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Syntheses, Characterization and x-ray Structures of Gold(III) Complexes Obtained by Addition of Bases to Gold(III)(2-Pyridinecarboxaldehyde)

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SYNTHESES, CHARACTERIZATION AND X-RAY STRUCTURES OF GOLD(III) COMPLEXES OBTAINED BY ADDITION OF BASES TO GOLD(III)(2-PYRIDINECARBOXALDEHYDE)

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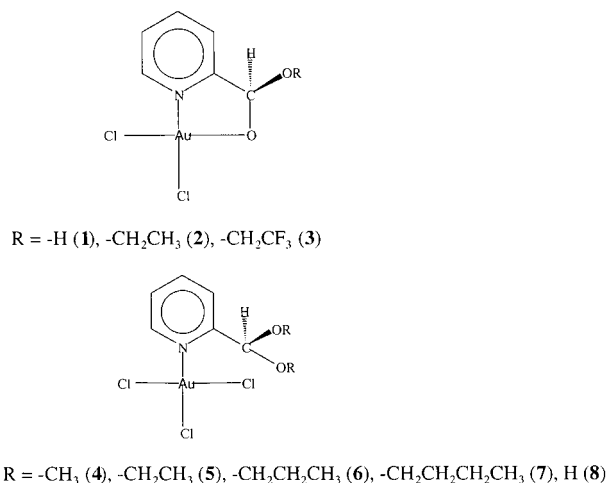
Reaction of potassium tetrachloroaurate(III), KAuCl_4 , with 2-pyridinecarboxaldehyde (2CHO-py) have been examined in protic HX (X=OH, OMe, OEt, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, OCH_2CF_3) solvents. Compounds in which the pyridine ligand is *N* or *N-O* coordinated in a newly carbonyl hydrated or in semi- and acetal-forms, derived by addition of one or two hydroxylic molecules, have been isolated; these include dichloro[pyridine-2(α -hydroxymethanolato)]gold(III) (1), dichloro[pyridine-2(α -ethoxymethanolato)]gold(III) (2), dichloro[pyridine-2(α -(2,2,2-trifluoroethoxymethanolato)]gold(III) (3), trichloro(2-pyridinecarboxaldehyde dimethyl acetal)gold(III) (4), trichloro(2-pyridinecarboxaldehyde diethyl acetal)gold(III) (5), trichloro(2-pyridinecarboxaldehyde di-1-propyl acetal)gold(III) (6) and trichloro(2-pyridinecarboxaldehyde di-1-butyl acetal)gold(III) (7). The crystal and molecular structures of (2), (5) and (7) have been determined by X-ray methods. Compound (2) crystallizes in space group $Pna2_1$ with $Z=4$, $a=7.8914(4)$, $b=17.3660(4)$ and $c=8.3873(5)$ Å; (5) crystallizes in space group $P1$ with $Z=2$, $a=7.7779(3)$, $b=8.2878(2)$ and $c=13.3202(6)$ Å, $\alpha=96.975(2)$, $\beta=95.096(2)$, $\gamma=115.027(2)^\circ$; (7) crystallizes in space group $P2_1/a$ with $Z=4$, $a=14.5438(12)$, $b=8.9865(7)$ and $c=15.0362(11)$ Å.

Keywords: Gold(III); Pyridinecarboxaldehyde; Bases; X-ray structures

INTRODUCTION

In a recent preliminary study [1] dealing with the reactions of 2-pyridinecarboxaldehyde (2-CHOpy) with a series of neutral and charged Pt(II), Pd(II) and Au(III) substrates, both in protic and aprotic solvents, we have found that the *N*-coordinated pyridine ligand undergoes addition of hydroxylic molecules as a consequence of the enhanced electrophilicity of the carbonyl carbon atom due to interaction with the metal ion. However, while Pt(II) and Pd(II) complexes are mainly obtained with the pyridine ligand *N*-coordinated in the aldehydic form, some analogous gold(III) species have

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SCHEME 1.

been isolated only as addition products. We have now extended the study of the reactivity of the Au(III)-2CHOp_y system towards a series of hydroxylic molecules and obtained a series of pure *N*-*O* chelated semiacetal complexes (Scheme 1: **2**, **3**) as well as acetal complexes (Scheme 1: **4**-**7**), depending on the solvents and the experimental conditions employed.

