NJC
Letter

Gold(I) complexes with amine ligands. 3.[1] Competition between auriophilic and hydrogen bonding interactions in dimeric species

Peter G. Jones* and Birte Ahrens

Institut für Anorganische und Analytische Chemie, Technical University of Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

The gold(I) complexes $(pip)_2Au^+Cl^-$ and $(Cy_2NH)AuCl$ (pip = piperidine, Cy = cyclohexyl) crystallise as loose dimers; in the ionic species $N{-}H\cdots Cl^-$ hydrogen bonding is the main secondary interaction, whereas in the neutral complex the $N{-}H\cdots Cl$ hydrogen bonding is weaker but is compensated by an auriophilic interaction.

Amine complexes of gold(I) have been little studied and are generally regarded as relatively unstable (in the absence of stabilising ligands as phosphines); this can be rationalized in terms of incompatibility of the soft metal centre with the hard nitrogen donor. Additional stabilisation may, however, be provided by secondary interactions such as auriophilic interactions (recognisable by formally non-bonded gold–gold distances of *ca.* 2.7–3.4 Å)[2] or $N{-}H\cdots X$ hydrogen bonds.

The stabilizing effect of hydrogen bonds was postulated for the imine complex $[Au(NH{=}CMe_2)_2](CF_3SO_3)$,[3] in which the cationic gold moieties, despite disadvantageous electrostatic effects, form chains with short $Au\cdots Au$ distances [3.1663(5), 3.1705(5) Å], and the triflate (trifluoromethanesulfonate) anions are involved in $N{-}H\cdots O$ hydrogen bonds.

Stabilization through hydrogen bonding can also be assumed for $[Au(NH_3)_2]Br$,[4] in which pairs of ammine–gold(I) cations are linked through auriophilic interactions [$Au\cdots Au$ 3.414(1) Å] with additional $N{-}H\cdots Br^-$ hydrogen bonds, forming a layer structure.

In isocyanidegold(I) thiosalicylates,[5] hydrogen bonding and auriophilic interactions are observed, but the former does not involve the donor atoms at gold; chains are built up *via* alternating secondary bonding types.

We have begun a systematic study of gold(I) complexes with aliphatic amine ligands, generally bearing an N—H function, as a potential donor group for stabilizing hydrogen bonds. We have not been able to obtain stable compounds with tertiary amine ligands, and attribute this to the lack of hydrogen bonds. Steric effects ('overcrowded nitrogen') could represent an alternative explanation (see below), but are difficult to quantify; similar considerations apply, in the case of ionic complexes, to Coulombic interactions.

We recently reported the structure of $(pyrr)_4Au_3Cl_3$[6] (pyrr = pyrrolidine), in which the $Au\cdots Au$ contacts were rather long and thus presumably weak [3.2041(7), 3.5834(4) Å], whereas the hydrogen bonds were more significant [$N\cdots Cl^-$ 3.179, 3.284(6) Å]. Here we report the structures of two dimeric species, obtained from (tht)AuCl and the corresponding amine: $(pip)_2Au^+Cl^-$, previously synthesised by us,[7] and $(Cy_2NH)AuCl$ (pip = piperidine, Cy = cyclohexyl). These reveal an interesting balance between the two types of secondary interaction.

$L_2Au^+Cl^-$ with L = piperidine and LAuCl with L = dicyclohexylamine: (tht)AuCl (160 mg, 0.5 mmol) was dissolved in neat amine (5 ml). The solution was stirred for 1 h with exclusion of light at room temperature; a white precipitate formed. Light petroleum was added and after cooling for 1 h at −18 °C the precipitate was filtered off and recrystallized from dichloromethane–light petroleum. Crystals were obtained by diffusion of light petroleum into dichloromethane solution. NMR spectra were measured in $CDCl_3$ solution, with TMS as internal standard.†

In $(pip)_2Au^+Cl^-$ (Fig. 1) an association of two cations and two anions about a twofold axis is observed, in which chloride anions accept two hydrogen bonds from the N—H groups [$N\cdots Cl^-$ 3.108(6), 3.122(7) Å]. The $Au\cdots Au$ contact is long [4.085(2) Å] and can represent at best a very weak interaction; this may be attributable to the positive charge associated with the gold moieties. The N—Au—N axes are rotated with respect to each other by 39.6(3)°.

