Comparison of Structure and Reactivity of Bis(2-aminoethyl)amine- and Bis(2-aminoethyl)amido-chlorogold(III) Complexes

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The crystal and molecular structures of the title compounds, $[AuCl\{NH(CH_2CH_2NH_2)_2\}]Cl[ClO_4]$ (1) and $[AuCl\{N(CH_2CH_2NH_2)_2\}][ClO_4]$ (2) have been determined by Patterson and Fourier methods. Compound (1) crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a cell of dimensions: a = 8.590(6), b = 12.745(8), c = 12.256(8) Å, and β = 113.6(1)°. Compound (2) crystallizes in the orthorhombic space group $P2_12_12_1$, with four molecules in a unit cell of dimensions: a = 12.976(8), b = 10.029(7), and c = 8.171(6) Å. Anisotropic least-squares refinement has reduced R to 0.119 and 0.103 for (1) and (2) respectively. In both compounds the co-ordination about the gold atom is approximately square planar but two atoms of the counter ions are about 3.1 Å from the metal along the axial co-ordination sites. In compound (1) the four donor atoms are essentially in a plane and the gold atom is displaced from this by 0.063 Å; in compound (2), instead, there is a pronounced tetrahedral distortion of the co-ordination geometry. Moreover, the pyramid about the central nitrogen of the tridentate ligand is much flatter in (1) than in (2). The Au–Cl bond is longer in the amido- than in the amino-complex [2.273(8) and 2.330(10) Å in (1) and (2) respectively] suggesting a greater *trans* influence of N^- as compared with NH. The reactivity of these substrates towards chloride substitution by bromide has been re-examined.

THE complexes $[MX(baa)]^{n+}$ [M = Pd^{II}, Pt^{II}, or Au^{III}; X = unidentate ligand; baa = bis(2-aminoethyl)amine] have been widely studied from a kinetic point of view.[1] The gold(III) complex is remarkable for the strong acidity of the central aminic group of the tridentate ligand,[2-4] and in order to compare the reactivity of $[AuX(baa)]^{2+}$ with that of the conjugate base $[AuX(baa - H)]^+$ the reaction of substitution of X by other nucleophiles has been studied in different conditions. Unfortunately, the kinetics of substitution at the protonated species are limited to the substitution of Cl^- by Br^- since other nucleophiles reduce the gold(III) complex [I^-, SCN^-, or $(NH_2)_2CS$] or cannot be used in acidic media (NO_2^-, N_3^-, or nitrogen bases).[5] Thus, from the reported rates of substitution of chloride by bromide ion, it appears that the amine complex reacts faster, by a factor of two, than the amido one. This behaviour contrasts with the rate increase observed in base-catalyzed substitution at six-co-ordinated metal amines,[6] and also with chloride substitution in $[AuCl(Et_4baa - H)]^+$ and $[AuCl(Et_4baa)]^{2+}$ [Et_4baa = bis(*NN*-diethyl-2-aminoethyl)amine] where the amido-complex reacts faster, by a factor of 70, than the amine one.[3]

In order to show, at least in the ground state, the effect of deprotonation of the central nitrogen, we have determined the crystal and molecular structure of $[AuCl(baa)]Cl[ClO_4]$ (1) and $[AuCl(baa - H)][ClO_4]$ (2) by *X*-ray diffractometry. We have also carried out some more kinetic studies on the reaction of substitution of Cl^- by Br^-.

RESULTS AND DISCUSSION

Positional and vibrational parameters are listed in Table 1, intramolecular bond lengths and angles in Table 2. Figure 1 gives the numbering scheme, the displacement of the donor atoms and of the central metal from the mean co-ordination plane, and a side view along the direction passing through N(2) and the middle point of the N(1)—N(3) segment. Figure 2 shows the interactions between anions and cations.