Here we report the synthesis and characterization of complexes **1**-**3** and **4**-**7** and the crystal structures of **2**, **5** and **7**, which allow correlation of structural data with the general mechanism of nucleophilic substitution at square-planar Au(III) complexes.

EXPERIMENTAL

Materials

Potassium tetrachloroaurate(III) dihydrate was prepared from the corresponding metal by the standard method. 2-Pyridinecarboxaldehyde (Aldrich) was vacuum distilled and stored at 4°C. The inorganic salts and solvents used were reagent grade products. High purity deuterated solvents of NMR measurements were used as received from Aldrich Chemical Co. The alcohols employed were distilled before use and stored over molecular sieves.

Instrumentation

IR spectra (4000-500 cm⁻¹, KBr disks; 600-50 cm⁻¹, polyethylene pellets) were recorded on a Nicolet Magna FT IR 750 spectrophotometer. ¹H NMR spectra were collected on a Bruker AC 200 F spectrometer. Conductivity measurements were carried out with a CDM 83 Radiometer Copenhagen conductivity meter and a CDC 334 immersion cell. Elemental analyses were performed by the Microanalytical Laboratory of the University of Padua.

Preparation of Complexes

Dichloro[Pyridine-2(α -hydroxymethanolato)]gold(III) (1)

To a stirred solution of $\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$ (0.414 g, 1 mmol) in H_2O (30 cm^3), a solution of 2-CHOpy (0.107 g, 1 mmol) in the same solvent (5 cm^3) was added and the resulting mixture warmed at 80°C . The solution and the yellow precipitate which formed rapidly were maintained for 1 h at 80°C with stirring. The solid was then filtered off, washed with water and dried *in vacuo* over P_2O_5 . This crude product resulted in a mixture (see results and discussion) of **1** and the diolic *N*-coordinated species with the aldehyde in the hydrated form (Scheme 1: **8**) and in a mol ratio of 85:15, respectively. The mixture was then suspended in warm water (30 cm^3 , 80°C) with stirring and a solution of NaHCO_3 was added dropwise to $\text{pH} \cong 6$ (initial $\text{pH} \cong 3$). After 1 h the yellow compound was filtered off, washed with water and dried *in vacuo* over P_2O_5 (0.353 g, 90%).

Dichloro[pyridine-2(α -ethoxymethanolato)]gold(III) (2)

(**1**) (0.196 g, 0.5 mmol) was dissolved in 15 cm^3 of EtOH at 60°C with stirring. The resulting yellow solution was concentrated to 5 ml and yellow crystals of the title compound formed by slow evaporation of the solvent at room temperatures in the dark. The compound was filtered off, washed with water and dried *in vacuo* over P_2O_5 (0.110 g, 52%).

Dichloro[pyridine-2(α -(2,2,2-trifluoroethoxymethanolato)]gold(III) (3)

The complex was prepared following the same procedure as for (**2**) by using 2,2,2-trifluoroethanol as solvent (0.090 g, 38%).

Trichloro(2-pyridinecarboxaldehyde dimethyl acetal)gold(III) (4)

2-Pyridinecarboxaldehyde (0.107 g, 1 mmol) was added to a solution of $\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$ (0.414 g, 1 mmol) in methanol (30 cm^3) and the resulting mixture was heated to 60°C for 15 min with stirring and then cooled to room temperature. The white microcrystalline precipitate (KCl) formed was filtered off. Fine yellow crystals of the product were obtained from the resulting solution by slow evaporation at room temperature in the dark (0.30 g, 67%).

The compounds trichloro(2-pyridinecarboxaldehyde diethyl acetal)gold(III), **5**, trichloro(2-pyridinecarboxaldehyde di-1-propyl acetal)gold(III), **6**, and trichloro(2-pyridinecarboxaldehyde di-1-butyl acetal)gold(III), **7**, were prepared by analogous procedures using ethanol, 1-propanol and 1-butanol, respectively. Yields were 0.302 g (62%), 0.320 g (63%), 0.278 g (52%), respectively.

