Crystal Structures of Tetraethylammonium Dichloroaurate(I) and Tetraethylammonium Diiodoaurate(I)*

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The structures of the title compounds have been determined from single-crystal X-ray diffraction data. $[N(C_2H_5)_4][AuCl_2]$ crystallizes in space group *Pnma* with a = 11.926(12), b = 12.611(10), c = 17.673(32) Å and Z = 8. Full-matrix least-squares refinement of 118 structural parameters gave R = 0.038 for 1897 observed [$I > 3.0\sigma(I)$] independent reflections, measured at 170 K. $[N(C_2H_5)_4][AuI_2]$ crystallizes in space group $P2_1/n$ with a = 12.806(9), b = 9.053(6), c = 12.811(10) Å, β = 111.50(5)° and Z = 4. Full-matrix least-squares refinement of 109 structural parameters gave R = 0.060 for 1916 observed [$I > 3.0\sigma(I)$] independent reflections, measured at 170 K. Both compounds contain monomeric anions. The two crystallographically independent anions in tetraethylammonium dichloroaurate(I) have Au–Cl distances of 2.281(5) and 2.282(5) Å, and 2.269(6) and 2.286(6) Å, and Cl–Au–Cl angles of 179.5(1)° and 175.9(1)°, respectively. In the anion in tetraethylammonium diiodoaurate(I), the Au–I distances are 2.530(2) and 2.540(2) Å, and the I–Au–I angle is 175.59(6)°.

In connection with structural studies on halocuprates(I) crystallizing with large cations with low effective positive charge, the coordination number of copper(I) has been found to increase with decreasing size of the cation (see e.g. Refs. 1–3 and references therein). Correlation of the concentration of halide ligand in crystalline halocuprates(I), containing symmetrical tetraalkylammonium and related cations,[1–3] with the coordination number of copper(I) in the anion formed suggests that dilution of the ligand ions by the cations is a determinative factor for the attainment of a particular copper(I) coordination number and thus for the resulting anionic configuration. Although the crystal structures of some tetraalkylammonium haloargentates(I)[4–8] and haloaurates(I)[9] are known, variation in coordination of silver(I) and gold(I) by the halide ions, as a function of the size of this type of cation, has yet to be examined.

The tetraethylammonium dihaloaurates(I) and tetrabutylammonium dihaloaurates(I) have been prepared, and the infrared and Raman spectra of the salts interpreted in terms of monomeric, linear anions.[10] Recently, the geometries of the anions in the tetrabutylammonium compounds have been determined by means of crystal structure analysis.[9] We wish to report the crystal structures of tetraethylammonium dichloroaurate(I) and tetraethylammonium diiodoaurate(I). Tetraethylammonium dibromoaurate(I) appears to be isostructural with the former compound;[11] we have not, however, been successful in obtaining a set of intensity data for tetraethylammonium dibromoaurate(I) of quality adequate to permit refinement of the crystal structure of this compound.

Experimental

Preparation of tetraethylammonium dichloroaurate(I). All operations were carried out under nitrogen. Gold(I) chloride (0.43 mmol) [ICN Biomedicals, Inc.; K&K] was dissolved in 10 ml of ethanol by stirring and warming, and a solution of 0.43 mmol of tetraethylammonium chloride in 5 ml of ethanol was added. The resulting solution was heated under reflux for approxi-

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mately 1 h and allowed to cool slowly to room temperature with stirring. Diethyl ether (5 ml) was added to the filtrate[10] and the solution was cooled to ca. 4 °C, colourless needles of $[N(C_2H_5)_4][AuCl_2]$, m.p. 68–70 °C, being obtained after approximately 24 h. The crystals decomposed after a few hours of exposure to X-ray radiation at room temperature; intensity data were therefore measured at 170 K.

