Synthesis of $[Au(NH_3)_2]^+$ Salts and the Crystal Structure of $[Au(NH_3)_2]Br$*

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The complexes $[Au(NH_2R)_2]X$ (R = H, Me, Et or Bu^t; X = Br, SbF_6 or BF_4) have been synthesised and characterised by IR, NMR spectra and by thermal gravimetric and differential scanning calorimetry techniques; the single-crystal structural determination of $[Au(NH_3)_2]Br$ has confirmed the linear co-ordination about gold and highlighted some interesting bond-length differences compared to $[Ag(NH_3)_2]NO_3$.

The development of gold(I) chemistry has been dominated by the perception that gold is a prototypical Class B (or soft) Lewis acid which forms its most stable complexes with soft Lewis bases. There is therefore an abundance of gold(I) phosphine complexes which are very commonly used as reagents in organometallic and cluster chemistry[1,2] and their biological role as drugs for the treatment of rheumatoid arthritis has been developed and investigated in some depth.[3] In contrast the chemistry of gold(I) with nitrogen ligands has been neglected, see ref. 4 for relevant structural analysis of chloro(piperidine)-gold(I). There have been reports that gold(I) halides[5] and cyanide[6] react with liquid ammonia to give the adducts $[AuX(NH_3)_n]$ (X = Cl, Br or I, n = 1–3; X = CN, n = 1) and $[AuCl(NH_3)]$ has been isolated when AuCl is dissolved in aqueous ammonia and acidified with HCl, but not structurally characterised. $[Au(NH_3)_2]^+$ has been identified in solution and its equilibrium constants measured,[7] but surprisingly salts of the cation have not been isolated and structurally characterised. This is particularly surprising given the stability of $[Ag(NH_3)_2]^+$,[8] which is quoted in elementary textbooks as the paradigm for linear co-ordination and whose structure was first investigated in 1934.[9] In this communication we describe the synthesis, isolation and spectroscopic characterisation of $[Au(NH_3)_2]^+$ and $[Au(NH_2R)_2]^+$ salts and the structure of $[Au(NH_3)_2]Br$.

Salts of $[Au(NH_3)_2]^+$ are formed when ammonia gas is bubbled through a solution of $[Au(NCPh)_2]^+$[10] in MeCN for 45 min at room temperature. The resulting colourless solution yields colourless crystals when the volume is decreased under reduced pressure. The BF_4^- and SbF_6^- salts may be recrystallised from MeCN–Et_2O and obtained in approximately 90% yields based on gold. The compounds are photosensitive, but may be stored under nitrogen in a darkened tube at −25 °C indefinitely. The related amine complexes $[Au(NH_2R)_2]BF_4$ (R = Me, Et or Bu^t) were synthesised in a similar fashion and their relative stabilities are Bu^t > Et > Me. The corresponding $[Au(NH_3)_2]Br$ salt has been obtained in lower yields by introducing NH_3 into a solution of $[AuBr_2]^-$ in MeCN and is less photosensitive than the corresponding BF_4^- salt and more amenable to single-crystal X-ray crystallographic analysis.

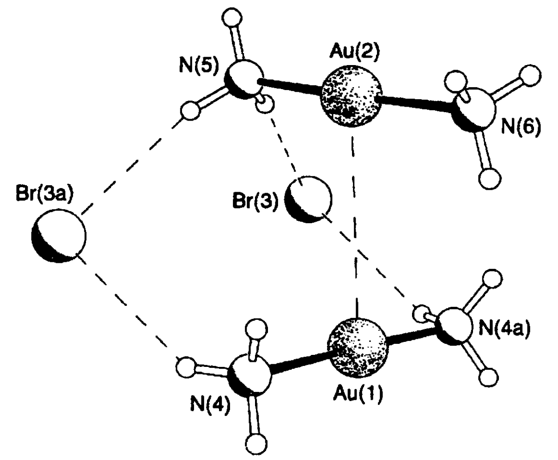

Fig. 1 The two crystallographically independent C_s-symmetric $[Au(NH_3)_2]Br$ molecules in the structure [in the molecule containing Au(1) the mirror plane is perpendicular to the Au–N bond, whilst the whole molecule containing Au(2) lies on the mirror plane]. Open circles depict bromide ions

