The Preparation, Properties, and Vibrational Spectra of Complexes containing the $AuCl_2^-$, $AuBr_2^-$, and AuI_2^- Ions

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The preparation and isolation of the complexes $[Et_4N][AuX_2]$ and $[Bu^n{}_4N][AuX_2]$, where X = Cl, Br, or I, are described. The i.r. and Raman spectra of the salts have been interpreted in terms of linear anions in each case. The fundamental frequencies of each anion are compared with those of the structurally similar HgX_2 molecules, and appropriate force constants are given.

ALTHOUGH gold(I) is known to form linear complexes with cyanide and many other ligands, simple salts of the AuX_2^- ions (X = Cl, Br, or I) have not been prepared and characterised. Earlier literature is confused.[1,2] Some stability constant data have suggested the existence of the $AuCl_2^-$ ion in aqueous and hydrochloric acid solutions of gold(I), and these have generally been taken to imply that $AuCl_2^-$ is an important water-stable ion; however, our observations on salts of the $AuCl_2^-$ ion show that the ion is rapidly decomposed by water with deposition of metallic gold. The $AuCl_2^-$ and $AuBr_2^-$ ions have also been assumed (probably correctly) to be present in certain ethanolic solutions of gold(I), but they had never been isolated except as part of the unusual mixed-valence compounds[3] $[Au(dtc)_2][AuX_2]$, where dtc = *NN*-di-n-butyldithiocarbamate, and X = Cl, Br, or I. The gold(I) halides, AuX, are either known (AuI)[4] or assumed (AuCl, AuBr)[5] to be long zig-zag polymers with linear co-ordination at the gold atom.

This paper reports the preparation, properties, and vibrational spectra of the new complexes $[Et_4N][AuX_2]$ and $[Bu^n{}_4N][AuX_2]$. The key to the isolation of the salts of the $AuCl_2^-$ and $AuBr_2^-$ ions has been the use of the reducing agents phenylhydrazinium chloride and acetone respectively, with the appropriate salt of the AuX_4^- ion. The new complexes are stable in air but are (except for $[Bu^n{}_4N][AuI_2]$) sensitive to moisture, and they are considered in each case to contain the linear $XAuX^-$ ion. The complex $[Bu^n{}_4N][AuI_2]$ is not decomposed by water because it is not soluble in it; if it is dissolved in ethanol and then water added it reprecipitates and gold is immediately deposited. The i.r. and Raman spectra of the anions are compared with those of the AuX_4^- ions, as well as with those of the neutral linear HgX_2 molecules.

EXPERIMENTAL

Preparation of Complexes.—Tetraethylammonium dichloroaurate(I). Tetraethylammonium tetrachloroaurate(III) (1·62 g, 3·46 mmol) was partly dissolved in absolute ethanol (30 ml) and gently heated. To this solution, phenylhydrazinium chloride ($PhNH\cdot NH_2,HCl$) (0·25 g, 1·73 mmol) in absolute ethanol (10 ml) was added with constant agitation. Gas was evolved and after 1½ h the initially yellow solution had become slightly orange. The solution was left to cool slowly, and then placed in a refrigerator for 10—12 h; pale yellow crystals precipitated. After filtration these were washed with diethyl ether and dried, to give $[Et_4N][PhAuCl_3]$ (280 mg, yield 16%). By adding diethyl ether to the filtrate, which was then cooled in a refrigerator for several hours, colourless needles of tetraethylammonium dichloroaurate(I) were obtained. These were filtered off, washed with diethyl ether, and dried (yield 0·8 g, 58%). Analyses and other physical data are in Table 1.

Tetra-n-butylammonium dichloroaurate(I). To tetra-n-butylammonium tetrachloroaurate(III) (1·11 g, 1·92 mmol), partly dissolved in absolute ethanol (20 ml), was added slowly phenylhydrazinium chloride (0·14 g, 0·96 mmol) in absolute ethanol (5 ml). A gas was evolved. After *ca.* 1 h at 40—50 °C the orange-red solution obtained was left to cool slowly, diethyl ether was added, and the solution placed in a refrigerator for 10 h. Colourless crystals of tetrabutylammonium dichloroaurate(I) precipitated (yield 0·41 g, 42%); this salt is less soluble than the analogous tetraethylammonium salt. The filtrate was left to evaporate slowly thus allowing long pale yellow prisms to crystallise.