X-ray Structure Determinations

Data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) at room temperature. Data were corrected for Lorentz polarization and absorption (SORTAV) [2] effects. Crystal parameters and other experimental details for data collection are summarized in Table III. Structures were solved by direct methods (SIR92) [3] and refined by full-matrix least-squares

methods with all non-hydrogen atoms anisotropic and hydrogens in calculated positions. All calculations were performed using SHELXL-97 [4] and PARST [5]. Selected bond distances and angles are shown in Table IV. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 187071 (for trichloro(2-pyridinecarboxaldehyde diethyl acetal)gold(III) (5), 187072 for trichloro(2-pyridinecarboxaldehyde di-*i*-butyl acetal)gold(III) (7) and 187073 for dichloro[pyridine-2(α -ethoxymethanolato)]gold(III) (2). Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

RESULTS AND DISCUSSION

Preparations

Elemental analyses and selected IR data for the complexes are collected in Table I. ^1H NMR data are reported in Table II. ^1H NMR assignments for coordinated 2CHO-py are given according to the following numbering scheme.

In all complexes the pyridine ligand always coordinates to the metal through the nitrogen atom. The stretching C=N frequency of the pyridine ring, which falls at 1586 cm^{-1} in the free ligand, shifts upon coordination to slightly higher frequency ($1600\text{--}1625\text{ cm}^{-1}$) [6]. Addition of the ligand to a hot aqueous solution of KAuCl_4

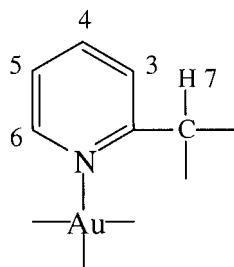


TABLE I Analytical and selected IR data for the complexes

Complex	Found (calcd) %				IR (cm^{-1})			
	C	H	N	Cl	$\nu(\text{O-H})$	$\nu(\text{C=N})$ pyridine ring	$\nu(\text{C-O-C})$ alkyl ether	$\nu(\text{Au-Cl})$
(1)	18.0 (18.4)	1.39 (1.54)	3.43 (3.57)	18.4 (18.1)	3262	1610		378, 360
(2)	22.7 (22.9)	2.24 (2.40)	3.26 (3.33)	16.9 (16.9)				
(3)	20.3 (20.3)	1.25 (1.49)	2.77 (2.95)	14.7 (15.0)	1617	1058	374, 357	
(4)	20.9 (21.0)	2.39 (2.43)	3.10 (3.07)	23.6 (23.3)				1611
(5)	24.6 (24.8)	3.11 (3.12)	2.95 (2.89)	22.1 (21.9)	1604	1005	366, 354	
(6)	27.8 (28.1)	3.49 (3.74)	3.08 (2.75)	20.6 (20.7)				1604
(7)	30.7 (31.1)	4.32 (4.29)	2.64 (2.59)	19.2 (19.7)	1604	1123	368, 354(sh)	

