Complexes of Gold(III) with Mononegative Bidentate N,O-Ligands†

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Gold(III) complexes of a variety of deprotonatable bidentate N,OH ligands have been prepared by direct reaction with $[AuX_4]^-$ (X = Cl or Br). Schiff-base ligands 2-$HOC_6H_4CH{=}NR$, (R = Me, Et, Pr^i, Bu^n, CH_2Ph, or C_6H_{11}) give predominantly $[Au(2\text{-}OC_6H_4CH{=}NR)_2][AuCl_4]$; the monomeric neutral form $[AuCl_2(2\text{-}OC_6H_4CH{=}NR)]$ is always a minor product. 2-Pyridyl-methanol and -ethanol (HL) give simple complexes $[AuX_3(HL)]$ in the presence of excess of halide ion. These ligands and a range of substituted pyridine-2-carboxylic acids and quinolinecarboxylic acids (HL′) give mono- and bis-chelated complexes $[AuX_2(L')]$ and $[AuL'_2]^+$. Some of the latter are capable of binding chloride ion to give five-co-ordinate complexes $[AuCl(L')_2]$. When the ligand substituent is a hydroxy or carboxylic acid group another deprotonation step is possible to give neutral hydrogen-bonded polymeric $[\{AuL'(L'-H)\}_n]$ or anionic $[Au(L'-H)_2]^-$ complexes. Crystal structure data are reported for $Na[Au(L'-H)_2]\cdot 4H_2O$ (HL′ = pyridine-2,5-dicarboxylic acid) and $[AuX_2(L')]$ (X = Cl or Br; HL′ = pyridine-2-carboxylic acid; X = Cl, HL′ = 3-hydroxypyridine-2-carboxylic acid), showing the expected square-planar geometry for gold with a *trans* arrangement for the bis(chelate).

Gold(III) forms a wide variety of complexes, predominantly with square-planar configuration. In recent years attention has focused on organometallic derivatives, and complexes with harder or chelate ligands have been relatively neglected. We have therefore initiated a programme to obtain complexes of mononegative bidentate ligands. Previous investigations with this type of ligand have shown that two forms of complex may be obtained. Thus, 8-hydroxyquinoline (Hquin) gives green and amber products which were assigned[1] as *cis* and *trans* isomers of $[Au(quin)_2][AuCl]_4$. However, a ^{197}Au Mössbauer spectroscopic re-examination showed the green form to be $[AuCl_2(quin)]$.[2] In other cases, ionic products involving two oxidation states have been reported, *e.g.* $[Au^I(Hhpro)_2][Au^{III}Cl_4]$ (Hhpro = 1-hydroxyproline) and $[Au^{III}(Hdmg)_2][Au^ICl_2]$ (Hdmg = dimethylglyoximate).[3] However, we have shown[4] that the first of these is actually a monomeric neutral gold(III) complex containing the deprotonated chelate, $[AuCl_2(hpro)]$.

We present now an investigation of gold(III) derivatives of a range of bidentate O,N-donor ligands, including anions of the Schiff bases 2-$HOC_6H_4CH{=}NR$ (R = Me, Et, Pr^i, Bu^n, CH_2Ph, or C_6H_{11}), some hydroxy- and carboxy-substituted pyridine-2-carboxylic acids, and 2-pyridylmethanol and 2-(2-pyridyl)ethanol. A preliminary report of part of this work has been given,[4] and other workers have reported kinetic studies with complexes of the last two ligands.[5]

Experimental

Schiff-base ligands were synthesised by direct reaction between salicylaldehyde and the appropriate primary amine in ethanol. Gold complexes were obtained by procedures of which those quoted are typical. Analytical data are given in Tables 1 and 2. The ^{197}Au Mössbauer spectra were obtained with the source (Pt) and sample immersed in liquid helium; the data are given in Table 3, where isomer shifts are quoted relative to gold metal at 4.2 K. The extensive overlapping of the sub-spectra in several cases necessitated constraining the individual doublets to be symmetrical. Unless otherwise specified, conductivity data refer to *ca.* 10^{-3} mol dm^{-3} solutions in acetonitrile.

Bis(N-n-*propylsalicylaldiminato*)*gold*(III) *Tetrachloroaurate*(III).—Sodium tetrachloroaurate(III) dihydrate (0.50 g, 1.26 mmol) in ethanol (20 cm^3) was warmed to 50 °C *N-n*-Propylsalicylaldimine (0.42 g, 2.54 mmol) in ethanol (10 cm^3) was added in four portions over 1 h. The mixture turned from yellow through gold to orange and finally became ruby red. After about 2 h a red-brown precipitate began to form, which was collected after about 3 h. It was washed with water, ethanol and diethyl ether, and recrystallised from warm acetone–light petroleum (b.p. 40–60 °C). Yield 60%.

Dichloro(N-*ethylsalicylaldiminato*)*gold*(III), $[AuCl_2(esal)]$.—Sodium tetrachloroaurate(III) dihydrate (0.10 g, 0.25 mmol) was dissolved in water (30 cm^3) and cooled to about −5 °C. *N*-Ethylsalicylaldimine (80 mg, 0.5 mmol) in methanol (*ca.* 3 cm^3) was added dropwise with stirring over 5–10 min. The mixture became a cloudy mustard-brown and was allowed to stand in a refrigerator for 1 week. The upper aqueous layer was decanted from the dark oil which had formed. Chlorobenzene was added to the oil, much of which dissolved to give a purple solution. Addition of diethyl ether gave a green-blue precipitate of the monomeric complex $[AuCl_2(esal)]$. Yield 0.10 g, 55%. The residual solid was the dark red ionic $[Au(esal)_2][AuCl_4]$ (44 mg, 12%). Reduction in volume of the decanted aqueous layer gave water-soluble yellow needles of $[NH_3Et][AuCl_4]$ [IR ν(N–H) 1510 and 1580 cm^{-1}; ^1H NMR (D_2O) δ 1.69 (t) and 3.45 (q)].