The Structure of Compound (1).—This species consists of the complex cation $[AuCl(baa)]^{2+}$ and Cl^- and ClO_4^- counter ions. The complex has a distorted square-planar geometry, the gold atom being displaced by 0.063 Å above the plane passing through the nitrogen atoms of the tridentate ligand and the covalent chloride which are coplanar within 0.004 Å.

TABLE 1

Atomic co-ordinates (× 10^4) for compounds (1) and (2) with estimated standard deviations in parentheses

	X	*Y*	*Z*
(*a*) Compound (1)			
Au	4 770(1)	3 019(1)	1 759(1)
Cl(1)	4 173(11)	1 298(6)	1 290(7)
Cl(2)	3 225(9)	2 676(6)	4 560(5)
Cl(3)	8 601(10)	1 126(5)	4 231(5)
O(1)	1 761(32)	2 559(24)	3 384(22)
O(2)	4 743(46)	2 727(34)	4 264(33)
O(3)	3 380(36)	1 727(26)	5 286(27)
O(4)	2 830(52)	3 505(38)	5 223(39)
N(1)	7 244(28)	2 820(19)	2 310(20)
N(2)	5 334(22)	4 545(16)	2 289(16)
N(3)	2 386(27)	3 426(20)	1 375(20)
C(1)	8 162(38)	3 897(28)	2 835(28)
C(2)	7 035(37)	4 532(26)	3 223(26)
C(3)	3 879(35)	4 977(25)	2 540(26)
C(4)	2 242(34)	4 601(25)	1 515(25)
(*b*) Compound (2)			
Au	2 317(1)	7 131(2)	5 508(2)
Cl(1)	3 187(9)	8 071(12)	3 292(15)
Cl(2)	200(9)	9 367(15)	3 619(16)
O(1)	857(43)	9 992(52)	4 896(68)
O(2)	281(41)	7 969(51)	3 840(65)
O(3)	531(45)	9 826(49)	1 966(67)
O(4)	−862(30)	9 788(38)	3 776(48)
N(1)	2 457(27)	8 768(35)	7 000(43)
N(2)	1 608(30)	6 199(39)	7 453(51)
N(3)	1 874(30)	5 503(36)	4 258(47)
C(1)	2 026(50)	8 392(64)	8 672(79)
C(2)	1 153(42)	7 354(53)	8 445(72)
C(3)	856(40)	5 395(52)	6 729(69)
C(4)	1 431(31)	4 521(40)	5 491(59)

The Au–N(1) and Au–N(3) bonds have similar length

[1.97(2) and 1.98(2) Å respectively], and both are slightly shorter than the Au–N(2) bond [2.05(2) Å]; the calculated value for a covalent Au–N bond is 2.04 Å.[7] Values of *ca.* 2.13 Å have been found in the four-co-ordinate $[Au(SO_3)_2(en)]^+$ complex (en = ethane-1,2-diamine),[8] while higher values (2.27—2.42 Å) have been found in five-co-ordinate $[AuCl_3(dmp)]$ [9] and $[AuBr_3(dmp)]$ species (dmp = 2,9-dimethyl-1,10-phenanthroline).[9] In another complex, $[AuCl_3(bquin)]$ (bquin = 2,2′-biquinolyl), the two Au–N bonds were very different (2.09 and 2.58 Å respectively).[10]

The Au–Cl bond [2.273(8) Å] is of normal length. Values in the range 2.27—2.29 Å have been reported for the five-co-ordinate $[AuCl_3(dmp)]$ complex,[9] for the chlorines *cis* to the phosphine of the four-co-ordinate $[AuCl_3(PPh_3)]$ complex,[11] and for the digonal $[AuCl(PPh_3)]$ species.[12] A much shorter length was reported for one of the Au–Cl bonds of $[AuCl_3(bquin)]$ (2.09 Å), while the other two were much longer (2.35 and 2.38 Å).[10] The Au–Cl bonds *trans* to PPh_3 in $[AuCl_3(PPh_3)]$ and *trans* to C_6F_5 in $[AuCl(C_6F_5)_2(PPh_3)]$ were also longer than normal (2.347 and 2.38 Å respectively).[11,13]