TABLE II ^1H NMR data of the complexes

Complex	Solvent	^1H NMR (δ , ppm; J , Hz)
(1)	CD_3NO_2	9.05 [1H, d, $J=5.9$, H_6], 8.37 [1H, td, $J=7.8$, 1.4, H_4], 7.87 [2H, m, $\text{H}_{3,5}$], 6.12 [1H, d, $J=6.3$ H_7], 4.76 [1H, d, $J=6.3$ OH]
(2)	CD_3NO_2	9.03 [1H, d, $J=5.9$, H_6], 8.38 [1H, td, $J=7.8$, 1.4, H_4], 7.85 [2H, m, $\text{H}_{3,5}$], 5.56 [1H, s, H_7], 3.96, 3.76 [2H, ABX ₃ system $J_{\text{AB}}=10.1$, $J_{\text{AX}}=J_{\text{BX}}=6.9$, CH_2], 1.29 [3H, t, $J=6.9$, CH_3]
(3)	CDCl_3	9.18 [1H, d, $J=5.7$, H_6], 8.27 [1H, td, $J=7.7$, 1.6, H_4], 7.80 [2H, m, $\text{H}_{3,5}$], 5.81 [1H, s, H_7], 4.24 [2H, m, CH_2]
(4)	CD_3NO_2	8.98 [1H, d, $J=5.4$, H_6], 8.34 [1H, td, $J=7.7$, 1.6, H_4], 8.17 [1H, dd, $J=7.7$, 1.6, H_3], 7.89 [1H, ddd, $J=7.7$, 5.4, 1.6, H_5], 6.01 [1H, s; H_7], 3.51 [6H, s, OCH_3]
(5)	CD_3NO_2	8.97 [1H, d, $J=5.8$, H_6], 8.35 [1H, td, $J=7.8$, 1.4, H_4], 8.19 [1H, dd, $J=7.8$, 1.8, H_3], 7.87 [1H, ddd, $J=7.8$, 5.8, 1.8, H_5], 6.10 [1H, s; H_7], 3.82 [4H, m, CH_2], 1.37 [6H, t, $J=7.0$, CH_3]
(6)	CD_3NO_2	8.97 [1H, d, $J=5.6$, H_6], 8.36 [1H, td, $J=7.8$, 1.6, H_4], 8.21 [1H, dd, $J=7.8$, 1.6, H_3], 7.87 [1H, ddd, $J=7.8$, 5.7, 1.6, H_5], 6.12 [1H, s; H_7], 3.72 [4H, m, $\text{OCH}_2\text{CH}_2\text{CH}_3$], 1.80 [H, m, $\text{OCH}_2\text{CH}_2\text{CH}_3$], 1.01 [6H, t, $J=7.3$, $\text{OCH}_2\text{CH}_2\text{CH}_3$]
(7)	CD_3NO_2	8.97 [1H, d, $J=5.6$, H_6], 8.36 [1H, t, $J=7.8$, H_4], 8.19 [1H, d, $J=7.8$, H_3], 7.87 [1H, dd, $J=7.8$, 5.6, H_5], 6.12 [1H, s, H_7], 3.76 [4H, m, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$], 1.77 [4H, m, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$], 1.48 [4H, m, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$], 0.98 [6H, t, $J=7.3$, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$]

^aChemical shifts for ^1H NMR are reported by reference to TMS.

TABLE III Crystallographic data for selected complexes

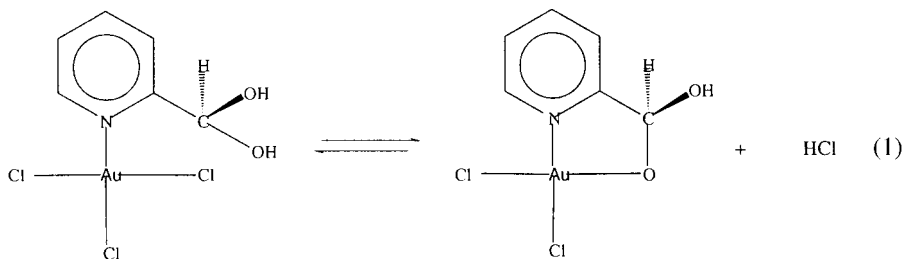
Compound	5	7	2
Formula	$\text{AuC}_{10}\text{H}_{15}\text{Cl}_3\text{O}_2\text{N}$	$\text{AuC}_{14}\text{H}_{23}\text{Cl}_3\text{O}_2\text{N}$	$\text{AuC}_8\text{H}_{10}\text{Cl}_2\text{O}_2\text{N}$
M	484.56	540.667	420.045
Space group	$P\bar{1}$	$P2_1/a$	$Pna2_1$
$a/\text{\AA}$	7.7779(3)	14.5438(12)	7.8914(4)
$b/\text{\AA}$	8.2878(2)	8.9865(7)	17.3660(4)
$c/\text{\AA}$	13.3202(6)	15.0362(11)	8.3873(5)
$\alpha/^\circ$	96.975(2)		
$\beta/^\circ$	95.096(2)	96.232(4)	
$\gamma/^\circ$	115.027(2)		
$U/\text{\AA}^3$	762.83(5)	1953.6(3)	1149.41(9)
Z	2	4	4
$D_c/\text{g cm}^{-3}$	2.110	1.838	2.427
$F(000)$	456	1040	776
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	101.578	79.431	132.377
Measured Refl.ns	8275	9253	6894
Unique Refl.ns	3600	3894	1759
R_{int}	0.041	0.048	0.049
Obs.Refl.ns [$I \geq 2\sigma(I)$]	3392	3206	1558
$\theta_{\text{min}}-\theta_{\text{max}}/^\circ$	3.4-27.8	3.8-27.5	2.7-30.0
hkl ranges	-10, 10; -10, 9; -17, 17	-18, 18; -11, 11; -19, 19	-10, 11; -0, 23; -11, 11
$R(F^2)$ (Obs. Refl.ns)	0.0325	0.0499	0.0318
$wR(F^2)$ (All Refl.ns)	0.0837	0.1440	0.0815
No. variables	156	192	126
Goodness-of-fit	1.109	1.128	1.071

