Bond	d	Bond	d	Bond	d
Complex I				Complex II	
Ag(1)—Ag(2)	2,902(3)	C(4)—C(5)	1,33(4)	Ag—Ag′*	2,915(8)
Ag(1)—O(1)	2,24(2)	C(5)—C(6)	1,40(5)	Ag—O(1)	2,206(8)
Ag(1)—O(4)	2,22(2)	C(6)—C(7)	1,44(4)	Ag′—O(2)	2,214(8)
Ag(2)—O(2)	2,22(2)	Average	1,41	O(1)—C(1)	1,28(1)
Ag(2)—O(3)	2,22(2)	C(8)—C(9)	1,48(38)	O(2)—C(1)	1,24(1)
O(1)—C(1)	1,21(3)	C(9)—C(10)	1,33(4)	O(3)—C(5)	1,38(2)
O(2)—C(2)	1,30(3)	C(9)—C(14)	1,44(4)	C(1)—C(2)	1,49(1)
O(3)—C(8)	1,34(3)	C(10)—C(11)	1,36(5)	C(2)—C(3)	1,41(2)
O(4)—C(8)	1,21(3)	C(11)—C(12)	1,31(5)	C(2)—C(7)	1,40(2)
C(1)—C(2)	1,53(3)	C(12)—C(13)	1,33(5)	C(3)—C(4)	1,36(2)
C(2)—C(3)	1,46(3)	C(13)—C(14)	1,37(5)	C(4)—C(5)	1,40(2)
C(2)—C(7)	1,38(4)	Average	1,36	C(5)—C(6)	1,34(2)
C(3)—C(4)	1,43(4)			C(6)—C(7)	1,39(2)
				Average	1,39

*Ag′−($\bar{x}$, $\bar{y}$, $\bar{z}$).

TABLE 4. Valence Angles ω (deg) in Complex I

Angle	ω	Angle	ω
Ag(2)Ag(1)O(1)	79,6(4)	C(3)C(2)C(7)	122,0(2,2)
Ag(2)Ag(1)O(4)	79,7(5)	C(2)C(3)C(4)	114,5(2,2)
O(4)Ag(1)O(1)	157,0(7)	C(3)C(4)C(5)	124,0(3,0)
Ag(1)Ag(2)O(2)	82,3(4)	C(4)C(5)C(6)	121,3(3,1)
Ag(1)Ag(2)O(3)	83,0(5)	C(5)C(6)C(7)	118,7(2,9)
O(3)Ag(2)O(2)	160,3(7)	C(6)C(7)C(2)	119,4(2,6)
Ag(1)O(1)C(1)	125,0(1,5)	Average	120,0
Ag(2)O(2)C(1)	119,2(1,4)	C(1)C(2)C(3)	117,2(1,9)
Ag(2)O(3)C(8)	121,7(1,5)	C(1)C(2)C(7)	120,7(2,1)
Ag(1)O(4)C(8)	127,3(1,7)	C(10)C(9)C(14)	113,2(2,6)
O(1)C(1)O(2)	128,7(2,1)	C(9)C(10)C(11)	124,9(2,7)
O(2)C(1)C(2)	114,2(2,1)	C(10)C(11)C(12)	118,3(3,2)
O(1)C(1)C(2)	117,1(2,1)	C(11)C(12)C(13)	123,4(3,5)
O(3)C(8)O(4)	124,6(2,3)	C(12)C(13)C(14)	117,3(3,0)
O(3)C(8)C(9)	116,7(2,2)	C(13)C(14)C(9)	121,9(3,0)
O(4)C(8)C(9)	118,8(2,5)	Average	119,8
		C(8)C(9)C(10)	121,0(2,5)
		C(8)C(9)C(14)	125,7(2,6)

In the structure of compound II, the dimeric molecule is centrosymmetric. The average distances Ag−O 2.21 Å and Ag−Ag 2.92 Å are close to the values in the structure of compound I. Within the limits of experimental accuracy, the valence distances and angles in the ligand are the same as in the structure of p-hydroxybenzoic acid itself [12] and its complexes with other metals [13]. The angle between the planes of the phenyl ring and the chelate ring AgOCOAg is 21.0°.

TABLE 5. Valence Angles ω (deg) in Complex II

Angle	ω	Angle	ω
Ag′AgO(1)	80,6	C(3)C(2)C(7)	117,2(1,0)
O(2)′AgAg′	80,4(4)	C(2)C(3)C(4)	123,0(1,2)
O(2)′AgO(1)	157,9(7)	C(3)C(4)C(5)	119,2(1,3)
AgO(1)C(1)	124,5(7)	C(4)C(5)C(6)	119,5(1,1)
O(1)C(1)O(2)	124,4(1,0)	C(5)C(6)C(7)	120,9(1,3)
C(1)O(2)Ag′	122,0(7)	C(6)C(7)C(2)	120,0(1,2)
C(1)C(2)C(3)	122,4(1,1)	Average	119,94
C(1)C(2)C(7)	120,5(1,1)	C(4)C(5)O(3)	118,2(1,8)
C(7)C(1)O(2)	118,5(1,0)	C(6)C(5)O(3)	122,2(1,2)
C(7)C(1)O(1)	117,0(9)		

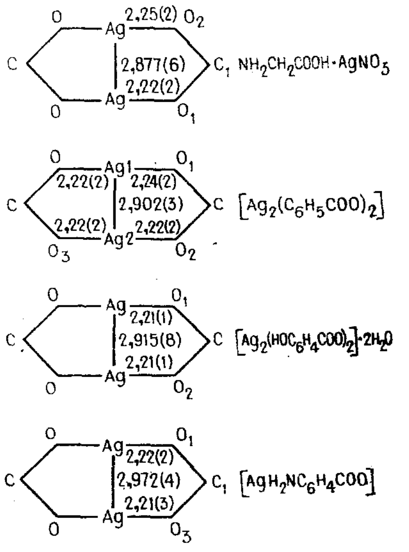

Fig. 3

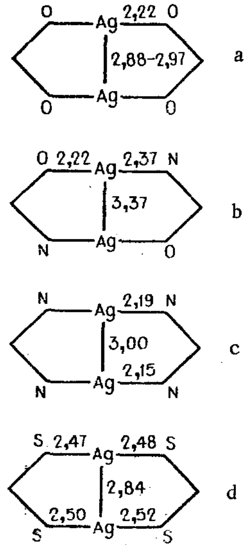

Fig. 4

Fig. 3. Ag–Ag distances in silver(I) carboxylates.

Fig. 4. Eight-membered rings in different complexes of silver(I); a) [2,8,14, present work], b) [6], c) [3], d) [4].

The molecule of water of crystallization detected in the determination of the structure of compound II forms a hydrogen bond with the hydroxyl group of p-hydroxybenzoic acid (O...O 2.699 Å). The shortest intermolecular distances in the structures of compounds I and II indicate that the interaction between the molecules of the complexes is van der Waals interaction.

Comparison of the two structures studied shows that the OH substituent in the para-position, within the limits of accuracy, has no significant influence on the configuration of the complex ring. The substituent and the nature of the acid have a significant influence on the Ag–Ag distance, which varies in the range 2.87–2.97 Å (Fig. 3).

The rings in complexes with different donors are represented schematically in Fig. 4; comparison of the Ag–Ag distances shows that there is no direct correlation between these distances and the distances from Ag to the donor atoms of the ligands.

As noted above, the nature of the packing of the molecules is the same in the two structures. A noteworthy feature is that the space group of each of the structures examined is the pseudo-space group of another structure. This feature apparently indicates the possible existence of corresponding modifications.

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