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The Endless Chain $[AcOHg]_n^{n+}$ Cation. Crystal Structure of Acetatomercury(II) Nitrate — Mercury(II) Acetate (1/1)

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Acetatomercury(II) nitrate-mercury(II) acetate (1/1), $(AcOHg)NO_3 \cdot Hg(AOc)_2$, not described so far in the chemical literature, was obtained by the reaction of mercury(II) nitrate hydrate with acetic anhydride. Orthorhombic-disphenoidal crystals, as shown by threedimensional X-ray diffraction analysis, are built of polymeric $[AcOHg]_n^{n+}$ cations, nitrate anions and mercury(II)-acetate molecules. The mercury ions in the cation are bridged over by the acetate ion through both oxygen atoms separately at the Hg—O distances of 213(3) and 212(2) pm under the O—Hg—O angle of 167(1)°. The mercury(II)-acetate molecule is in *syn* conformation with the Hg-O distances of 204(3) and 209(3) pm and the O—Hg—O angle of 173(1)°. Crystal structure, determined from 1330 intensity data, was refined by full-matrix least-squares method to $R = 0.076$ and $R_w = 0.090$.

INTRODUCTION

When mercury(II) acetate is heated in acetic anhydride a condensation polymer of trimercurated acetic acid is obtained.[1] When mercury(II) nitrate is used, instead of acetate, mercurated acetic acid is obtained[2] whose structure has not been determined yet. Very likely it belongs to the nitrates of trimercurated acetic acid.[3] But, when mercuric nitrate hydrate, $Hg(NO_3)_2 \cdot H_2O$, is added to acetic anhydride at room temperature, bright transparent crystals are separated from the solution immediately after a part of mercury(II) nitrate has been disolved. The separation of crystals proceeds in this way until all mercury(II) nitrate added has been consumed. The separation of the crystals is accompanied by the evolution of nitrogen dioxide. Acetic anhydride has not been mercurated in this reaction, since the crystals tested with aqueous sodium hydroxide give abundant precipitate of mercury(II) oxide. The composition of the crystals, according to chemical analysis, is defined by the formula $Hg_2NO_3(OAc)_3$.

The acetate ion in the product obviously resulted from the hydrolysis of acetic anhydride by water of the hydrated mercury(II) nitrate which was used. Nitrogen dioxide appeared as the decomposition product of nitric acid set free by the action of acetic acid on mercury(II) nitrate in the nonaqueous medium. The proper formula of the new salt, $(AcOHg)NO_3 \cdot Hg(OAc)_2$, was

found from its crystal structure determined by X-ray diffraction analysis. It is an addition compound of mercury(II) acetate with acetatomercury(II) nitrate containing polymeric $[AcOHg]_n^{n+}$ cation which has not been reported so far.[4]

EXPERIMENTAL

Preparation

The compound $(AcOHg)NO_3 \cdot Hg(OAc)_2$ was prepared by dissolving $Hg(NO_3)_2 \cdot H_2O$ in (*i*) acetic anhydride or (*ii*) in a mixture of glacial acetic acid with acetic anhydride.

(*i*) Mercury(II) nitrate monohydrate (1 g), finely ground, was added in small portions to acetic anhydride (10 ml) and the mixture was left for one hour at room temperature with occasional shaking. The solid was filtered off, washed with carbon tetrachloride and dried *in vacuo*. Yield: 0.84 g (89 %). *Anal.* Calcd. for $C_6H_9Hg_2NO_9$ ($M_r = 640.32$): C 11.26, H 1.42, Hg 62.65%; found: C 11.33, H 1.37, Hg 62.64%.

(*ii*) Mercury(II) nitrate monohydrate (3.34 g), finely ground, was added in portions to a mixture of glacial acetic acid (6 ml) and acetic anhydride (1.3 ml) and the mixture was gently heated (~50 °C) until complete dissolution of the nitrate and appearance of crystalline precipitate. After the mixture was left for one hour at room temperature, the solid was isolated as described above. Yield: 2.54 g (79%). *Anal.* Found: C 11.32, H 1.50, Hg 62.61%.

X-Ray Diffraction Analysis

Crystal data were determined with a Philips PW 1100 computer controlled diffractometer (graphite monochromatized Mo—Kα radiation, $\lambda = 71.07$ pm).

Single crystal data. — $C_6H_9Hg_2NO_9$, mol. wt. 640.32, orthorhombic-dispheno-idal, space group $P2_12_12_1$ with $Z = 4$ formula units in the unit cell of dimensions $a = 1741.5(9)$, $b = 872.9(8)$, $c = 825.4(5)$ pm, $V = 1.254$ nm^3, $D_o = 3.26$ Mg m^{-3}, $D_c = 3.39$ Mg m^{-3}, F(OOO) = 1136, μ (Mo—Kα) = 250.0 cm^{-1}, crystal dimensions (mm from centroid): (011), ($0\bar{1}\bar{1}$), ($01\bar{1}$), ($0\bar{1}1$) 0.130; (100), ($\bar{1}00$) 0.090; maximum and minimum transmission coefficients, 0.080 and 0.015.