rapidly affords (mainly) the complex with the ligand in the hydrated aldehyde form (**8**) [1]. Then, one of the two OH groups intramolecularly substitutes the Cl atom in the *cis* position with respect to the pyridine nitrogen atom by eliminating HCl. The rate and the extent of the whole process depend on the experimental

TABLE IV Selected bond distances (Å) and angles (°) for the complexes

Compound	5	7	2
Au1–N1	2.058(5)	2.054(8)	2.022(3)
Au1–C11	2.261(2)	2.258(3)	2.240(3)
Au1–C12	2.279(2)	2.275(3)	2.276(2)
Au1–C13	2.279(2)	2.282(3)	
Au1–O1	2.902(4)	2.889(2)	1.988(6)
N1–Au1–C11	178.9(1)	177.6(2)	172.7(2)
N1–Au1–C12	90.6(2)	88.7(2)	94.8(2)
N1–Au1–C13	88.4(2)	90.6(2)	
N1–Au1–O1	69.1(3)	68.7(3)	82.2(3)
C11–Au1–C12	90.4(1)	89.4(1)	92.5(1)
C11–Au1–C13	90.7(1)	91.2(1)	
C11–Au1–O1	110.2(2)	112.8(2)	90.6(2)
C12–Au1–C13	174.5(1)	176.8(1)	
C12–Au1–O1	91.4(2)	93.5(2)	176.8(2)
C13–Au1–O1	93.3(2)	90.6(2)	

conditions. Addition of one molecule of water at the carbonyl group is fast, while subsequent intramolecular reaction leading to formation of *N*–*O* chelated complexes, **1**, requires about 20 min for completion, as confirmed by pH measurements. The reaction mixture at this stage contains the two complexes **1** and **8**. The experimental evidence for these reactions are found in the infrared spectrum of the mixture. The characteristic stretching signal of the carbonyl group in its keto form that occurs in the free ligand at 1720 cm^{-1} and in the complex $\text{Pd}(2\text{-CHOPy})_2\text{Cl}_2$ at 1712 cm^{-1} [7], is absent. In addition, a strong broad absorption centred at 3262 cm^{-1} and assignable to $\nu(\text{O-H})$ of coordinated ligand in **1** and **8** is seen. The aqueous solution from which the mixture precipitates with time becomes strongly acidic, owing to the formation of HCl. Finally, the $^1\text{H NMR}$ spectrum of the mixture obtained after 1 h and before treatment with NaHCO_3 reveals two series of signals assignable to two different species in mol ratio 15 : 100 (**8** : **1**). This ratio is calculated by integration of $^1\text{H NMR}$ signals of the H_7 (Scheme 1) atom of the ligand. $^1\text{H NMR}$ signals of hydrogen atoms of the pyridine ring (H_6 , H_5 , H_4 and H_3 in Scheme 1) attributable to complex **8** are almost completely masked by the more intense signals of the corresponding atoms in complex **1**. The mol ratio of **8**–**1** species seems to depend mainly on experimental conditions (time and temperature), but to completely convert the mixture to species **1** it is necessary to completely eliminate HCl formed, by adding NaHCO_3 to an aqueous mixture of the previously filtered crude product (**8** + **1**). This suggests that the formation of **1** from **8** is a reversible reaction (1). A kinetic study of the reverse reaction is in progress. The chelate compounds **2** and **3** were obtained from the reaction of pure **1** with the corresponding alcohols. The acetalic compounds **4**–**7** were obtained by reacting



$\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$ and 2-CHOp_y in the appropriate alcohol. Crystals of **2**, **5** and **7** suitable for X-ray structure determinations were obtained from solution by slow evaporation of solvent at room temperature in the dark.