Preparation of tetraethylammonium diiodoaurate(I). All operations were carried out under nitrogen. Gold(I) iodide (0.31 mmol) [ICN Biomedicals Inc., K&K] was dissolved in 10 ml of ethanol, as above, and a solution of 0.31 mmol of tetraethylammonium iodide in 10 ml of ethanol was added. The solution was heated under reflux for ca. 1 h and cooled slowly to room temperature, after which precipitated AuI was filtered off. The pale-yellow filtrate was cooled to ca. 4 °C, pale-yellow plates of $[N(C_2H_5)_4][AuI_2]$, m.p. 103–104 °C, being deposited after approximately 48 h.

Crystal and experimental data for the two compounds are given in Table 1. Space groups and preliminary unit cell dimensions were determined

Table 1. Crystal and experimental data for tetraethylammonium dichloroaurate(I) and tetraethylammonium diiodoaurate(I).

	$[N(C_2H_5)_4][AuCl_2]$	$[N(C_2H_5)_4][AuI_2]$
M_r	398.1	581.0
Unit cell dimensions	$a = 11.926(12)$, $b = 12.611(10)$, $c = 17.673(32)$ Å	$a = 12.806(9)$, $b = 9.053(6)$, $c = 12.811(10)$ Å, $\beta = 111.50(5)°$
Space group[a]	*Pnma* (No. 62)	$P2_1/n$ (No. 14, non-standard setting)
Z	8	4
D_c/g cm^{-3}	1.99	2.79
Habit	Colourless needles	Pale-yellow plates
m.p./°C	68–70	103–104
μ(Mo$K\alpha$)/mm^{-1}	11.77	15.45
Crystal size/mm	0.31×0.22×0.15	0.13×0.17×0.09
Temperature (data collection)/K	170	170
$2\theta_{max}$/°	50	50
Scan mode	ω-2θ	ω-2θ
2θ scan rate/° min^{-1}	2.5–15.0	2.5–15.0
No. of independent reflections excluding these systematically absent	2372	2453
No. of observed independent reflections [$I > 3.0\sigma(I)$]	1897	1916
Correction for absorption	Empirical[b]	Empirical[b]
Method used to solve structure	Direct methods (MITHRIL[c]); successive electron density maps	Patterson; successive electron density maps
No. of parameters refined	118	109
Weights calculated according to	$w = [\sigma^2(F_o) + 0.0001\ F_o^2]^{-1}$	$w = [\sigma^2(F_o) + 0.0016\ F_o^2]^{-1}$
R	0.038	0.060
Maximum residual electron density/ e Å^{-3}	0.92	2.1

[a]Ref. 16a. [b]Ref. 14. [c]Ref. 15.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for $[N(C_2H_5)_4][AuCl_2]$. B_{eq} is defined as $\frac{8\pi^2}{3}\sum_i\sum_j U_{ij}\, a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. Estimated standard deviations are given in parentheses.

Atom	*x*	*y*	*z*	B_{eq}
Au(1)	0.33744(5)	0.2500	0.60311(3)	3.61(1)
Cl(1)	0.2060(3)	0.2500	0.6969(2)	4.5(1)
Cl(2)	0.4677(3)	0.2500	0.5085(2)	4.4(1)
Au(2)	0.48443(4)	0.2500	0.13320(3)	3.29(1)
Cl(3)	0.4882(3)	0.2500	0.2625(2)	4.4(1)
Cl(4)	0.4942(3)	0.2500	0.0050(2)	4.9(1)
N	0.7486(5)	−0.0074(5)	0.1244(4)	2.6(2)
C(1)	0.6550(6)	−0.0887(7)	0.1374(5)	3.1(2)
C(2)	0.7400(7)	0.0438(8)	0.0453(5)	3.4(3)
C(3)	0.8590(6)	−0.0681(7)	0.1313(5)	3.0(2)
C(4)	0.7437(7)	0.0828(7)	0.1812(5)	3.1(2)
C(5)	0.5363(7)	−0.0422(7)	0.1373(6)	3.9(3)
C(6)	0.7450(9)	−0.0316(10)	−0.0211(5)	4.7(3)
C(7)	0.9653(7)	−0.0029(8)	0.1203(5)	3.4(3)
C(8)	0.7501(8)	0.0505(8)	0.2643(5)	4.0(3)