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After filtration, the crystals were washed with diethyl ether, giving [Bu^n_4N][$PhAuCl_3$] (yield 0·16 g, 13%)

Tetraethylammonium dibromoaurate(I). Tetraethylammonium tetrabromoaurate(III) (1·81 g, 2·8 mmol) was partly dissolved in absolute ethanol (15 ml) together with acetone (1 ml). After having been heated at 60—70 °C on a water-bath, the initially red solution became colourless and the reaction was complete. A lachrymatory substance was evolved (bromoacetone). The final colourless solution was left to cool slowly, and then placed in a refrigerator for 10 h. Long colourless needles precipitated, which were filtered off, rapidly washed with diethyl ether, and dried. These were tetraethylammonium dibromoaurate(I) (yield 1·14 g, 2·35 mmol, 84%).

TABLE 1

Analytical data and physical properties of gold(I) and gold(III) complexes

	C (%)		H(%)		N (%)		X (%)					Conductance	
Complex	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Description	M.p./ °C	Yield (%)	Λ cm² Ω⁻¹ mol⁻¹	10^3 Concn./ M
[Et_4N] [$AuCl_2$]	24·12	$24{\cdot}3_5$	5·02	4·98	3·52	3·28	17·84	17·9	Colourless needles	69	58	102	0·7
[Bu^n_4N] [$AuCl_2$]	37·65	37·9	7·06	6·94	2·75	2·79	13·92	13·9	Colourless prisms	82	42	105	0·9
[Et_4N] [$AuBr_2$]	19·71	$19{\cdot}6_5$	4·11	4·03	2·87	2·85	32·85	33·1	Colourless needles	88	99	106	0·64
[Bu^n_4N] [$AuBr_2$]	32·05	$32{\cdot}2_5$	6·01	6·09	2·34	2·32	26·71	$26{\cdot}6_5$	Colourless needles	93	98	99	1·15
[Et_4N] [AuI_2]	16·52	$16{\cdot}3_5$	3·44	3·42	2·41	2·45	43·72	43·7	Pale yellow plates	103	33	110	0·86
[Bu^n_4N] [AuI_2]	27·71	$27{\cdot}5_5$	5·19	5·20	2·02	2·18	36·65	$36{\cdot}0_5$	Yellow needles	79	89	108	0·58
[Et_4N] [$AuCl_4$]	20·47	$20{\cdot}4_5$	4·26	4·12	2·98	3·00	30·28	30·5	Bright yellow plates	215—218	—	111	0·66
[Bu^n_4N] [$AuCl_4$]	33·05	33·1	6·20	6·19	2·41	2·33	24·44	$24{\cdot}2_5$	Bright yellow needles	157—160	—	105	1·25
[Et_4N] [$AuBr_4$]	14·84	14·7	3·09	3·00	2·16	2·12	49·46	50·0	Dark maroon prisms	189—192	—	105	0·31
[Bu^n_4N] [$AuBr_4$]	25·31	25·2	4·75	4·70	1·85	1·81	42·13	42·3	Dark maroon prisms	163—166	—	107	0·53

By addition of diethyl ether to the filtrate, a further 0·21 g of tetraethylammonium dibromoaurate (I) was obtained, making an overall yield of 99%.

Tetra-n-butylammonium dibromoaurate(I). This compound can be obtained in 98% yield by the previously described procedure, with tetra-n-butylammonium tetrabromoaurate(III) replacing tetraethylammonium tetrabromoaurate(III).