Trichloro(2-*pyridylmethanol*)*gold*(III), $[AuCl_3(Hpm)]$.—A solution of 2-pyridylmethanol (Hpm) (0.11 g, 1.0 mmol) in water (10 cm^3) was added dropwise to a stirred solution containing $Na[AuCl_4]\cdot 2H_2O$ (0.20 g, 0.50 mmol) and sodium chloride (1.03 g, 4 mmol) in water (15 cm^3) at 0 °C. A yellow solid separated immediately. Stirring was continued for 45 min. The solid was filtered off, washed with water and extracted with diethyl ether (50 cm^3). The ether solution was concentrated to

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Analytical and conductivity data for Schiff-base complexes[a]

		Analysis (%)[b]				
Complex	Colour	C	H	N	Cl	$\Lambda_M{}^c$/S mol^{-1}
$[Au(msal)_2][AuCl_4]$	Red-brown	24.1	2.0	3.4		
		(23.9)	(2.0)	(3.5)		
$[AuCl_2(msal)]$	Grey	24.2	1.9	3.4	17.6	16
		(23.9)	(2.0)	(3.5)	(17.7)	
$[Au(esal)_2][AuCl_4]$	Dark red	26.0	2.6	3.4	16.9	92
		(26.0)	(2.4)	(3.4)	(17.1)	
$[AuCl_2(esal)]$	Blue-green	25.6	2.5	3.4		
		(26.0)	(2.4)	(3.4)		
$[Au(psal)_2][AuCl_4]$	Red-brown	27.9	3.1	3.2	16.3	95
		(27.9)	(2.8)	(3.2)	(16.5)	
$[AuCl_2(psal)]$	Dark green	27.6	2.8	3.3	17.0	17
		(27.9)	(2.8)	(3.2)	(16.5)	
$[Au(ipsal)_2][AuCl_4]$	Red-brown	28.0	2.8	3.2	16.6	91
		(27.9)	(2.8)	(3.2)	(16.5)	
$[Au(bsal)_2][AuCl_4]$	Red-brown	29.7	3.3	3.1	16.1	96
		(29.6)	(3.2)	(3.2)	(16.0)	
$[Au(bzsal)_2][AuCl_4]$	Red-brown	35.1	2.5	3.0	14.6	86
		(35.2)	(2.5)	(2.9)	(14.9)	
$[Au(csal)_2][AuCl_4]$	Red-brown	33.5	3.7	3.1	15.1	89
		(33.2)	(3.4)	(3.6)	(15.1)	
$[Au(salen)][AuCl_4]$	Brown	24.0	1.8	3.5	17.0	
		(23.9)	(2.0)	(3.6)	(17.7)	
$[Au(salpd)][AuCl_4]$	Brown	24.8	2.0	3.4	17.5	
		(25.0)	(2.0)	(3.4)	(17.4)	
$[Au(salhxn)][AuCl_4]$	Brown	33.7	4.0	3.0	15.1	
		(33.1)	(3.6)	(3.0)	(15.5)	

[a] 2-$OC_6H_4C{=}NR$, where R = Me (msal), Et (esal), Pr^n (psal), Pr^i (ipsal), Bu^n (bsal), CH_2Ph (bzsal), or C_6H_{11} (csal); 2-$OC_6H_4CH{=}N$-$[CH_2]_n$-$N{=}CHC_6H_4O$-2, where *n* = 2 (salen), 3 (salpd) or 6 (salhxn). [b] Calculated values in parentheses. [c] *ca.* 10^{-3} mol dm^{-3} in $MeNO_2$.

Table 2 Analytical data for complexes of pyridine-type ligands

	Analysis (%)						Analysis (%)				
Complex	C	H	N	Halide	Au	Complex	C	H	N	Halide	Au
$[AuCl_3(Hpm)]$	17.7	1.7	3.3	25.8	47.9	$[Au(pyca)_2]ClO_4$	25.8	1.3	4.9	6.1	34.9
	(17.5)	(1.7)	(3.4)	(25.5)	(47.8)		(26.6)	(1.5)	(5.2)	(6.6)	(36.4)
$[AuCl_3(Hpe)]$	19.8	2.1	3.3	24.7	46.6	$[Au(pm)_2]BF_4$	28.9	2.4	5.5		39.4
	(19.7)	(2.1)	(3.3)	(25.0)	(46.2)		(28.8)	(2.4)	(5.6)		(39.4)
$[AuBr_3(Hpm)]$	13.3	1.2	2.5	43.8	36.6	$[Au(pm)_2]ClO_4$	27.9	2.2	5.3	6.9	38.8
	(13.2)	(1.2)	(2.6)	(44.0)	(36.6)		(28.1)	(2.3)	(5.5)	(6.9)	(38.4)
$[AuBr_3(Hpe)]$	15.1	1.6	2.5	42.3	36.6	$[Au(pe)_2]BF_4$	31.7	2.9	5.4		37.4
	(15.0)	(1.6)	(2.5)	(42.8)	(36.1)		(31.8)	(3.0)	(5.3)		(37.3)
$[AuCl_2(pyca)]$	18.2	0.9	3.5	18.2	50.0	$[Au(pe)_2]ClO_4$	31.2	2.8	5.2	6.6	36.4
	(18.5)	(1.0)	(3.6)	(18.2)	(50.5)		(31.1)	(3.0)	(5.2)	(6.6)	(36.4)
$[AuCl_2(hpyca)]$	17.5	0.8	3.4	17.4	48.6	$[Au(pyca)_2][AuCl_4]$	18.2	0.9	3.4	18.0	51.0
	(17.7)	(1.0)	(3.5)	(17.5)	(48.5)		(18.5)	(1.0)	(3.6)	(18.2)	(50.5)
$[AuCl_2(2,4\text{-}Hpydca)]$	19.6	1.0	3.2	16.1	44.0	$[Au(pm)_2][AuCl_4]$	18.9	1.3	3.5	18.9	52.1
	(19.3)	(0.9)	(3.2)	(16.3)	(45.4)		(19.1)	(1.6)	(3.7)	(18.9)	(52.3)
$[AuCl_2(2,5\text{-}Hpydca)]\cdot 0.33\,thf$	21.5	1.2	2.6	15.1	42.3	$[Au(pe)_2][AuCl_4]$	21.0	1.9	3.3	18.5	50.8
	(21.7)	(1.5)	(3.1)	(15.1)	(43.0)		(21.5)	(2.1)	(3.6)	(18.2)	(50.5)
$[AuCl_2(pm)]$	19.0	1.2	3.4	19.1	51.8	$[Au(qnca)_2][AuCl_4]$	27.2	1.4	3.5	15.7	45.2
	(19.1)	(1.6)	(3.7)	(18.9)	(52.3)		(27.3)	(1.4)	(3.2)	(16.1)	(44.7)
$[AuCl_2(pe)]$	21.6	2.0	3.5	18.0	50.4	$[Au(hpyca)(Hhpyca)]$	30.2	1.3	5.7		41.3
	(21.5)	(2.1)	(3.6)	(18.2)	(50.5)		(30.5)	(1.5)	(5.9)		(41.7)
$[AuBr_2(pyca)]$	14.9	0.7	2.8	33.0	42.0	$[Au(2,3\text{-}pydca)(2,3\text{-}Hpydca)]$	31.5	1.3	5.1		37.4
	(15.0)	(0.8)	(2.9)	(33.4)	(41.1)		(31.8)	(1.3)	(5.3)		(37.3)
$[AuBr_2(hpyca)]$	14.6	0.7	2.8	32.5	39.3	$[Au(2,5\text{-}pydca)(2,5\text{-}Hpydca)]$	31.5	1.2	5.1		37.5
	(14.5)	(0.8)	(2.8)	(32.3)	(39.8)		(31.8)	(1.3)	(5.3)		(37.3)
$[AuBr_2(pm)]$	15.6	1.3	3.0	34.2	42.4	$[Au(hqnca)(Hhqnca)]$ *	41.9	2.0	4.8		32.3
	(15.5)	(1.3)	(3.0)	(34.4)	(42.3)		(41.9)	(1.9)	(4.9)		(34.4)
$[Au(pyca)_2]BF_4$	27.2	1.4	5.0		37.5	$Na[Au(2,5\text{-}pydca)_2]\cdot 4H_2O$	29.0	1.7	4.6		35.2
	(27.3)	(1.5)	(5.3)		(37.3)		(28.7)	(1.7)	(4.8)		(33.6)