from rotation and Weissenberg photographs, the metric *C*-centred orthogonal cell for $[N(C_2H_5)_4][AuI_2]$ obtained by the matrix $101/\bar{1}01/0\bar{1}0$ thus being shown to be non-orthorhombic. Diffracted intensities were measured with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo$K\alpha$ radiation. A 96-step profile was recorded for each reflection and the intensities were calculated[12] using the Lehmann and Larsen profile-analysis method.[13] Correction was made for Lorentz and polarisation effects; empirical corrections for the effects of absorption[14] were made after solution of the structures. Unit cell dimensions were determined from diffractometer setting angles for 15 reflections.

Structure determination and refinement

Tetraethylammonium dichloroaurate(I). The positions of the gold and the chlorine atoms were determined by direct methods (MITHRIL),[15] and those of the remaining atoms were obtained from successive electron-density maps. Full-matrix least-squares refinement of positional and isotropic thermal parameters gave $R = 0.10$; an empirical correction for the effects of absorption[14] then gave $R = 0.093$. In the final cycles of refinement, anisotropic thermal parameters were refined for the non-hydrogen atoms and the hydrogen atoms were included as a fixed contribution with C–H distance = 1.08 Å and $B = B_{eq}$ of the carrying carbon atom, assuming staggered conformation of the ethyl groups. A final R of 0.038 was thus obtained for 118 parameters and 1897 reflections.

Tetraethylammonium diiodoaurate(I). The atomic coordinates of the anion were obtained from the Patterson map, and those of the cation from successive electron-density calculations. Full-matrix least-squares refinement of positional and isotropic thermal parameters gave $R = 0.092$; an empirical correction for the effects of absorption[14] then gave $R = 0.069$. Inclusion of anisotropic thermal parameters for the non-hydrogen atoms, and of the hydrogen atoms as a fixed contribution (see above), gave a final R of 0.060 for 109 parameters and 1916 reflections.

Further details concerning the refinement of both structures are summarized in Table 1. Atomic scattering factors and anomalous dispersion corrections were taken from Ref. 16b. The computer programs employed are described in Refs. 17 and 18. Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Tables 2 and 3. Lists of structure factors, anisotropic thermal parameters, hydrogen atom coordinates and connectivity

Table 3. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for $[N(C_2H_5)_4][AuI_2]$. B_{eq} is defined as $\frac{8\pi^2}{3}\sum_i\sum_j U_{ij}\, a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. Estimated standard deviations are given in parentheses.

Atom	*x*	*y*	*z*	B_{eq}
Au	0.20486(7)	0.19612(9)	0.38685(6)	2.34(3)
I(1)	0.1476(1)	0.3590(2)	0.5173(1)	3.02(5)
I(2)	0.2598(1)	0.0156(2)	0.2640(1)	2.59(4)
N	0.627(1)	0.214(2)	0.374(1)	2.0(5)
C(1)	0.628(2)	0.291(2)	0.480(2)	2.7(6)
C(2)	0.596(2)	0.052(2)	0.381(2)	2.9(7)
C(3)	0.742(2)	0.230(2)	0.366(2)	2.5(6)
C(4)	0.542(2)	0.284(2)	0.270(2)	2.4(6)
C(5)	0.514(2)	0.294(3)	0.492(2)	3.5(7)
C(6)	0.604(2)	−0.041(3)	0.287(2)	3.3(7)
C(7)	0.836(2)	0.153(3)	0.456(2)	2.7(6)
C(8)	0.555(2)	0.438(3)	0.253(2)	2.8(6)