Intensity measurements. — Integrated intensities of 1330 reflections with $I > 5\sigma(I)$ were collected within the interval of $2^\circ < \Theta < 30^\circ$ using the $\omega - 2\Theta$ scan technique, with scan range 1.2° and scan rate 0.04 s^{-1}. Correction for the absorption,[5] Lorentz and polarization effects were applied.

Determination and refinement of the structure. — The structure was solved by means of three-dimensional Fourier synthesis based upon the mercury atom coordinates obtained from the Patterson synthesis and then refined by the full-matrix least-squares method. Weights of $1/(\sigma F_o)$ were alloted to 1324 reflections. The anisotropic temperature factors were assigned to the mercury atoms. The atomic scattering factors were those of Cromer and Mann[6] with corrections for the real and imaginary parts of the anomalous dispersion for the mercury atom only.[7] The final values of the reliability indices were $R = 0.076$ and $R_w = 0.090$. The final values of the atomic coordinates and thermal parameters with e. s. d's are listed in Table I. Calculations were carried out on the UNIVAC 1100 of SRCE, The University Computing Centre, Zagreb, using the XRAY System.[8]

RESULTS AND DISCUSSION

The correct formula $(AcOHg)NO_3 \cdot Hg(OAc)_2$ of the compound was obtained as the result of the X-ray crystal structure analysis. It excluded the formula $Hg(NO_3)_2 \cdot 3Hg(OAc)_2$, which was first supposed on the basis of the chemical composition and properties. Therefore, the formation of the compound by the reaction of mercury(II) nitrate monohydrate with acetic anhydride at room temperature is represented by the overall equation:

$$2\,Hg(NO_3)_2\cdot H_2O + 3.5\,OAc_2 \rightarrow (AcOHg)NO_3\cdot Hg(OAc)_2 + 3\,NO_2 + 0.75\,O_2 + 4\,HOAc.$$

Nitrogen dioxide and oxygen, as the reaction products, were proved quantitatively: from the gas evolved, nitrogen dioxide was separated by condensation in a U-tube cooled in a mixture of ice and salt, the remaining oxygen was identified by means of a glowing chip of wood.[9] Accordingly, only one of four moles of the nitrate ion, brought into the reaction, entered into the composition of the product. Nitric acid, formed by the reaction with nitrate (three of the four moles) with acetic acid, decomposed to nitrogen dioxide, oxygen and water. It follows that, in the given conditions, the nitrate ion is displaced from its compound with mercury by the acetate ion. Even the nitrate ion contained in the product is not bound to mercury but, as a discrete anion, belongs only to its effective coordination.[10]

Description of the Structure. The crystal structure of $(AcOHg)NO_3 \cdot Hg(OAc)_2$, projected along the *b*-axis direction, is shown in Figure 1. The interatomic distances and bond angles are given in Table II. The crystal structure is built up of three distinct components: the $[AcOHg]_n^{n+}$ cation, the nitrate anion and the mercury(II)-acetate molecule.

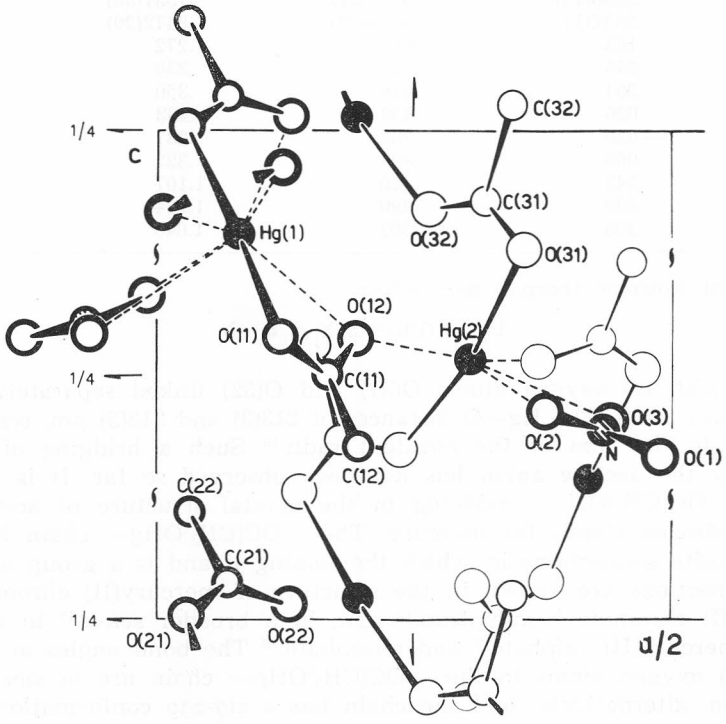

Figure 1. The structure of acetatomercury(II) nitrate — mercury(II) acetate (1/1), viewed along the *b*-axis direction.