TABLE 2

Bond lengths (Å) and angles (°) of (1) and (2), with estimated standard deviations in parentheses

	(1)	(2)
Au–Cl(1)	2.273(8)	2.33(1)
Au–N(1)	1.97(2)	2.05(4)
Au–N(2)	2.05(2)	2.06(4)
Au–N(3)	1.98(2)	2.01(4)
N(1)–C(1)	1.59(4)	1.52(7)
C(1)–C(2)	1.48(5)	1.55(8)
C(2)–N(2)	1.45(3)	1.53(7)
N(2)–C(3)	1.51(4)	1.40(7)
C(3)–C(4)	1.54(4)	1.53(7)
C(4)–N(3)	1.52(4)	1.52(6)
Cl(1)–Au–N(1)	93.8(7)	95(1)
Cl(1)–Au–N(2)	176.4(6)	176(1)
Cl(1)–Au–N(3)	94.9(8)	94(1)
N(1)–Au–N(2)	85.9(9)	87(1)
N(1)–Au–N(3)	170(1)	168(1)
N(2)–Au–N(3)	85.3(9)	84(2)
Au–N(1)–C(1)	109(2)	108(3)
N(1)–C(1)–C(2)	109(3)	109(5)
C(1)–C(2)–N(2)	110(2)	107(4)
C(2)–N(2)–C(3)	120(2)	113(4)
N(2)–C(3)–C(4)	106(2)	106(4)
C(3)–C(4)–N(3)	108(2)	105(3)
C(4)–N(3)–Au	111(2)	107(3)
Au–N(2)–C(2)	106(2)	104(3)
Au–N(2)–C(3)	108(2)	104(3)

The geometry of the baa ligand is similar to that found in the analogous palladium(II) and platinum(II) derivatives of formula $[M(baa)X]^+$.[14,15] In all cases the N(1)–M–N(2) and N(2)–M–N(3) angles are smaller than the N(1)–M–X(1) and N(3)–M–X(1) angles due to a slight strain of the tridentate ligand. Moreover, the sum of the angles around N(2) in (1) [334(2)°] is similar to that found in $[Pd(NO_2)(baa)]^+$ [333(1)°] [14] and in $[PtBr(baa)]^+$ [334.5 (1.5)°].[15]

There are several interactions, along the axial co-ordination sites, between Au and the anions Cl^- and $[ClO_4]^-$, as shown in Figure 2. One oxygen atom, from $[ClO_4]^-$, and the Cl^- ion are 3.10 and 3.05 Å, respectively from gold. These distances are very long compared with the sum of the covalent radii for these atoms (2.06 and 2.39 Å respectively), although still shorter than the non-bonded distances (3.6 and 4.0 Å respectively).[7] The situation is somewhat similar to that found in the pseudo-octahedral complex $[AuI_2(pdma)]I$ [pdma = *o*-phenylenebis(dimethylarsine)] where the Au–I bond lengths along the *z* axis are 3.35 Å compared with a covalent bond length of 2.73 Å and with a non-bonded distance of 4.4 Å.[16]

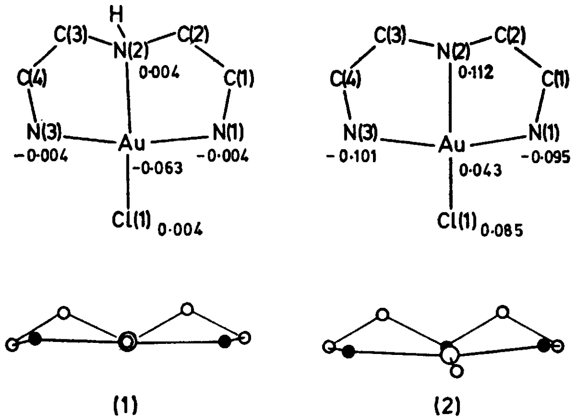

FIGURE 1 Numbering scheme and displacement of the donor and metal atom from the mean co-ordination plane together with a side view along the direction passing through N(2) and the middle point of the N(1)—N(3) segment for $[AuCl(baa)]^{2+}$ (1), and $[AuCl(baa - H)]^+$, (2)