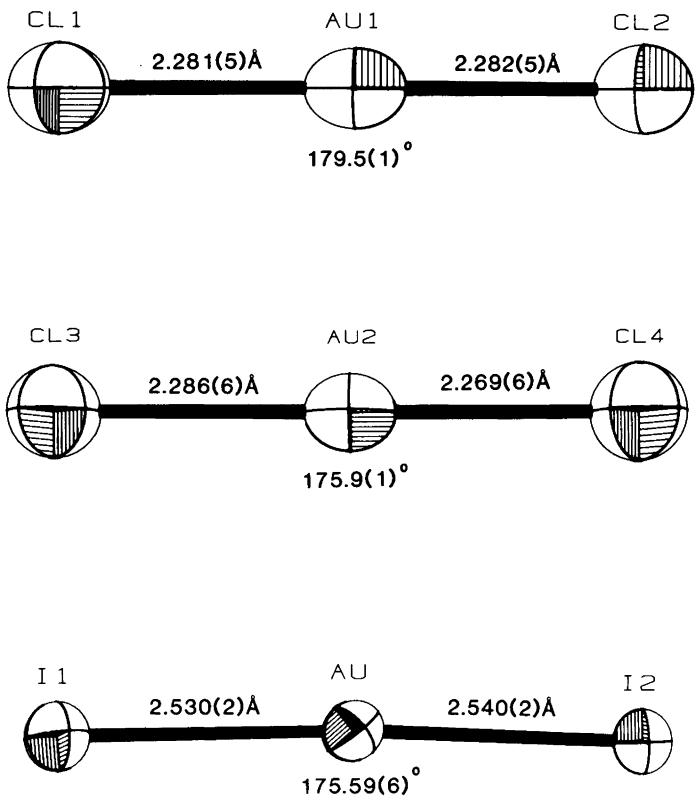

Fig. 1. The dichloroaurate(I) ions and the diiodoaurate(I) ion in $[N(C_2H_5)_4][AuCl_2]$ and $[N(C_2H_5)_4][AuI_2]$, respectively. Estimated standard deviations in the distances and angles are given in parentheses. The thermal ellipsoids enclose 50 % probability.[19]

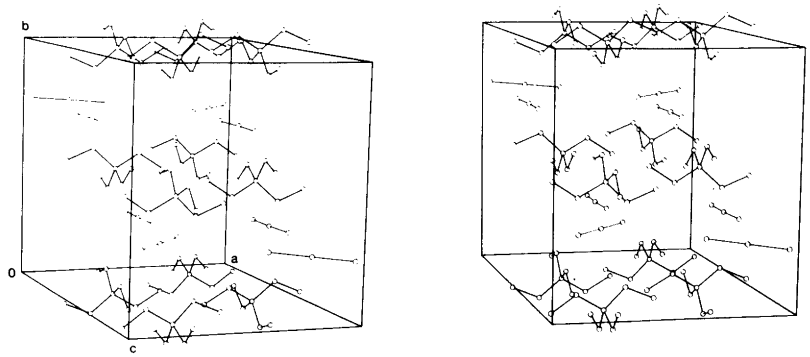

Fig. 2. Stereoscopic view[19] of the structure of $[N(C_2H_5)_4][AuCl_2]$. All atoms are represented as spheres of radius 0.08 Å.

relationships within the cations may be obtained from the authors on request.

Discussion

As expected, both compounds contain monomeric anions in which gold(I) is two-coordinated (Fig. 1). In tetraethylammonium dichloroaurate(I) there are two crystallographically independent anions, both of which are situated on a mirror plane. The presence of crystallographically inequivalent chlorine sites has been predicted from the chlorine n.q.r. frequencies for the compound.[20] Perturbation of the anion in the solid state was also inferred from vibrational spectra.[10,20] The Au–Cl and Au–I distances in the tetraethylammonium compounds (Fig. 1) are similar to those determined for the tetrabutylammonium counterparts, viz. 2.257(4) and 2.529(1) Å, respectively, gold(I) being situated at a centre of symmetry in both the latter compounds.[9] Slight differences in Au–X distances between monomeric dihaloaurate(I) ions in different solid-state environments have been noted previously.[9] Similar variations have been found to occur for Cu–Cl or Cu–Br distances in monomeric dichlorocuprate(I) and dibromocuprate(I) ions crystallizing with different cations (see e.g. Ref. 21).