In the uncharged complex $(Cy_2NH)AuCl$ dimers are also observed (Fig. 2), but with inversion symmetry, making the N—Au—Cl axes antiparallel to each other. They have shorter and presumably stronger $Au\cdots Au$ interactions [3.2676(14) Å], whereas the $N\cdots Cl$ distances are longer at 3.391(8) Å. Thus, the reduction of charge of the gold species from +1 to 0 makes the hydrogen bonding weaker, as expected, but the auriophilic interactions stronger. It remains to be seen if this is a general effect, but the same trend can also be recognised in the neutral complex (pip)AuCl [7] [$Au\cdots Au$ 3.301(5), $N\cdots Cl$ 3.346, 3.580 Å], which forms loose tetramers with secondary

---

† Bis(piperidine)gold(I) chloride. Yield 91%, dec. > 86 °C. ^1H NMR (200.13 MHz, $CDCl_3$): δ 1.73 (m, 4 H, β-CH_2), 3.25 (m, 4 H, α-CH_2). ^{13}C NMR (50.32 MHz, $CDCl_3$) 23.41 (β-CH_2), 26.52 (γ-CH_2), 53.50 (α-CH_2). EI-MS, *m/z* 84 (100%, [M-Au-Cl-H]). Anal. calcd for $C_{10}H_{22}AuClN_2$ (402.72): C, 29.82; H, 5.51; N 6.96. Found: C, 29.34; H, 5.35; N, 7.06%.

Chloro(dicyclohexylamine)gold(I). Yield 75%, dec. > 114 °C. ^1H NMR (200.13 MHz, $CDCl_3$) 1.26–1.84 (16 H, CH_2), 2.12, 2.40 [m, 4 H, 2-, 2′-CH_2 (eq.)], 2.99 (m, 2 H, CH). ^{13}C NMR (50.32 MHz, $CDCl_3$) 25.05 (3-C), 35.50 (4-C), 34.82 (2-C) 58.73 (1-C). EI-MS, *m/z* = 181 (16%, [M-Au-Cl]). IR (KBr) ν(AuCl): 345 cm^{-1} (w). Anal. calcd for $C_{12}H_{23}AuClN$ (413.74): C, 34.84; H, 5.60; N, 3.39. Found: C, 34.86; H, 5.55; N, 3.34%.

X-Ray structure determinations. Data were measured using Mo-Kα radiation. Absorption corrections were based on ψ-scans. Structures were refined anisotropically on F^2 using all reflections (program SHELXL-97[9]). Hydrogen atoms were included using a riding model except for those bonded to nitrogen, which were refined 'freely' with restrained N—H bond lengths. Crystal data: $(pip)_2Au^+Cl^-$: $C_{10}H_{22}AuClN_2$, $M = 402.71$, monoclinic, $C2/c$, $a = 21.346(5)$, $b = 6.480(2)$, $c = 19.630(5)$ Å, $\beta = 111.54(3)°$, $V = 2525.8(13)$ Å^3, $Z = 8$, $\mu = 11.8$ mm^{-1}, $T = -130$ °C, Stoe STADI-4 diffractometer, 3568 reflections, 2228 unique, $wR2$ 0.067, $R1$ 0.030. $(Cy_2NH)AuCl$: $C_{12}H_{23}AuClN$, $M = 413.73$, triclinic, $P(-1)$, $a = 8.306(3)$, $b = 8.978(2)$, $c = 10.132(3)$ Å, $\alpha = 68.24(2)$, $\beta = 85.17(3)$, $\gamma = 77.71(3)°$, $V = 685.7(3)$ Å^3, $Z = 2$, $\mu = 10.9$ mm^{-1}, $T = -100$ °C, Siemens P4 diffractometer, 2399 reflections, 2336 unique, $wR2$ 0.088, $R1$ 0.036. CCDC reference number 440/051.