* H_2hqnca = 4-Hydroxyquinoline-2-carboxylic acid.

about 5 cm^3 and the complex reprecipitated by addition of light petroleum (b.p. 40–60 °C, 60 cm^3). Yield 53%. The orange diethyl ether-insoluble residue was $[AuCl_2(pm)]$ (12%).

Dibromo(3-*hydroxypyridine*-2-*carboxylato*)*gold*(III), $[AuBr_2(Hhpyca)]$.—A solution of 3-hydroxypyridine-2-carboxylic acid (H_2hpyca) (70 mg, 0.5 mmol) in water (15 cm^3) was

Table 3 Gold-197 Mössbauer data [isomer shift (i.s.), quadrupole splitting (q.s.) in mm s^{-1}, at 4.2 K]

	Cation/neutral complex		Anion		
Compound	i.s.	q.s.	i.s.	q.s.	Ref.
$[Au(esal)_2][AuCl_4]$[a]	3.01	2.32	2.27	1.65	
$[Au(psal)_2][AuCl_4]$[b]	3.02	2.65	2.33	1.23	
$[Au(ipsal)_2][AuCl_4]$[c]	3.00	2.65	1.97	1.11	
$[Au(bsal)_2][AuCl_4]$[d]	2.87	1.9	2.36	1.67	
$[Au(bzsal)_2][AuCl_4]$[e]	3.07	2.54	2.45	1.48	
$[Au(salhxn)][AuCl_4]$[f]	3.04	2.66	2.44	1.66	
$[AuCl_2(pyca)]$	2.72	1.83			
$[AuCl_2(2,3\text{-}Hpydca)]$	2.75	1.79			
$[AuCl_2(Hhpyca)]$	2.72	1.84			
$[Au(pyca)_2]BF_4$	3.21	2.72			
$[Au(pyca)_2][AuCl_4]$[g]	3.52	2.72	2.15	2.07	
$[Au(hpyca)(Hhpyca)]$	3.24	2.64			
$[Au(2,3\text{-}pydca)(2,3\text{-}Hpydca)]$	3.24	2.51			
$[Au(2,5\text{-}pydca)(2,5\text{-}Hpydca)]$	3.25	2.54			
$[Au(hqnca)(Hhqnca)]$	3.10	1.97			
$Na[Au(2,5\text{-}pydca)_2]\cdot 4H_2O$			3.48	2.85	
$[AuCl_2(hpro)]$	2.61	1.72			3
$[AuCl_2(quin)]$	2.91	1.72			2
$[AuCl_2(cquin)]$[h]	2.72	1.62			2
$[Au(quin)_2][AuCl_4]$	3.64	2.64	2.43	1.49	2

[a–g] Area ratios, observed (calc., see text): 2.0 (1.7), 1.9 (1.9), 1.7 (1.9), 2.2 (2.0), 2.6 (2.1), 2.3 (2.2) and 1.3 (1.5). [h] cquin = 5-Chloroquinolin-8-olate.

adjusted to pH 7 by addition of dilute sodium hydroxide solution. This solution was added dropwise with stirring to a solution of $Na[AuCl_4]\cdot 2H_2O$ (0.20 g, 0.50 mmol) and sodium bromide (0.31 g, 3 mol) in water (15 cm^3). An orange solid slowly separated and was filtered off after 2 h. It was washed with water (30 cm^3) and extracted with acetone (60 cm^3). The volume of the extract was reduced to about 5 cm^3 and the complex was precipitated by the addition of light petroleum. Yield 77%.