The structures of tetraethylammonium dichloroaurate(I) and tetraethylammonium diiodoaurate(I) are illustrated in Figs. 2 and 3. The shortest cation–anion distances in tetraethylammonium dichloroaurate(I) are Au(2)···C(5) and Au(2)···C(5^{i}) = 3.74(1) Å, and Cl(4)···C(5^{ii}) and Cl(4)···C(5^{iii}) = 3.65(1) Å; in tetraethylammonium diiodoaurate(I) the closest anion–cation contacts are Au···C(5) = 3.79(2) Å and

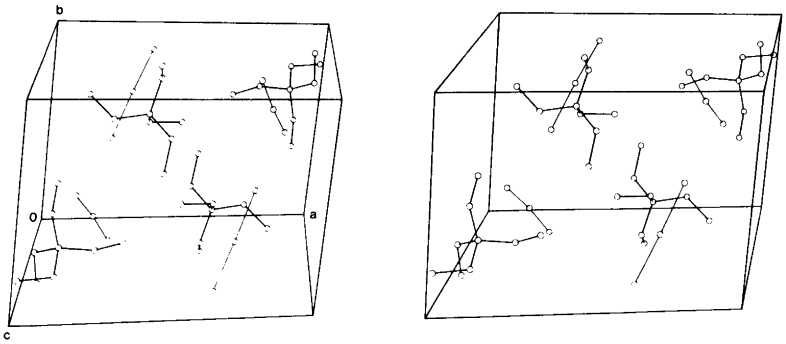

Fig. 3. Stereoscopic view[19] of the structure of $[N(C_2H_5)_4][AuI_2]$. All atoms are represented as spheres of radius 0.08 Å.

I(2)···C(1^{iv}) = 3.83(2) Å [symmetry code: (*i*): $x,\frac{1}{2}-y,z$; (*ii*): $1-x,\frac{1}{2}+y,-z$; (*iii*): $1-x,-y,-z$; (*iv*): $x-\frac{1}{2},\frac{1}{2}-y,z-\frac{1}{2}$]. There are no Au···Au contacts of <4 Å in either of the compounds.

That monomeric dihaloaurate(I) anions are obtained with both the tetraethylammonium and the tetrabutylammonium cation contrasts with the corresponding halocuprates(I): Whereas tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I) both contain monomeric anions,[22,23] the tetraethylammonium cation crystallizes with a $[Cu_7Cl_{10}]^{3-}$ chain containing two- and three-coordinated copper(I),[24] and with a $[Cu_2Br_4]^{2-}$ dimer containing three-coordinated copper(I).[25] In the iodocuprate(I) series, $[Cu_2I_4]^{2-}$ dimers containing three-coordinated copper(I) have been obtained with tetrabutylammonium[26] and tetraethylammonium,[27] the latter cation also crystallizing with a discrete $[Cu_6I_{11}]^{5-}$ ion[27] and with an infinite $[Cu_2I_3]^-$ chain,[28] both composed of copper(I)–iodide tetrahedra. In the haloargentate(I) system, double $[Ag_2X_3]^-$ (X=Cl,Br,I) chains of edge-sharing silver(I)–halide tetrahedra similar to those in $[N(CH_3)_4][Ag_2Br_3]$[8] and $[N(CH_3)_4][Ag_2I_3]$[5,6] have been obtained with the tetraethylammonium cation.[29,30] The crystal structures of the tetrabutylammonium chloroargentate(I) and the tetrabutylammonium bromoargentate(I) are not yet known; tetrabutylammonium tetraiodotriargentate(I) contains, however, an infinite $[Ag_3I_4]^-$ chain composed of silver(I)–iodide tetrahedra.[4]

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