The $[AcOHg]_n^{n+}$ cation is an endless chain in which the —$OC(CH_3)OHg$— unit is repeated along the *c*-axis direction by the 2_1 symmetry operation. In other words, the mercury(II) cations, Hg(2), are bridged over by the ace-

TABLE I

Atomic coordinates and thermal parameters ($pm^2 \times 10^4$) with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*	*U* or U_{eq}
Hg(1)	.0808(1)	.1175(2)	.7880(2)	.048(0)[a]
Hg(2)	.3051(1)	.4120(2)	.5332(2)	.039(0)[a]
N	.4347(16)	.2329(38)	.3346(42)	.043(7)
O(1)	.4897(16)	.1545(36)	.3387(39)	.057(8)
O(2)	.3732(17)	.1720(40)	.4263(45)	.066(9)
O(3)	.4394(17)	.3793(43)	.4039(45)	.069(9)
C(11)	.1705(22)	.1039(52)	.5150(55)	.053(10)
C(12)	.1993(27)	.0641(57)	.3455(67)	.070(13)
O(11)	.1215(16)	.0325(36)	.5744(41)	.057(8)
O(12)	.1943(15)	.2322(34)	.5760(38)	.057(7)
C(21)	.0698(21)	.2760(45)	.0797(53)	.047(9)
C(22)	.0359(32)	.3506(71)	.2277(80)	.085(17)
O(21)	.0307(15)	.1800(33)	.0088(38)	.054(7)
O(22)	.1333(15)	.3296(38)	.0345(47)	.063(9)
C(31)	.3204(28)	.4035(69)	.8700(74)	.069(13)
C(32)	.3426(27)	.3653(62)	1.0435(71)	.067(13)
O(31)	.3536(14)	.3347(32)	.7551(36)	.047(6)
O(32)	.2632(11)	.4899(28)	.8472(29)	.032(5)
H(121)	.163	.091	.272	
H(122)	.246	.121	.330	
H(123)	.204	.046	.350	
H(221)	.026	.453	.233	
H(222)	—.020	.288	.237	
H(223)	.065	.304	.322	
H(321)	.343	.440	1.107	
H(322)	.309	.280	1.104	
H(323)	.305	.301	1.046	

[a] Equivalent isotropic thermal parameters:

$$U_{cq} = (1/6\pi^2)\, \Sigma_i \Sigma_j \beta_{ij}\, a_i \cdot b_j$$

tate ion with its oxygen atoms O(31) and O(32) linked separately each to one mercury atom. The Hg—O distances of 213(3) and 212(2) pm, respectively, are close to the sum of the covalent radii.[10] Such a bridging of mercury cations by the acetate anion has not been observed so far. It is analogous to the ...$OC(CH_3)OH$... bridging in the crystal structure of acetic acid,[11] where hydrogen stands for mercury. The —$OC(CH_3)OHg$— chain belongs to the composite connections in which the joining ligand is a group of atoms.[12] Such connections are known in the structure of mercury(II) chromate[13] and mercury(II) chromate hemihydrate[14] and, in a broader sense,[12] in the structure of mercury(II) sulphate[15] and phosphate.[16] The bond angles at the O(31) and O(32) oxygen atoms in the —$OC(CH_3)OHg$— chain are in *syn* and *anti* orientation, alternatively, and the chain has a *zig-zag* conformation like the —OHg— chain in the orthorhombic mercuric oxide.[17] The more so since the —$OC(CH_3)OHg$— chain is actually a ribbon of approximately coplanar atoms in a plan nearly parallel to the (320) crystallographic plane.