Bis(pyridine-2-carboxylato)gold(III) *Perchlorate*, $[Au(pyca)_2]ClO_4$.—A solution of pyridine-2-carboxylic acid (Hpyca) (0.18 g, 1.5 mmol) in water (15 cm^3) was adjusted to pH 7, and a solution of $Na[AuCl_4]\cdot 2H_2O$ (0.220 g, 0.5 mmol) in water (15 cm^3) was added dropwise. A yellow solid separated and was redissolved by gently warming the mixture (45 °C). Heating was removed and stirring continued for 2 h. The clear solution was filtered, reduced to about 3 cm^3 under reduced pressure, and filtered into a hot solution of lithium perchlorate trihydrate (1.2 g, 7 mmol) in water (*ca.* 3 cm^3). The mixture was stirred for 5 min and allowed to stand in a refrigerator, when beige crystals separated after about 2 h. These were collected, washed with water and acetone, and dried. Yield 61%.

[*Pyridine-2,3-dicarboxylato*(2 –)][*pyridine-2,3-dicarboxylato*(1 –)]*gold*(III), $[Au(2,3\text{-}pydca)(2,3\text{-}Hpydca)]$.—A solution of pyridine-2,3-dicarboxylic acid ($2,3\text{-}H_2pydca$) (0.25 g, 1.5 mmol) in water (15 cm^3) was adjusted to pH 5. To this was added, dropwise with stirring, a solution of $Na[AuCl_4]\cdot 2H_2O$ (0.20 g, 0.5 mmol) in water (10 cm^3). The pale yellow product separated and was collected by centrifugation after about 2.5 h. It was washed with water, ethanol, acetone and diethyl ether and dried. Yield 70%.

Sodium Bis[*pyridine-2,5-dicarboxylato*(2 –)]*aurate*(III). *Tetrahydrate*, $Na[Au(2,5\text{-}pydca)_2]\cdot 4H_2O$.—An aqueous solution of $Na[AuCl_4]\cdot 2H_2O$ (0.10 g, 0.25 mmol) was slowly added to an aqueous solution of pyridine-2,5-dicarboxylic acid (2,5-pydca) (0.125 g, 0.75 mmol) while the pH was maintained at 7. No precipitation occurred. Slow diffusion of the vapour from 50% nitric acid into the solution yielded colourless crystals.

Crystal-structure Determinations.—Data were collected on a CAD4 diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.710 69 Å). Intensity standards measured at 3 h intervals showed no systematic drift. Lorentz polarisation and absorption corrections were applied and standard heavy-atom techniques were used to solve the phase problems. Structures were solved by Patterson techniques. Full-matrix least-squares refinement using SHELX 76[6] or TEXSAN[7] subjected vibrational parameters for all non-hydrogen atoms to anisotropic refinements. Hydrogen atoms attached to carbon were placed in chemically reasonable positions while the remainder were ignored. Other pertinent data are given in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre, comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results

Preparation and Characterisation.—The two pyridyl alcohols, Hpm and Hpe [2-(2-pyridyl)ethanol)], co-ordinate without loss of a proton provided excess of halide is present, to give $[AuX_3(HL)]$ (X = Cl or Br). The retention of the hydroxy group is shown by the IR spectra (3520–3530 cm^{-1}).

If the additional halide is omitted, simple chelated complexes are obtained, $[AuX_2(L)]$ (HL = Hpm or Hpe). For pyridine-2-carboxylic acid ligands this type of complex is obtained even in the presence of added halide, when the pH is kept below about 6. Best yields are obtained with a 2:1 ligand:gold ratio; the excess of ligand acts as a weak base and binds the liberated proton [equation (1)]. Chelation of L^- is indicated by the IR

$$[AuCl_4]^- + 2HL \longrightarrow [AuCl_2(L)] + 2Cl^- + H_2L^+ \quad (1)$$

spectra and lack of conductivity (Table 6) and, in three cases, by X-ray crystallography (see below).

When the pH of the reaction mixture is slightly raised and a two-fold excess of HL is present bis(chelate) cations $[AuL_2]^+$ are obtained, which can be isolated with a range of anions. In some cases (HL = Hpyca or Hpm) there is initial precipitation of $[AuCl_2(L)]$ and/or $[AuL_2][AuCl_4]$ which redissolves on stirring or warming. In other cases (HL = $2\text{-}HOC_6H_4CH{=}NR$ or quinoline-2-carboxylic acid) reaction leads directly to rapid precipitation of $[AuL_2][AuCl_4]$ under nearly all conditions. Although these materials cannot be distinguished analytically