Structure of (2).—The crystals consist of $[AuCl(baa - H)]^+$ cations and $[ClO_4]^-$ anions. A side view of the cation and the displacement of the donor atoms from the mean co-ordination plane are shown in Figure 1. The complex has a square-planar stereochemistry, tetrahedrally distorted. The Au–N bond lengths are equal within the accuracy of the present analysis, ranging from 2.01(4) to 2.06(4) Å. The Au–Cl bond length of 2.33(1) Å is significantly longer than that of 2.273(8) Å found in the parent amine complex.

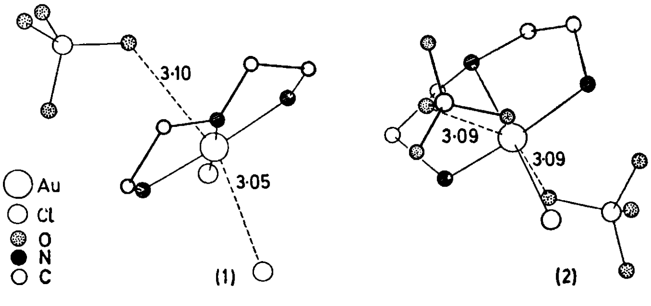

FIGURE 2 A view of $[AuCl(baa)]Cl[ClO_4]$, (1), and $[AuCl(baa - H)][ClO_4]$, (2), showing the interactions between anions and cations

In this case, as in the case of compound (1), the N–Au–N angles are smaller than the Cl–Au–N ones due to steric strain. The sum of the angles around N(2), however, is 321(3)°, which appears to be significantly smaller than that found in compound (1) and in all other complexes with a non-deprotonated baa ligand.

The existence of a weak interaction between the oxygens of the $[ClO_4]^-$ anions, in approximately axial positions, and the metal, is suggested by the Au • • • O distances which are 3.09 Å. These interactions are shown in Figure 2.

The main differences between the amino- and the amido-complex concern: (*i*) the distortion of the co-ordination geometry; (*ii*) the difference in Au–Cl bond lengths; and (*iii*) difference in the geometry around the N(2) atoms. Whereas in (1) the donor atoms are essentially coplanar and the gold atom is displaced by 0.063 Å above the co-ordination plane, in compound (2) they are tetrahedrally distorted. In both cases the bond angles follow the same trend (Table 2), but a slight difference appears in the Au–N bond lengths. The Au–Cl(1) bond distances are 2.273 and 2.33 Å in (1) and (2) respectively suggesting a greater *trans* influence of N^- than of NH. This is in agreement with the σ-donor power which is smaller for NH than for N^-. A comparable difference in bond lengths (0.07 Å) was observed between the *cis* and *trans* chlorines, with respect to phosphine, in the $[AuCl_3(PPh_3)]$ complex.[11] It can therefore be suggested that the difference of *trans* influence between the amino- and the amido-nitrogen is comparable to that existing between a Cl^- ion and a PPh_3 ligand. It is also worth noting that a tetrahedral distortion from planarity, as in (2), was observed in the phosphine complex. In the phosphine complex this distortion was related to its high reactivity.

The angles around N(2) show a significant flattening of the N(2) pyramid in (1) as compared with (2). This is in agreement with Gillespie's stereochemical model.[17] In fact substitution of a H atom with a lone pair in N(2) should result in a decrease of the other bond angles.