Crystallography

It is well known that square planar Au(III) complexes can expand their coordination from SQP geometry to square pyramidal (SQPY) or square bipyramidal (SQBPY) structures [8–11]. These secondary coordinations, observed in crystals, induce perturbations which seem to be related to geometric changes involved in incipient nucleophilic substitution at low-spin Au(III) SQP complexes. A simple molecular orbital model has been used to derive a double-humped potential-energy surface for the substitution of a simple ligand in a low spin d^8 square-planar transition-metal complex [12]. It has been shown that, once formed, the SQPY species will undergo transformation to a trigonal bipyramidal (TBP) structure, which may exist either as an activated complex or as a true intermediate, then to a new square pyramidal complex, which through losing an apical atom or group passes to a new square planar species. Furthermore, the reaction pathway of the analogous nucleophilic substitution at SQP d^8 Ni(II) centres has been investigated using the principle of structural correlation [13,14] applied to the crystal structures of 78 different five-coordinated nickel complexes [15]. The resulting mechanism can be summarized in the following steps: (i) nucleophilic attack at the d^8 Ni(II) centre with the formation of an intermediate SQPY species; (ii) formation of a trigonal bipyramidal complex through the Berry mechanism [16]; (iii) dissociation of an axial ligand and (iv) rearrangement to a new square planar complex. It is reasonable to assume that this mechanism can be also transferred to the nucleophilic substitution at d^8 Au(III), although structural correlations are not possible because Au(III) does not form “true” five coordinated species. Its tendency to expand its coordination using a fifth weak contact, however, can be considered as the first step in the formation of the activated trigonal bipyramidal complex in the nucleophilic substitution mechanism.

ORTEP [17] views of the three molecules whose structures have been determined are displayed in the Figs. 1–3, respectively. In complexes **5** and **7** the four positions of the square-planar coordination of Au(III) are occupied by three chlorine atoms and the nitrogen of the pyridine (derivative) ligand. The Au–N(pyridine) distances of 2.058(5) and 2.054(8) Å well correspond to those found in gold(III) complexes containing a pyridine ligand which is not strained [9,18]. Distances between Au and Cl1 in *trans* positions of the pyridine nitrogen of 2.261(2) in **5** and 2.258(3) Å in **7** are slightly shorter than those of Au–Cl2 and Au–Cl3 bonds which are *trans* to each other [Au–Cl = 2.279 and 2.278 Å (on average) for compounds **5** and **7**, respectively] owing to the reciprocal *trans* influence of Cl atoms [19]. The most interesting feature of these square-planar complexes is their ability to expand their coordination to SQPY geometry by forming a fifth secondary Au–O bond with an acetalic oxygen. Au–O1 distances of 2.902(4) and 2.889(2) Å, for **5** and **7**, respectively, are longer than normal Au–O bonds of 2.00–2.07 Å, found in Au-carboxylate and hydroxo complexes [10], but much shorter than the usual non-bonded van der Waals contact between these atoms (3.6 Å) [8]. Such a secondary coordination produces distortions in square planar geometry which can be considered as the first step of an incipient transformation, through square pyramidal modes, to a trigonal bipyramidal geometry which is the transition state in the nucleophilic substitution process at d^8 square planar complex. The distortions can be

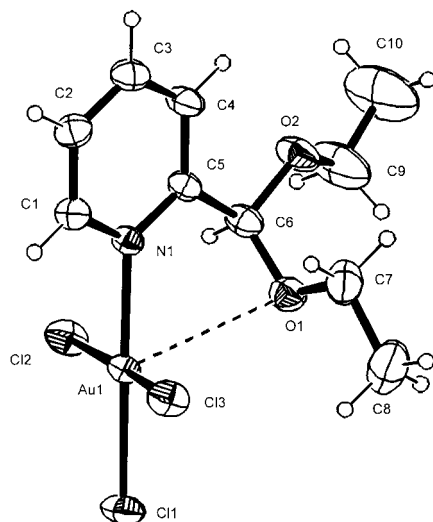


FIGURE 1 ORTEP view and atom numbering of Compound **5** showing thermal ellipsoids at 30% probability.