Table 4 Experimental data for the crystallographic analyses

Compound	$[AuBr_2(pyca)]$	$[AuCl_2(Hhpyca)]$	$[AuBr_2(Hhpyca)]$	$Na[Au(2,5\text{-}pydca)_2]\cdot 4H_2O$
Formula	$C_6H_4AuBr_2NO_2$	$C_6H_4AuCl_2NO_3$	$C_6H_4AuBr_2NO_3$	$C_{14}H_{14}AuN_2NaO_{12}$
M	478.88	405.97	494.88	622.2
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a/Å	8.185(2)	6.887(2)	7.144(2)	7.049(2)
b/Å	7.995(3)	15.137(1)	14.894(4)	7.581(2)
c/Å	14.356(2)	10.216(1)	10.645(4)	8.8660(3)
α/°	—	—	—	96.59(3)
β/°	96.95(2)	120.71(1)	123.34(4)	103.29(4)
γ/°	—	—	—	95.38(3)
U/Å^3	932.5	915.7	946.3	440.3
Z	4	4	4	1
D_c/Mg m^{-3}	3.41	2.94	3.47	2.35
No. of reflections for lattice parameters	25	25	25	25
θ range/°	8.5–12.2	7.1–14.0	9.3–15.6	5.5–9.8
$F(000)$	848	736	880	298
Crystal size/mm	0.05 × 0.05 × 0.25	0.03 × 0.18 × 0.25	0.2 × 0.2 × 0.2	0.04 × 0.13 × 0.3
μ/mm^{-1}	23.55	15.98	23.84	8.42
Absorption correction (minimum, maximum)	0.978, 1.594	0.491, 1.307	0.634, 1.511	0.701, 1.891
ω Scan speed/° min^{-1}	0.2–5	0.2–5	0.2–5	1.8–5
ω Scan width	$0.8 + 0.35 \tan\theta$	$0.6 + 0.35 \tan\theta$	$0.6 + 0.35 \tan\theta$	$0.8 + 0.34 \tan\theta$
θ range/°	0–25	0–25	0–25	0–25
h range	−9 to 9	−8 to 7	−9 to 9	0 to 8
k range	0–9	0–17	0–18	−8 to 8
l range	0–16	0–12	0–12	−10 to 9
Standard reflections	1 −3 2 −2 0 6 −4 0 −4	4 0 −4 3 0 −2 0 −6 0	0 0 4 −1 2 3 4 0 −2	2 −1 0 0 2 −1 0 1 3
No. of measured reflections	1967	1922	2351	1568
No. of reflections used in refinement	1174 unique $[F \geqslant 3\sigma(F)]$	1356 $[F \geqslant 3\sigma(F)]$	1578 $[F \geqslant 3\sigma(F)]$	1531 $[F \geqslant 5\sigma(F)]$
R(int)	0.015	0.024	0.024	0.040
Maximum shift-to-error ratio	0.01	0.004	0.02	0.07
Minimum, maximum height in final ΔF map/e Å^{-3}	−1.5, 1.7	−2.5, 1.8	−3.0, 3.0	−3.2, 2.8
No. of refined parameters	112	120	119	144
R	0.042	0.037	0.050	0.060
R'	0.049	0.045	0.057	0.065
c in $w = [\sigma^2(F_o) + cF_o^2]^{-1}$	0.0006	0.0002	0.0003	0.0003

from $[AuCl_2(L)]$, their far-IR spectra, conductivities and Mössbauer spectra are distinctive. It was found extremely difficult to obtain significant quantities of $[AuX_2(2\text{-}OC_6H_4CH{=}NR)]$, which always occurred mixed with a considerable proportion of the ionic form.

When solutions containing $[AuL_2]^+$ (L = pyridine-2,*n*-carboxylate, n = 3–5; or Hhpyca) are allowed to stand or are warmed white precipitates are formed which have a ligand : gold ratio of 2 : 1 but contain no other anion. The IR spectra show very broad absorptions in the O–H bending and stretching regions indicative of considerable hydrogen bonding. The Mössbauer parameters are very similar to those of the parent bis(chelate) cationic complexes. For the dicarboxylate ligands, the complexes show only a single set of carboxylate absorptions in the IR spectra, with frequencies intermediate between those of the acid and the salt form. It seems likely that one substituent hydroxyl or carboxylic acid group has undergone deprotonation and forms hydrogen bonds to a non-deprotonated group on an adjacent molecule, giving a polymeric structure. These materials dissolve in dilute alkali, presumably giving the completely deprotonated anionic complexes $[Au(L - H)_2]^-$. Recrystallisation of the 2,5-H_2pydca-derivative by slow acidification of an alkaline solution of $[Au(2,5\text{-}pydca)_2]^-$ gave colourless crystals which were characterised by X-ray crystallography as $Na[Au(2,5\text{-}pydca)_2]\cdot 4H_2O$. The IR spectrum of this material does not show the broad hydrogen-bonded OH absorptions which characterise the polymers, and has carboxylate absorptions characteristic of a salt (1730 and 1620 cm^{-1}).

Mössbauer Spectra.—The ^{197}Au Mössbauer parameters of selected complexes are shown in Table 3. All are consistent with the formulations suggested. In particular, there is an increase in both parameters when two chloride ligands are replaced by a chelate; this behaviour is consistent with the O,N ligand being a better donor than Cl^- to gold(III), and is analogous to the trend found for the quinolinolate complexes. Deprotonation of the substituent groups on the pyridine chelates has no discernible effect on donation to gold except perhaps in the anionic dichelate $[Au(2,5\text{-}pydca)_2]^-$.

The variation in parameters observed for the $[AuCl_4]^-$ anions is seen for other salts, and is due to changes in the extent of polarisation of the anion by the cation.[8]

It was also noticeable that the areas of the two sub-spectra for $[AuL_2][AuCl_4]$ were not equal, that for the cation being the greater. Similar phenomena have been seen in other systems containing non-equivalent gold atoms,[2,9–11] and are due to the dependence of the recoil-free fraction (f) on the molar mass (M) of the complex.[8,12] The data presently available[8] lead to the empirical expression $\ln f = -1.8 - (605/M)$, and on this basis the cations should give intensities about 70–120% greater than those of the anions. The observed intensity ratios were in good agreement with these estimates, considering the extensive overlapping of the sub-spectra.