The single-crystal X-ray structural determination of $[Au(NH_3)_2]Br$† has confirmed the presence of linear cations in the crystal with N–Au–N 178.7(8) and 178.0(8)° for the two independent C_s-symmetric molecules in the unit cell as shown in Fig. 1. The packing diagram shown in Fig. 2 reveals a layer structure based on crinkled $[Au(NH_3)_2]^+$ and Br^- sheets. The

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* *Non-SI unit employed:* cal ≈ 4.184 J.

† Crystal data: $H_{12}Au_2Br_2N_4$, $M = 621.89$, orthorhombic, $a = 6.905(1)$, $b = 11.294(1)$, $c = 12.975(1)$ Å, space group *Pnma*, $Z = 4$, $D_c = 4.082$ g cm^{-3}, μ(Mo-Kα) = 36.80 mm^{-1}, $F(000) = 1072$, final $R1 = 0.037$, $wR2 = 0.096$ for 604 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 45°$], $w^{-1} = \sigma^2(F_o^2) + (0.0603P)^2$ where $P = (F_o^2 + 2F_c^2)/3$. Data were measured on a Siemens P4/PC diffractometer with graphite-monochromated Mo-Kα radiation using ω scans. The structure was solved by the heavy-atom method. The gold and bromine atoms were refined anisotropically and the nitrogen atoms isotropically using absorption-corrected data. Computations were carried out using SHELXTL/SHELXL program systems.[11] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

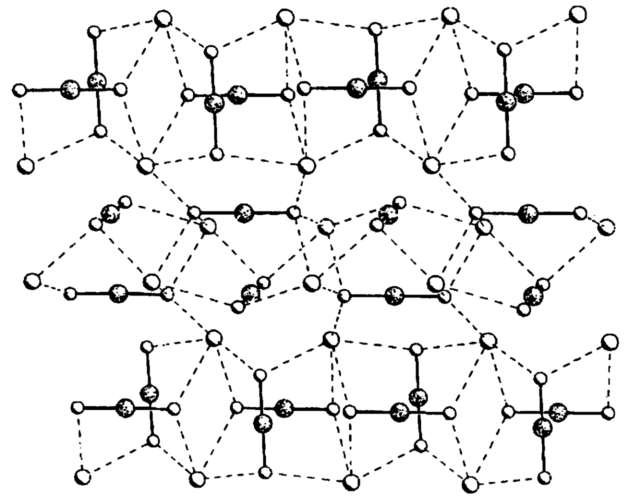

Fig. 2 Part of the array of hydrogen-bonded anions and cations in the structure of $[Au(NH_3)_2]Br$

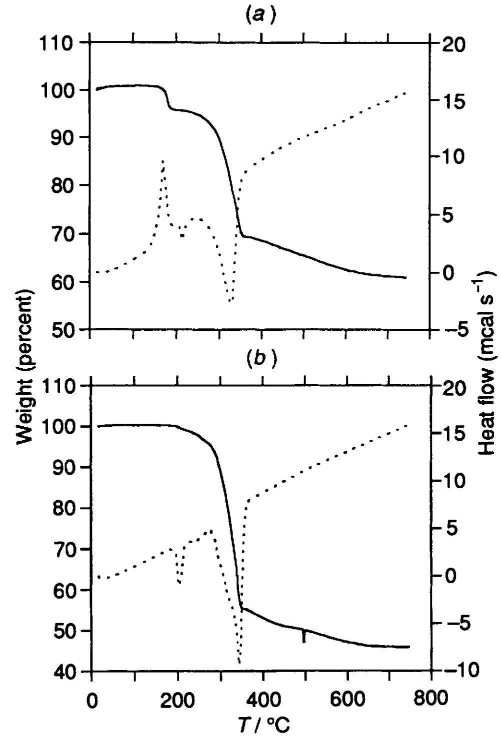

Fig. 3 Comparison of the TGA–DSC traces for $[Au(NH_3)_2]BF_4$ (*a*) and $[Ag(NH_3)_2]BF_4$ (*b*): heat flow (– – – –), weight (——)