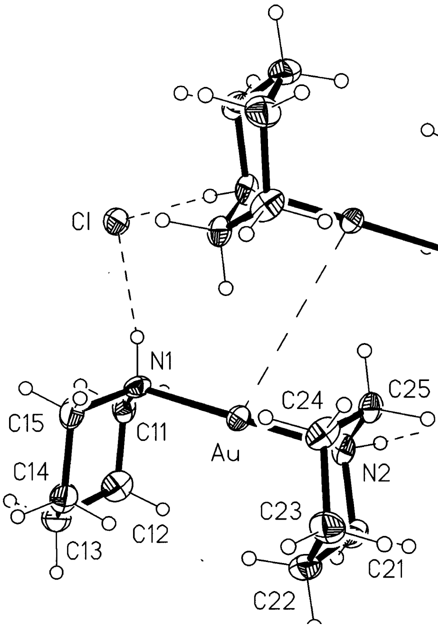

Fig. 1 Structure of the dimer of $(pip)_2Au^+Cl^-$ in the crystal. Ellipsoids represent 50% probability levels; H atom radii are arbitrary. Bond lengths and angles at gold: Au—N1 2.050(6) Å, Au—N2 2.055(6) Å, N1—Au—N2 179.0(3)°

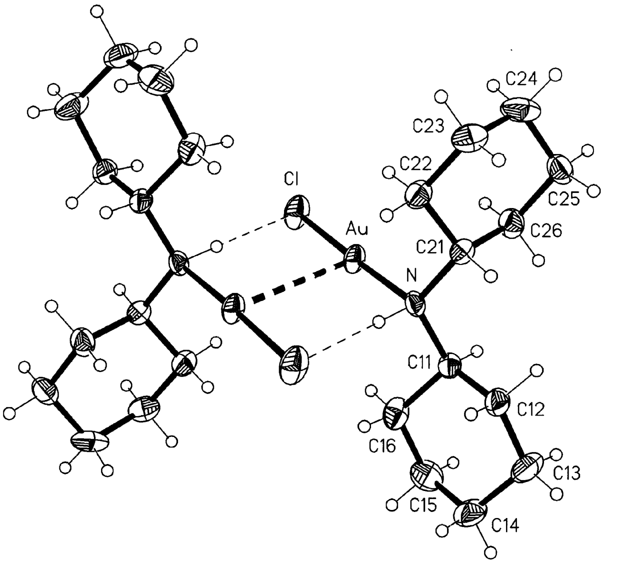

Fig. 2 Structure of the dimer of $(Cy_2NH)AuCl$ in the crystal. Ellipsoids represent 50% probability levels; H atom radii are arbitrary. Bond lengths and angles at gold: Au—N 2.077(7) Å, Au—Cl 2.266(2) Å, N—Au—Cl 177.7(2)°

bonds similar to those in the $(Cy_2NH)AuCl$ dimers; the considerably smaller size of the piperidine ligands suggests also that steric effects are not of central importance in determining either stability or the strengths of other secondary interactions.

A recent theoretical study of copper(I) complexes[8] has predicted a structure analogous to $(Cy_2NH)AuCl$ for $(NH_3)CuCl$, and presumably also reflects the relative contributions of attractive $Cu^I\cdots Cu^I$ interactions and hydrogen bonding.

We conclude that the contributions of auriophilic and hydrogen bonding are likely to stabilise gold(I) complexes of many protic amines, and thus to render invalid a rigid application of the hard–soft principle; the relative contributions will depend on the charge of the gold complex. Further investigations (to be published) have provided preliminary confirmation of this supposition.

Acknowledgements

We thank the Fonds der Chemischen Industrie (Frankfurt) for financial support.

References

1 P. G. Jones and B. Ahrens, *Z. Naturforsch. B*, 1998, **53**, 653.
2 H. Schmidbaur, *Gold Bull.*, 1990, **23**, 11; *Chem. Soc. Rev.*, 1995, 391.
3 J. Vicente, M.-T. Chicote, M.-D. Abrisqueta, R. Guerrero and P. G. Jones, *Angew. Chem.*, 1997, **109**, 1252.
4 D. M. P. Mingos, J. Yau, S. Mentzer and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1995, 319.
5 W. Schneider, A. Bauer and H. Schmidbaur, *Organometallics*, 1996, **15**, 5445.
6 P. G. Jones and B. Ahrens, *Chem. Ber./Recueil*, 1997, **130**, 1813.
7 J. J. Guy, P. G. Jones, M. J. Mays and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1977, 8.
8 X.-Y. Liu, F. Mota, P. Alemany, J. J. Novoa and S. Alvarez, *Chem. Commun.*, 1998, 1149.
9 G. M. Sheldrick, SHELXL-97, Program for Refining Crystal Structures, University of Göttingen, Göttingen, 1997.

Received in Basel, Switzerland, 15*th June* 1998;
Letter 8/05587D