Table 5 Fractional atomic coordinates for non-hydrogen atoms

Atom	x	y	z	Atom	x	y	z
$[AuBr_2(pyca)]$							
Au	0.202 55(6)	0.420 33(8)	0.558 35(4)	C(4)	0.388 7(24)	0.002 7(22)	0.357 9(15)
Br(1)	0.075 8(2)	0.256 2(3)	0.666 6(2)	C(5)	0.306 2(22)	−0.050 1(18)	0.430 4(16)
Br(2)	0.132 0(2)	0.668 3(3)	0.636 4(1)	C(6)	0.250 3(10)	0.058 3(18)	0.490 6(14)
N	0.275 1(13)	0.225 1(14)	0.480 0(8)	C(7)	0.371 8(18)	0.470 8(10)	0.401 7(12)
C(2)	0.354 1(16)	0.284 8(16)	0.408 9(11)	O(1)	0.311 9(12)	0.557 3(10)	0.465 6(7)
C(3)	0.412 3(20)	0.171 9(22)	0.347 1(12)	O(2)	0.437 5(14)	0.529 7(12)	0.339 3(8)
$[AuCl_2(Hhpyca)]$							
Au	0.591 03(6)	0.487 32(3)	0.701 29(4)	C(5)	0.866 1(17)	0.237 4(7)	0.674 5(13)
Cl(1)	0.255 0(4)	0.422 4(2)	0.546 7(3)	C(6)	0.711 3(17)	0.302 0(7)	0.656 5(12)
Cl(2)	0.412 8(5)	0.613 8(2)	0.693 1(3)	C(7)	1.061 3(17)	0.490 8(6)	0.862 7(11)
N	0.782 9(12)	0.380 5(5)	0.719 0(8)	O(1)	0.891 6(11)	0.542 6(5)	0.836 67(7)
C(2)	1.009 0(15)	0.399 5(6)	0.803 8(10)	O(2)	1.259 8(12)	0.515 3(5)	0.942 7(9)
C(3)	1.168 5(16)	0.338 4(7)	0.826 5(11)	O(3)	1.390 0(11)	0.354 8(5)	0.907 7(8)
C(4)	1.092 9(19)	0.254 8(7)	0.757 3(13)				
$[AuBr_2(Hhpyca)]$							
Au	0.593 51(11)	0.485 231(45)	0.702 754(82)	C(2)	1.005 6(27)	0.041 2(12)	0.797 2(22)
Br(1)	0.239 15(31)	0.418 05(15)	0.533 50(24)	C(3)	1.164 4(32)	0.338 9(12)	0.816 8(24)
Br(2)	0.407 33(35)	0.617 11(14)	0.702 60(26)	C(4)	1.090 5(32)	0.257 1(12)	0.748 2(28)
O(1)	0.898 3(19)	0.540 001(86)	0.844 0(14)	C(5)	0.866 8(32)	0.238 8(12)	0.660 2(23)
O(2)	1.258 3(21)	0.512 455(83)	0.945 7(16)	C(6)	0.712 6(32)	0.300 5(12)	0.645 9(22)
O(3)	1.384 5(21)	0.357 02(85)	0.902 2(17)	C(7)	1.060 2(27)	0.491 2(11)	0.865 0(18)
N	0.787 4(23)	0.381 2(10)	0.715 5(18)				
$Na[Au(2,5\text{-}pydca)_2]\cdot 4H_2O$							
Au(1)	0	0	0	C(1)	0.068 0(22)	0.221 5(16)	0.296 7(16)
Na	−0.459 1(57)	0.498 0(65)	0.017 5(64)	C(2)	0.135 6(23)	0.282 8(16)	0.456 3(16)
O(1)	−0.091 2(20)	0.240 4(13)	0.031 3(11)	C(3)	0.224 1(22)	0.169 1(16)	0.556 1(15)
O(2)	−0.092 5(19)	0.468 3(12)	0.211 5(13)	C(4)	0.248 0(20)	−0.004 9(15)	0.492 0(15)
O(3)	0.358 9(16)	−0.286 7(11)	0.531 3(11)	C(5)	0.182 5(21)	−0.057 9(15)	0.331 4(15)
O(4)	0.395 2(18)	−0.079 0(12)	0.746 7(11)	C(6)	−0.044 0(23)	0.323 7(18)	0.174 9(16)
O(5)	−0.560 6(17)	0.503 8(12)	0.260 4(12)	C(7)	0.342 9(21)	−0.135 2(17)	0.599 8(15)
O(6)	−0.608 7(16)	0.196 9(11)	−0.013 9(12)	Au(2)	0	1/2	1/2
N(1)	0.090 4(18)	0.050 9(12)	0.234 5(12)				

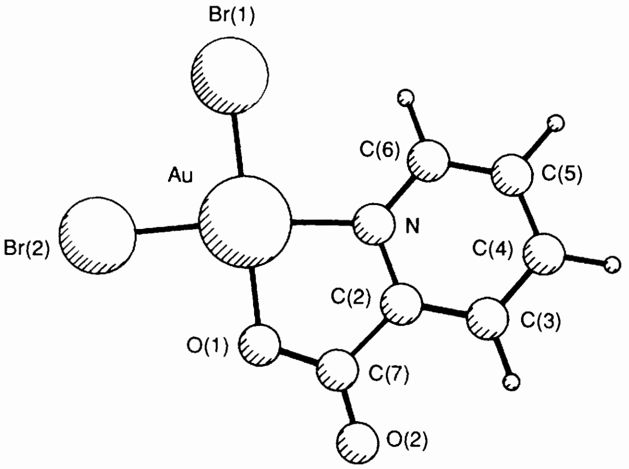

Fig. 1 Structure of $[AuBr_2(hpyca)]$. Other complexes of this type are isomorphous and isostructural. Crystallographic data are given in Tables 4 and 5, and bond lengths and angles in Table 7

Crystal Structures.—Full X-ray crystal-structure determinations have been made for $[AuX_2(L)]$ (X = Cl or Br, HL = H_2hpyca; X = Br, HL = Hpyca) and for $Na[Au(2,5\text{-}pydca)_2]\cdot 4H_2O$. For $[Au(esal)_2][AuCl_4]$ crystals were too small for full analysis but it was established that the unit cell was monoclinic and both the gold atoms (cation and anion) lay on centres of symmetry (space group $P2_1/n$, a = 14.8, b = 6.8, c = 10.7 Å, β = 108°, Z = 2).[13] This implies a *trans* configuration for the cation.