crinkling results from the gold cations forming pairs of parallel linear infinite chains which are mutually perpendicular. The bromide ions form extensive hydrogen bonds with the hydrogens of the ammonia ligands (the Br ··· N distances are in the range 3.38–3.58 Å). The pattern of NH ··· Br hydrogen bonds also extends out of the plane of the paper in Fig. 2 cross linking adjacent sheets to form a three-dimensional hydrogen-bonding network. The gold cations are well separated from the bromide ions with the closest Au ··· Br contact equal to 4.147(2) Å, but show reasonably short contacts to other gold cations Au ··· Au = 3.414(1) Å. The structure shows two surprising features when compared with $[Ag(NH_3)_2]NO_3$—the Au–N distances [2.03(2)–2.01(2) Å] are shorter than the Ag–N distances [2.116(10)–2.125(10) Å] and the Au ··· Au shortest contact is longer, 3.414(1) *vs.* 3.131(2) Å. For related palladium and platinum compounds the M–N bond lengths follow the more intuitively obvious trend. The longer gold–gold contacts are particularly surprising in view of the 'aurophilicity' effect which has been discussed extensively by Schmidbaur.[12] The pronounced tendency of gold(I) linear fragments to approach each other in such a manner that the gold–gold contacts begin to approximate to those distances found in the bulk metal is widespread and has been attributed to relativistic effects and d–s hybridisation phenomena.[13] Therefore, it is rather surprising that the Au ··· Au contacts in the present structure are longer than those reported for the related silver compounds.[9] Attempts are currently being made to complete structures on gold and silver cations with identical formulae.

The FAB mass spectrum of $[Au(NH_3)_2]BF_4$ shows a single parent ion peak for $[Au(NH_3)_2]^+$ (m/z = 231), but no peaks for $[Au(NH_3)]^+$. The infrared spectrum (KBr disc) shows bands at 3355, 3289, 3231 and 3177 cm^{-1} [ν(N–H)], 1306, 1294 and 1277 cm^{-1} [δ(N–H)] and 534 and 523 cm^{-1} [ν(Au–N)]. The ^{1}H NMR spectrum shows a (1 : 1 : 1) triplet at δ 3.5 which is attributed to the NH_3 protons with $^1J(^{14}N–H)$ = 47 Hz.

The thermogravimetric analysis–differential scanning calorimetry (TGA–DSC) scans for $[Au(NH_3)_2]BF_4$ and $[Ag(NH_3)_2]BF_4$ show some interesting differences (see Fig. 3). $[Au(NH_3)_2]BF_4$ loses only one of the NH_3 ligands in an exothermic process between 140 and 184 °C and the remaining NH_3 and BF_3 between 272 and 337 °C and finally the decomposition of AuF to gold metal occurs between 340 and 750 °C; the latter processes are endothermic. In contrast $[Ag(NH_3)_2]BF_4$ decomposes at a higher temperature 195–350 °C, by an endothermic process to form AgF, without the intermediate formation of the ion with a single ammonia molecule. Therefore, the previous lack of solid-state data on $[Au(NH_3)_2]^+$ can be attributed to the lower thermal stability of the gold compound and its more favourable decomposition to $[Au(NH_3)]BF_4$.

The chemistry of gold(I) with polydentate nitrogen ligands is currently being investigated and the possibility of developing the organometallic chemistry of gold(I) with nitrogen ligands is being studied.

Acknowledgements

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