The nitrate ion, with the interatomic distances and bond angles (Table II) in agreement with the literature data, is coordinated to the Hg(2) mercury atom as a bidentate ligand with the O(2) and O(3) oxygen atoms at a distance

TABLE II

*Interatomic distances (pm) and bond angles (°), with estimated standard deviations in parentheses**

(a) Distances

Hg(1)—O(11)	204(3)	C(12)—H(123)	97
Hg(1)—O(21)^{i}	209(3)	C(22)—H(221)	91
Hg(2)—O(31)	213(3)	C(22)—H(222)	112
Hg(2)—O(32)^{ii}	212(2)	C(22)—H(223)	101
N—O(1)	124(4)	C(32)—H(321)	81
N—O(2)	124(4)	C(32)—H(322)	105
N—O(3)	129(5)	C(32)—H(323)	107
C(11)—C(12)	153(7)	Hg(1) . . . O(1)^{iii}	271(3)
C(11)—O(11)	117(5)	Hg(1) . . . O(1)^{iv}	275(3)
C(11)—O(12)	130(5)	Hg(1) . . . O(2)^{iii}	289(4)
C(21)—C(22)	151(8)	Hg(1) . . . O(3)^{iv}	293(3)
C(21)—O(21)	123(5)	Hg(1) . . . O(12)	282(3)
C(21)—O(22)	126(5)	Hg(1) . . . O(22)^{i}	290(4)
C(31)—C(32)	156(8)	Hg(2) . . . O(22)^{v}	250(3)
C(31)—O(31)	126(7)	Hg(2) . . . O(12)	251(3)
C(31)—O(32)	126(6)	Hg(2) . . . O(32)	278(2)
C(12)—H(121)	91	Hg(2) . . . O(2)	256(3)
C(12)—H(122)	95	Hg(2) . . . O(3)	259(3)

(b) Angles

O(11)—Hg(1)—O(21)	173(1)	O(11)—C(11)—O(12)	122(4)
O(31)—Hg(2)—O(32)	167(1)	C(22)—C(21)—O(21)	118(4)
O(1)—N—O(2)	121(3)	C(22)—C(21)—O(22)	115(4)
O(1)—N—O(3)	122(3)	O(21)—C(21)—O(22)	127(4)
O(2)—N—O(3)	116(3)	C(32)—C(31)—O(31)	120(5)
C(12)—C(11)—O(11)	120(4)	C(32)—C(31)—O(32)	118(5)
C(12)—C(11)—O(12)	117(4)	O(31)—C(31)—O(32)	122(5)

* Transformation of the asymmetric unit (x, y, z): (i) x, y, 1 + z; (ii) 0.5 — x, 1 — y, z — 0.5; (iii) 0.5 — x, —y, z + 0.5; (iv) x — 0.5, 0.5 — y, 1 — z; (v) 0.5 — x, 1 — y, z + 0.5.

of 256(3) and 259(3), pm, respectively. These oxygen atoms belong also to the coordination of the Hg(1) mercury atom in the molecule of mercury(II) acetate, at distances of 289(4) and 293(3) pm, and bind together these two components of the structure. The oxygen atoms of the bridging acetate ions in the chain cation are not involved in the contacts with the Hg(1) atom, the Hg(1) . . . O(32) and Hg(1) . . . O(31) distances of 457 and 512 pm, respectively, being considerably larger than the sum of the van der Waals radii.[10,12]

The mercury(II)-acetate molecule appears in the structure in *syn* conformation in contrast to the *anti* conformation in the crystal structure of $Hg(OAc)_2$.[18] The preference for the *syn* conformation is caused by the donor function of the O(12) and O(22) carboxyl oxygen atoms towards the Hg(2) mercury atom in the cation, realized at Hg . . . O distances of 251(3) and 250(3) pm, respectively. There are also two intramolecular contacts of the O(12) and O(22)^{i} carboxyl oxygen atoms of 282(3) and 290(4) pm, respectively. The bond lengths and angles (Table II) in the acetate ion are in agreement with the known data.[18]

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SAŽETAK

Beskonačni lančasti kation $[AcOHg]_n^{n+}$. Kristalna struktura acetatoživa(II)-nitrata-živa(II)-acetata (1/1)

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Acetatoživa(II)-nitrat-živa(II)-acetat (1/1), $(AcOHg)NO_3 \cdot Hg(OAc)_2$, do sada nepoznat u kemijskoj literaturi, dobiven je reakcijom živa(II)-nitrat-hidrata s acetanhidridom. Trodimenzijskom rendgenskom difrakcijskom analizom ustanovljeno je da su rompsko-sfenoidalni kristali spoja građeni od polimernih kationa $[AcOHg]_n^{n+}$, nitratnih aniona i molekula živa(II)-acetata. Živini ioni u kationu premošteni su acetatnim ionima preko oba kisikova atoma odjelito na razmacima Hg—O od 213(3) i 212(2) pm pod kutem O—Hg—O od 167(1)°. Molekula živa(II)-acetata ima *syn*-konformaciju, a veze Hg—O od 204(3) i 209(3) pm čine kut O—Hg—O od 173(1)°. Kristalna struktura, određena na temelju izmjerenih intenziteta 1330 refleksa, utočnjena je metodom najmanjih kvadrata s potpunom matricom do indeksa $R = 0{,}076$ i $R_w = 0{,}090$.