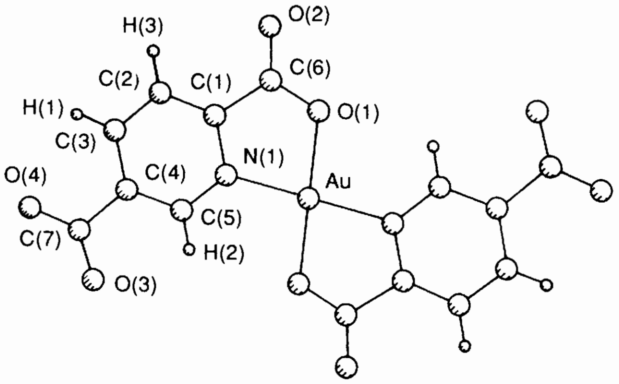

Fig. 2 Structure of the anion $[Au(2,5\text{-}pydca)_2]^-$. Bond lengths and angles are given in Table 7

The neutral complexes $[AuX_2(L)]$ show conventional *cis*-chelated structures (Fig. 1), selected data for which are shown in Table 7. The bond lengths appear normal, although there appears to be only one strictly comparable structure in the literature: for $[AuCl_2(phen)]^+$ (phen = 1,10-phenanthroline) the Au–Cl bond lengths are 225.7 and 225.8 pm.[14] There is no evidence of a significant difference in *trans* influence between the O- and N-donor atoms of the pyridine carboxylic acid ligands. In the two 3-hydroxy-substituted complexes the molecules are held together in centrosymmetric pairs by hydrogen bonding between the OH groups and the C=O groups of the co-ordinated carboxylate groups; this probably accounts for the lowering of the C=O stretching frequency.[15]

Table 6 Infrared and conductivity data for complexes of pyridine-type ligands

	IR/cm^{-1}			
Complex	ν(Au–X)	$\nu_{asym}(CO_2)$[a]	Λ_M/S mol^{-1}	Concentration/mmol dm^{-3}
$[AuCl_3(Hpm)]$	360vs, 340m (sh)		3.8	2.1
$[AuBr_3(Hpm)]$	260m, 250m (sh)		4.7	1.7
$[AuCl_3(Hpe)]$	355vs (br), 366m (sh)		3.6	1.3
$[AuBr_3(Hpe)]$	255vs (br), 240m (sh)		5.4	1.5
$[AuCl_2(pyca)]$	379ms, 366ms	1700vs (br)	7.0	1.8
$[AuBr_2(pyca)]$	332m, 292m	1695vs (br)	0.5	1.3
$[AuCl_2(Hhpyca)]$	376m, 366m	1675vs (br)	0.9	1.5
$[AuBr_2(Hhpyca)]$	328m, 268m	1665vs (br)	1.7	1.5
$[AuCl_2(2,4\text{-}Hpydca)]$	385vs, 370vs	1710vs (br)	0.25	2.0
$[AuCl_2(2,5\text{-}Hpydca)]$	375m, 365m (sh)	1720vs (br)	1.0	1.5
$[AuCl_2(pm)]$	365s, 350s		6.8	1.1
$[AuBr_2(pm)]$	308m, 265m		2.0	1.5
$[AuCl_2(pe)]$	368s, 350s		8.0[b]	1.5
$[Au(pyca)_2][AuCl_4]$	360ms	1730vs (br)	127	1.2
$[Au(pyca)_2]BF_4$		1720vs (br)	144	1.1
$[Au(pyca)_2]ClO_4$		1720vs (br)	121	1.3
$[Au(qnca)_2][AuCl_4]$	366s	1730vs (br)	122	0.6
$[Au(pm)_2][AuCl_4]$	350vs (br)		131	1.9
$[Au(pm)_2]BF_4$			149	1.3
$[Au(pm)_2]ClO_4$			149	1.1
$[Au(pe)_2][AuCl_4]$	350vs (br)		135	1.1
$[Au(pe)_2]BF_4$			146	1.2
$[Au(pe)_2]ClO_4$			141	1.4
$[Au(hpyca)(Hhpyca)]$		1710vs (br)		
$[Au(2,3\text{-}pydca)(2,3\text{-}Hpydca]$		1715vs (br)		
$[Au(2,4\text{-}pydca)(2,4\text{-}Hpydca)]$		1720vs (br)		
$[Au(2,5\text{-}pydca)(2,5\text{-}Hpydca)]$		1710vs (br)		
$[Au(hqnca)(Hhqnca)]$		1725vs (br)		
$Na[Au(2,5\text{-}pydca)_2]\cdot 4H_2O$		1730vs (br)		

[a] For the co-ordinated carboxylate group. [b] In $PhNO_2$.

Table 7 Selected bond length (pm) and angle (°) data for $[AuX_2(L)]$ and $Na[Au(2,5\text{-}pydca)_2]\cdot 4H_2O$ (X = Cl or Br, L = Hhpyca; X = Br, L = pyca)

L	pyca	Hhpyca	Hhpyca	2,5-pydca
X	Br	Br	Cl	
Au–X, *trans*-O	236.8(2)	237.6(2)	225.4(3)	
trans-N	238.2(2)	237.2(2)	225.3(3)	
Au–N	205(1)	203(1)	203.7(8)	196(1)
Au–O	201.5(9)	202(1)	199.4(6)	198.5(9)
X–Au–X	90.1(1)	89.13(8)	90.0(1)	
N–Au–O	82.5(4)	80.9(6)	82.8(3)	81.5(4)

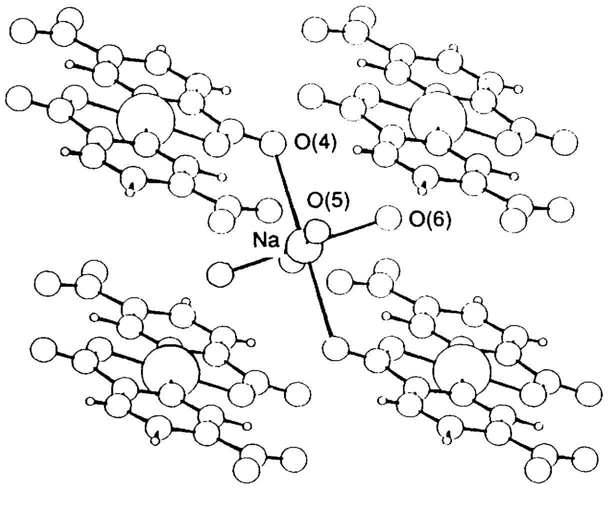

Fig. 3 The sodium ion environment in $Na[Au(2,5\text{-}pydca)_2]\cdot 4H_2O$ viewed down the *c* axis

The structure of $Na[Au(2,5\text{-}pydca)_2]\cdot 4H_2O$ shows that the gold atom is chelated in *trans* fashion by two doubly deprotonated ligands giving a planar anion (Fig. 2). The Au–N bond is slightly but significantly (7σ) shorter than for the neutral complexes. This is presumably due to the presence of the anionic substituent, since the replacement of two halides by the chelate might be expected to have the opposite effect. The sodium cations are square-planar co-ordinated by four water molecules (Na–O 230–244 pm), and also make two long bonds (307 pm) to the carbonyl oxygen atoms of the 2-carboxylate groups of two different complex anions (Fig. 3). The 5-carboxylate groups are not co-ordinated to either metal, but form a three-dimensional network of hydrogen bonds with the sodium-bound water molecules.