On the basis of this structural information we could have expected an increase in the rate of chloride substitution going from the amino- to the amido-complex paralleling the lengthening of the Au–Cl bond. The kinetic data from the literature do not fulfil this expectation although it must be recognized that: (*i*) the structural information refers to the ground state only, whereas reactivity relates to the free-energy difference between the ground and the transition state; and (*ii*) the interpretation of the kinetic data in this particular case is not straightforward. In fact, because of the relative acidity of the central aminic group (pK_a = 4.0 in 0.5 mol dm^{-3} $[ClO_4]^-$), the kinetics of substitution of Cl^- by Br^- in the protonated species (1) had to be followed in strongly acidic media, under which conditions displacement of one end of the baa ligand can occur.[18] On the other hand, the kinetics of substitution in the deprotonated species (2) had to be followed in neutral or basic media where hydrolysis and the formation of hydroxo-species can also occur.[2]

Because of these facts we had some difficulties in setting up the kinetic experiments and in handling the data obtained therefrom. In two sets of runs performed at pH 2.7 and 4.7 and in the presence of chloride ion to suppress hydrolysis we had evidence for a subsequent rapid reaction preceding that which had a kinetic constant in accord with the literature data (162 ± 14 and 164 ± 6 dm^3 mol^{-1} s^{-1} at pH 2.7 and 4.7 respectively).

We believe that more decisive information can be obtained by following the kinetics of substitution of Cl^- in $[AuCl(baa)]^{2+}$ and $[AuCl(bama)]^{2+}$ complexes [bama = bis(2-aminoethyl)methylamine] by other nucleophiles. Since the reactivity of these two substrates can be assumed to be the same, but only the former can give the amido-species $[AuCl(baa - H)]^+$ at higher pH, it follows that any difference observed in the reactivity of these two complexes at higher pH (as required by several entering nucleophiles) can be confidently ascribed to the different *trans*-labilizing effect of an amino- and of an amido-group.

EXPERIMENTAL

Hydrogen tetrachloroaurate(III) trihydrate was obtained from Johnson, Matthey and Co.; bis(2-aminoethyl)amine trihydrochloride (baa•3HCl) and inorganic salts were reagent grade products.

Preparation of Complexes.—The preparation of $[AuCl(baa)]Cl_2$ has already been reported [2] but we used a different procedure. A solution of baa•3HCl (1.00 g, 4.7 mmol) in water (1 cm^3) was added slowly, with stirring, to a solution of $HAuCl_4{\cdot}3H_2O$ (0.70 g, 1.8 mmol) in the same solvent (2 cm^3); a yellow precipitate immediately formed. A solution of Na[OH] (0.32 g, 8.0 mmol in 1 cm^3 of water) was then added to the reaction mixture and this left stirring at 0 °C for 2 h. The light yellow precipitate was then filtered off, washed twice with cold ethanol, and dried over P_2O_5. The yield was *ca.* 70% {Found: C, 11.7; H, 3.1; Cl, 26.1; N, 10.3. $[AuCl(baa)]Cl_2$ requires C, 11.8; H, 3.2; Cl, 26.2; N, 10.3%}.

Crystals of $[AuCl(baa)]Cl[ClO_4]$ were obtained by slow evaporation of an aqueous solution of $[AuCl(baa)]Cl_2$ (0.20 g in 3 cm^3) brought to pH 1.5 with $HClO_4$; crystallization was induced with $Li[ClO_4]$.