Tetraethylammonium di-iodoaurate(I). Tetraethylammonium dibromoaurate(I) (0·487 g, 1 mmol) in absolute ethanol (4 ml) was mixed with tetraethylammonium iodide (0·504 g, 2 mmol) in the same solvent (4 ml). The solution was held at *ca.* 40 °C for 1 min and then left to cool slowly while being continuously shaken during 2 h. The solution was then placed in a refrigerator for 10 h, whereupon yellow plates precipitated. These were filtered off, washed with cold absolute ethanol and then with diethyl ether, and dried. Tetraethylammonium di-iodoaurate(I) was obtained (yield 0·191 g, 0·33 mmol, 33%). More product could be obtained by addition of diethyl ether to the filtrate, but the product frequently contained tetraethylammonium bromide and was more deeply coloured (orange, or orange-red) owing to the presence of tetraethylammonium tri-iodide. The latter is produced by a redox reaction between gold(I) and iodide ions, which results in the precipitation of metallic gold and the formation of the I_3^- ion. Tetraethylammonium di-iodoaurate(I) can be recrystallised from ethanol.

Tetra-n-butylammonium di-iodoaurate(I). This was prepared by treating tetra-n-butylammonium dibromoaurate(I) (1·92 g, 3·2 mmol) with tetra-n-butylammonium iodide in absolute ethanol (20 ml). The mixture was heated at *ca.* 50 °C for 30 min, and then left to cool slowly. After 5 h in the refrigerator, long yellow crystals precipitated. These were filtered off, washed with diethyl ether, and dried. Tetra-n-butylammonium di-iodoaurate(I) (yield 1·98 g, 2·86 mmol, 89%) was obtained.

Tetraethylammonium tetrachloroaurate(III). An ethanolic solution of $HAuCl_4,xH_2O$ was treated with the stoicheiometric quantity of tetraethylammonium chloride. The resulting yellow precipitate of the required complex was recrystallised from ethanol. The yield was quantitative.

Tetra-n-butylammonium tetrachloroaurate(III). The previous procedure was used, with tetra-n-butylammonium chloride in place of tetraethylammonium salt. The yield was quantitative.

Tetraethylammonium tetrabromoaurate(III). An ethanolic solution of $HAuCl_4,xH_2O$ was treated at 50—60 °C with an 8—10-fold excess of tetraethylammonium bromide. Substitution of bromide for chloride took place immediately to give quantitatively a deep maroon precipitate of the required complex, which could be recrystallised from ethanol.

Tetra-n-butylammonium tetrabromoaurate(III). The previous procedure was used, with tetra-n-butylammonium bromide in place of tetraethylammonium bromide, giving tetra-n-butylammonium tetrabromoaurate(III) quantitatively.

Instrumental.—Raman spectra were recorded on a Spex 1401 spectrometer in conjunction with a Coherent Radiation Kr^+ model 52 laser, and 90° collection optics. The method of detection was photon counting (cooled FW130 phototube) with linear response. The power available at the exciting wavelengths 5682 and 6471 Å of Kr^+ was *ca.* 100 and *ca.* 600 mW respectively. The 5682 Å line was only used for the complex $[Et_4N][AuCl_2]$; the 6471 Å line, which was used for obtaining the spectra of the other complexes, was normally attenuated to powers of 50—100 mW in order to avoid decomposition of the samples. Raman spectra on solutions of the complexes in capillaries were generally unobtainable owing to sample decomposition and deposition of metallic gold. The spectra were calibrated by reference to the emission lines of neon. The spectra of the solids were recorded as compressed discs.

I.r. spectra were recorded on a Perkin-Elmer 225 spectrometer (to 200 cm^{-1}) as Nujol mulls, and on an R.I.I.C. interferometer (200—20 cm^{-1}) as paraffin wax discs (P.C.M.U. Service, Harwell). In the latter case, spectra were recorded for 10—20 mg compound to 80 mg paraffin wax in 13 mm discs.