Conductivity Studies.—Solutions of several of the neutral complexes were found to undergo changes in conductivity on standing. In the case of $[AuCl_2(psal)]$ (psal = *N*-propylsalicylaldiminate) in nitromethane the molar conductivity rose from 17 to 47 S mol^{-1} over 5 d. Simultaneously there was change in colour from purple to yellow, and the absorption spectrum of the final solution was identical to that of $[Au(psal)_2][AuCl_4]$; the final conductivity value was compatible with this disproportionation when account is taken of the change in molecular weight. Comparable increases occurred for $[AuX_3(HL)]$ (HL = Hpm or Hpe). In this case, the most likely reaction is formation of the chelate, with liberation of HX.

The chelated complexes also show some increase in conductivity, the change being most marked for the pyridylalcohol derivatives $[AuX_2(L)]$ (L = pm or pe). In this case it is likely that the principal reaction is displacement of a halide by a solvent molecule, which is consistent with the greater basicity (and hence *trans* influence) of the alkoxy group. It was also noticeable that reaction was less extensive for X = Br than Cl, and there was no evidence of disproportionation to give the ionic complexes.

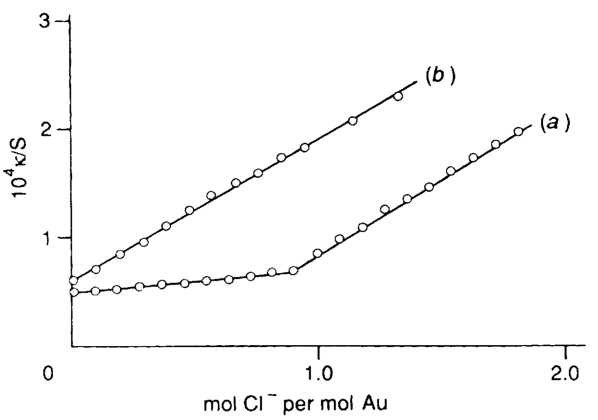

Fig. 4 Conductimetric titration of (*a*) $[Au(pyca)_2]BF_4$ and (*b*) $[Au(pm)_2]BF_4$ with Cl^-

The complexes $[Au(pyca)_2]Y$ ($Y = BF_4$ or ClO_4) are stable in solution. However, when $Y = AuCl_4$, there is a substantial decrease in conductivity (*e.g.* from 127 to 61 S mol^{-1} over 30 h, falling to 19 S mol^{-1} after 96 h). Here the most likely reaction is displacement of Cl^- from the anion by a solvent molecule. However, this might be expected to give a small rise in conductivity, owing to the greater mobility of Cl^- than $[AuCl_4]^-$. It appears that the liberated chloride ion is bound by the cation. This was demonstrated by a conductimetric titration of $[Au(pyca)_2]BF_4$ with $[NEt_4]Cl$ [Fig. 4(*a*)]; a sharp end-point was obtained after the addition of 0.9 mol equivalents of Cl^-. This behaviour is analogous to that of $[Au(pdma)_2]^+$, which also binds halide ions (pdma = *o*-phenylenebis(dimethylarsine)].[16] Interestingly, titration of $[Au(pm)_2]BF_4$ with $[NEt_4]Cl$ gave an immediate, linear rise in conductivity [Fig. 4(*b*)] with no breaks. Evidently the greater donor power of the alkoxy O-donor atom places sufficient negative charge on the gold atom to inhibit the formation of the five-co-ordinate complex.

Discussion

Bidentate ligands of the type N–OH (HL) can in principle form three types of complex with a trivalent metal halide: the simple unchelated derivative $[MX_3(HL)]$ and two chelate forms derived from the deprotonated ligand, $[MX_2(L)]$ and $[ML_2]^+$ (the chelated non-deprotonated form is most unlikely when co-ordinated to a trivalent metal). Representatives of all these types have been found in this work, the principal determining experimental conditions being the pH and the presence or absence of additional halide ion.

The reaction of $[AuX_4]^-$ (X = Cl or Br) with the O,N-bidentate ligands used here give products which depend principally on the pH and only slightly on the nature of the ligand. Only the pyridyl alcohols Hpm and Hpe show monodentate behaviour, and then only in the presence of a considerable excess of halide ion which serves to inhibit the chelation reaction. Monochelate derivatives are formed readily by all the pyridinecarboxylic acids but yields are satisfactory only in the presence of an excess of the ligand which presumably acts as a buffering agent. At slightly higher pH, with a larger excess of the ligand, bis(chelate) cationic complexes are formed. This type of complex is also formed very readily by the Schiff-base ligands, for which it is difficult to obtain significant yields of the neutral monochelates. In these cases some hydrolysis of the ligand also occurs and the liberated base encourages reaction of the second ligand; it is necessary to postulate that attack by the ligand on $[AuX_2(2\text{-}OC_6H_4\text{-}CH{=}NR)]$ is faster than on $[AuCl_4]^-$, presumably because of the difference in charge.

For bis(chelated) complexes of the ligands with hydroxy- and carboxylic acid substituents, deprotonation of the substituent on one ligand readily occurs, to give insoluble hydrogen-bonded polymers, and complete deprotonation leads to the centrosymmetric anions $[Au(L\text{–}H)_2]^-$.

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Received 7*th November* 1991; *Paper* 1/05677H