TABLE 3

Values of $k_{obs.}$ for the reaction of $[AuCl(baa)]Cl_2$ with an excess of bromide ion in acetate buffer solution and at constant $[Cl^-]$ of 3×10^{-3} mol dm^{-3}. I = 0.2 mol dm^{-3}, 25 °C

pH	$10^3[Br^-]$/mol dm^{-3}	$k_{obs.}$ (360 nm)/s^{-1}
2.7	1.25	0.20
	5.0	0.81
	8.5	1.50
	12.5	2.04
	20.0	3.24
4.7	1.25	0.56
	5.0	1.18
	8.5	1.71
	12.5	2.43
	20.0	3.63

Crystals of $[AuCl(baa - H)[ClO_4]$ were obtained by slow evaporation of a solution of $[AuCl(baa)]Cl_2$ (0.20 g) in water (3 cm^3) brought to pH 6 with Li[OH]; crystallization was induced by adding LiCl and $Li[ClO_4]$ in excess.

Kinetics.—Rate data were obtained spectrophotometrically with a Gibson–Durrum stopped-flow instrument by rapid mixing of the solutions of substrate and reagents. The rate constants were calculated from conventional plots of log $(A_\infty - A_t)$ against time. The data are collected in Table 3. All kinetic runs were performed in the presence of an excess of entering reagent and at constant ionic strength (0.2 mol dm^{-3}). Kinetic runs at pH 2.7 were performed in a solution of sodium acetate (0.20 mol dm^{-3}) and $HClO_4$ (0.20 mol dm^{-3}); at pH 4.7 the corresponding concentrations were 0.20 and 0.10 mol dm^{-3}. A constant chloride concentration of 3×10^{-3} mol dm^{-3} was used throughout.

X-*Ray Analysis*.—*Crystal data*. (*i*) $C_4H_{13}AuCl_3N_3O_4$ (1), $M = 470.6$, Monoclinic, $a = 8.590(6)$, $b = 12.745(8)$, $c = 12.256(8)$ Å, $\beta = 113.6(1)°$, $U = 1\,229.5$ Å^3, $Z = 4$, $D_c = 2.54$ g cm^{-3}, μ(Mo-K_α) = 130 cm^{-1}, $\mu r = 3.25$, space group $P2_1/n$.

(*ii*) $C_4H_{12}AuCl_2N_3O_4$, (2), $M = 434.0$, Orthorhombic, $a = 12.976(8)$, $b = 10.029(7)$, $c = 8.171(6)$ Å, $U = 1\,063.3$ Å^3, $Z = 4$, $D_c = 2.71$ g cm^{-3}, μ(Mo-K_α) = 147 cm^{-1}, $\mu r = 3.69$, space group $P2_12_12_1$.

Three-dimensional data were collected for both compounds on a Siemens diffractometer by means of the θ—2θ scan technique using Mo-K_α radiation for a maximum 2θ of 54°. Reflections having $I_o < 3\sigma(I_o)$ were rejected, the remainder being corrected for Lorentz-polarized factors. Totals of 2 520 reflections for (1) and 1 140 for (2) were used in the subsequent calculations. Absorption corrections were applied for both compounds; the crystals used were approximately cylindrically shaped.

Structure Determination and Refinement.—Both structures were solved by conventional Patterson and Fourier methods. After least-squares refinement R was 0.119 for (1) and 0.103 for (2), anisotropic temperature factors being used only for Au and Cl. Owing to the nature of the crystals, which affects the quality of the data in both cases, no attempt was made to locate the hydrogen atoms. The final weighting scheme was: $w = 1/(A + B|F_o| + C|F_o|^2)$ [$A = 18.0$, $B = 1.0$, and $C = 0.030$ for (1); and $A = 27.0$, $B = 1.0$, and $C = 0.027$ for (2)], and was chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin \theta)/\lambda$.

Final atomic co-ordinates are listed in Table 1 together with their estimated standard deviations calculated from the residual and the diagonal elements of the inverse matrix of the last least-squares cycle. The numbering scheme for the atoms of (1) and (2) is shown in Figure 1. Atomic scattering factors were those of ref. 19. Isotropic and anisotropic temperature factors and observed and calculated structure factors are listed in Supplementary Publication No. SUP 22651 (14 pp.).*

All calculations were carried out on a CDC 6200 computer, with programs described in ref. 20.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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