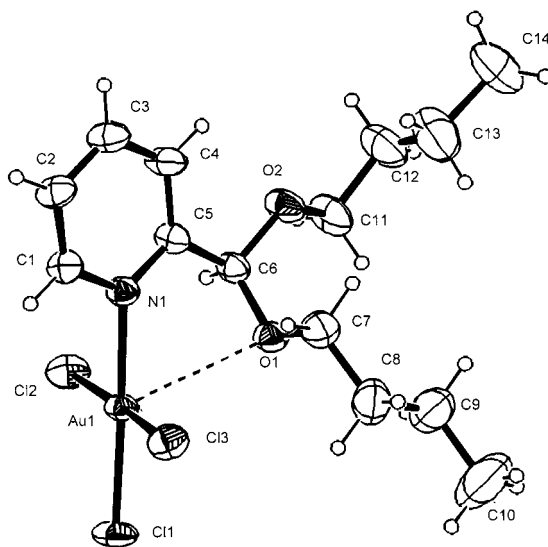


FIGURE 2 ORTEP view and atom numbering of Compound **7** showing thermal ellipsoids at 30% probability.

evidenced by calculating the deviations from the weighted least-square planes passing through the square planar coordinated atoms. It is seen that C12 and C13 deviate significantly [0.107(2) and 0.107(2) Å in **5**, and 0.061(3) and 0.059(3) Å in **7**] in the opposite direction of the approaching O1 oxygen, while the apical Cl1 atoms deviate from the same plane only by 0.002(2) and 0.007(3) Å for **5** and **7**, respectively.

Compound **2** displays the structural result obtained after the substitution of Cl atom by oxygen. The formation of the Au–O1 bond forces the pyridine ring to be almost parallel to the coordination plane, the dihedral angle between the mean planes being

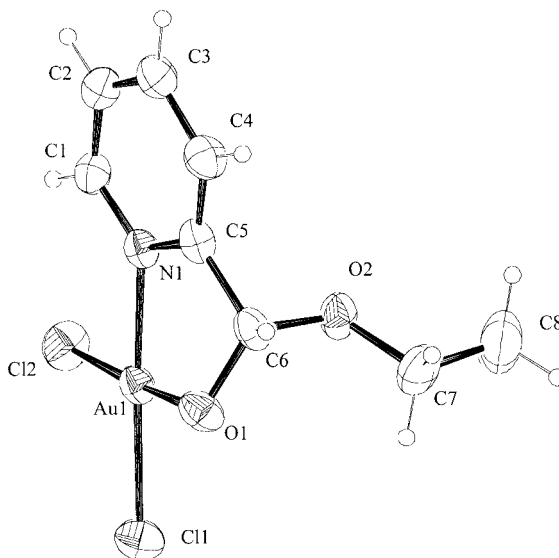


FIGURE 3 ORTEP view and atom numbering of Compound **2** showing thermal ellipsoids at 30% probability.

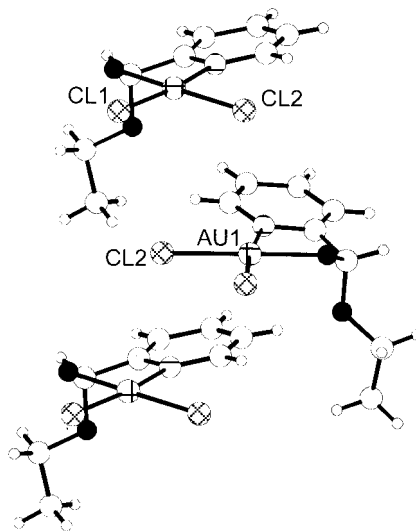


FIGURE 4 Observed packing motif in Compound **2** showing short Au1...Cl2 contacts.

12.9(3)°. This favours π -conjugation between the pyridine ring and Au with Au–N1 being (2.022(3) Å) shorter than that observed in **5** and **7** where the pyridine rings are rotated with respect to the coordination plane by angles of 67.2(2) and 73.6(2)°, respectively. This complex displays small distortion from SQP geometry because the C11 and C12 atoms deviate from the mean plane defined by Au1, N1, O1, C11 and C12 atoms only by 0.002(3) and 0.011(4) Å, while the significantly greater deviation of O1 of 0.069(8) Å, is probably due to strain effects in the chelate ring. Also in this structure, Au(III) displays secondary coordination as shown in Fig. 4, an intermolecular

contact between Au1 and C12 of 3.708(4) Å slightly shorter than the van der Waals contact 4.00 Å.

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