TABLE 2

Vibrational spectra of the complexes $R[AuX_2]/cm^{-1}$ [a]

Assignment	$[Et_4N]$ $[AuCl_2]$		$[Bu^n_4N]$ $[AuCl_2]$		$[Et_4N]$ $[AuBr_2]$		$[Bu^n_4N]$ $[AuBr_2]$		$[Et_4N]$ $[AuI_2]$		$[Bu^n_4N]$ $[AuI_2]$	
($D_{\infty h}$ nomenclature)	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman
$\nu_3(\Sigma_u^+)$	356s											
	349vs	353w	350vs		252vs		254vs		209vs		210vs	
$\nu_1(\Sigma_g^+)$		334sh										
		329m		329m		208vs		209vs		156vs [b]		158vs
		324sh		326wm								
$\nu_2(\pi_u)$	134m		120ms		*ca.* 95m,br		79m		82m		67sh	
	122s	119s	112s		83s,br		75s		69s		59m	
		116m										
		111m										

[a] Weak bands occur in the Raman spectra of all the tetra-n-butylammonium salts at 251 ± 1 and 261 ± 3 cm^{-1}. [b] This fundamental occurs at 154 cm^{-1} in ethanol solution, in which it is polarised.

The equivalent conductance of the salts were recorded for methanol solutions at $0{\cdot}5$—$1{\cdot}2 \times 10^{-3}$M (*ca.* 20 °C). Measurements were taken within 2 min of the preparation of the solution by use of a Wayne-Kerr Universal Bridge B221.

RESULTS AND DISCUSSION

In order to reduce gold(III) to gold(I) species, it is necessary to make a very careful choice of reducing agent to avoid reduction to metallic gold. The $AuCl_2^-$ ion has been isolated as the tetraethylammonium and tetra-n-butylammonium salts by use of phenylhydrazinium chloride as reducing agent as in reaction (1). Phenylhydrazinium chloride likewise reduces the $AuBr_4^-$ ion

$$2R[AuCl_4] + PhNH{\cdot}NH_2,HCl \longrightarrow R[AuCl_2] + R[PhAuCl_3] + N_2 + 4HCl \quad (1)$$
$$R = Et_4N \text{ or } Bu^n_4N$$

to form the $AuBr_2^-$ ion as well as the $[PhAuBr_3]^-$ ion. The phenylgold(III) derivatives will be discussed elsewhere.[6]

The bromo-salts were also isolated by use of acetone as reducing agent, according to reaction (2). Acetone

$$R[AuBr_4] + Me_2CO \longrightarrow R[AuBr_2] + CH_2BrCOMe + HBr \quad (2)$$

is a very clean reducing agent, since (*a*) its oxidation product is volatile and thus easily eliminated and (*b*) the ethanolic solution resulting from the above reaction is sufficiently stable to be boiled without decomposition. However, acetone fails to react similarly with the $AuCl_4^-$ ion.

For the preparation of the iodo-species, simple displacement reactions of bromide by iodide have been employed, *viz.*, (3).

$$R[AuBr_2] + 2RI \longrightarrow R[AuI_2] + 2RBr \quad (3)$$

The complexes (Table 1) are colourless ($AuCl_2^-$ and $AuBr_2^-$ ions) or pale yellow (AuI_2^- ion) crystalline solids with relatively low m.p.s and are 1 : 1 electrolytes in methanol.

Vibrational Spectra.—I.r. and Raman spectra are listed in Table 2 in terms of $D_{\infty h}$ nomenclature. Only ν_1 is Raman-active, and only ν_2 and ν_3 are i.r.-active. However, these stringent selection rules are not expected to be obeyed in the solid state, for which the (generally) more relaxed selection rules pertaining to the appropriate factor group are operative. Indeed, the spectra of the tetraethylammonium salts in particular display clear evidence for the presence of strong lattice forces in the solid state, *viz.*, for $[Et_4N][AuCl_2]$ ν_3 occurs as a doublet in the i.r. spectrum, and also appears in the Raman (*cf.* the VCl_4^- and the $SnCl_3^-$ ions.[7,8]) No chlorine isotopic effect was clearly evident. The fundamental ν_3 invariably occurs as a very strong sharp i.r. band with no significant difference between its frequency for the two different series of salts. The frequency of ν_1 is likewise not significantly dependent on the counter-ion; this fundamental gives rise to only medium Raman intensity for the $AuCl_2^-$ ion, which is not a very good scatterer, but gives rise to much greater Raman intensity for the $AuBr_2^-$ and AuI_2^- ions. The ν_2 (π_u) fundamental is in all cases split into a doublet in the i.r. spectrum, with the lower-frequency component being the more intense. The splitting amounts to 12—14 cm^{-1} in the case of the tetraethylammonium salts, and to 4—9 cm^{-1} in the case of the tetra-n-butylammonium salts. The frequency of

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ν_2 is consistently 12 cm^{-1} higher for the tetraethylammonium than for the tetra-n-butylammonium salts, *again suggesting* the presence of stronger restraining lattice forces in the case of the former cation (as expected from lattice energy considerations).

The frequencies of the ν_3 fundamental of the $AuCl_2^-$ and $AuBr_2^-$ ions are closely similar to the frequencies of the ν_6 (e_u) fundamental of the $AuCl_4^-$ (356 cm^{-1}) and $AuBr_4^-$ (252 cm^{-1}) ions respectively,[9,10] presumably on account of the counterbalancing effects on metal–ligand stretching frequencies of decrease in co-ordination number (from four to two) and decrease in the oxidation state of the metal atom (from three to one).[11] The frequencies $\nu_1(\Sigma_g^+)$ and ν_1 (a_{1g}) of the AuX_2^- and AuX_4^- ions respectively are likewise similar, for the same reasons. The gold–chlorine stretching frequencies of the $AuCl_2^-$ ion may also be compared with that of the neutral gold(I) complex $Ph_3PAu^{35}Cl$ (329 cm^{-1}).[12] The $AuCl_2^-$ ion also exists in the complex $Cs_2Au_2Cl_6$, for which an *X*-ray analysis[13] has shown the presence of alternate square planar $AuCl_4^-$ and linear $AuCl_2^-$ ions. However, the interpretation of the vibrational spectrum of such a compound is unlikely to be straightforward.

The mean frequencies of the fundamentals of the AuX_2^- ions (as the $Bu^n{}_4N^+$ salts) are compared in Table **3** with the corresponding frequencies of the mercury(II) halides in the vapour state.[14-16] For the AuX_2^- ions, the stretching force constant k is 11—22% lower than for the analogous mercury(II) halide, in agreement with well-established trends in force constants with change in oxidation state of the central metal atom.[11] For each series, k varies in the order $MCl > MBr > MI$. The interaction constant k_{12} is fairly constant for the AuX_2^- ions at $0{\cdot}20 \pm 0{\cdot}01$ mdyn/Å, whereas the interaction constant for the mercury(II) halides is about an order of magnitude smaller. Like k, the bending force constant k_δ/l^2 within each series falls in the order $ClMCl > BrMBr > IMI$, the values for the gold(I) series being about three times greater than for the mercury(II) series.

TABLE 3

Comparison of the average fundamental frequencies and force constants of the AuX_2^- ions [a] and the gaseous mercury(II) halides, HgX_2 [b]

				Force constants (mdyn/Å) [c]		
Species	$\nu_1(\Sigma_g^+)$ / cm^{-1}	$\nu_2(\pi_u)$ / cm^{-1}	$\nu_3(\Sigma_u^+)$ / cm^{-1}	k	k_{12}	k_δ/l^2
$AuCl_2^-$	329	116	350	$2{\cdot}07_1$	$0{\cdot}19_0$	$0{\cdot}10_3$
$HgCl_2$(g) [b]	358	70	413	$2{\cdot}65_5$	$0{\cdot}02_2$	$0{\cdot}03_8$
$AuBr_2^-$	209	77	254	$1{\cdot}86_6$	$0{\cdot}19_0$	$0{\cdot}07_7$
$HgBr_2$(g) [b]	222	41	293	$2{\cdot}28_5$	$0{\cdot}03_5$	$0{\cdot}02_2$
AuI_2^-	158	63	210	$1{\cdot}65_3$	$0{\cdot}21_3$	$0{\cdot}06_5$
HgI_2(g) [b]	158	33	237	$1{\cdot}86_0$	$0{\cdot}00_6$	$0{\cdot}01_8$

[a] $Bu^n{}_4N^+$ salts. [b] Refs. 14—16. [c] 1 mdyn/Å = 10^2 N/m.

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