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Implications of the Crystal Structure of the Ammonia Solvate $[Au(NH_3)_2]Cl\cdot4NH_3$

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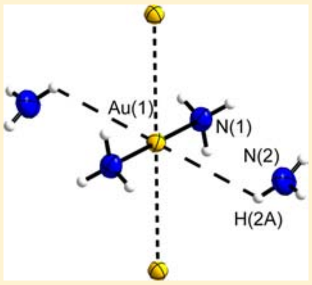
ABSTRACT: Crystals of diammine gold(I) chloride ammonia (1/4), $[Au(NH_3)_2]Cl\cdot4NH_3$, have been grown from solutions of AuCl in liquid ammonia. The X-ray diffraction analysis (at 123 K) has shown that the crystals feature an extensive network of hydrogen bonds between the $[H_3N{-}Au{-}NH_3]^+$ cations (with C_i symmetry) and the Cl^- anions, including also the ammonia molecules. There is no evidence for an emerging increase of the coordination number of the gold atom by adopting another ammonia molecule or by approaching a chloride anion. Moreover, the geometry of two distant and angular N−H···Au contacts is not a strong support of hydrogen bonds recently amply discussed in the literature.

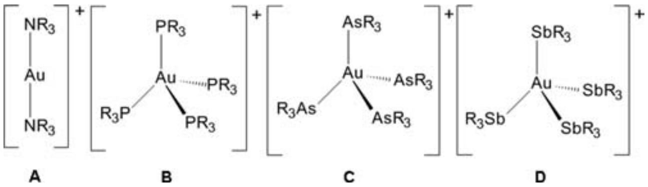


■ INTRODUCTION

The coordination chemistry of gold is expanding rapidly since gold complexes have been recognized to be very effective and specific catalysts for many organic transformations.[1−6] For quite some time, tertiary phosphines R_3P were the favorite ligands, and a large variety of complexes with mono-, bi-, and tridentate P-donors have been designed and explored.[7] More recent developments have concentrated now on carbene complexes.[8]

Both gold(III) and gold(I) centers were found to accept up to four P-donors to form square-planar or tetrahedral complexes, respectively, but the acceptor properties for phosphines appeared to be much lower for gold(I) than for gold(III).[7] Nevertheless, tetracoordination (**B**) could be realized if competition with other ligands was excluded. Up to four tertiary arsines R_3As (**C**) and even stibines R_3Sb (**D**) have also been attached to a gold(I) center (Scheme 1).[9−11]

Scheme 1. Difference in Coordination Numbers and Geometries around Au(I) with A(m)mine, Phosphine, Arsine, and Stibine Ligands

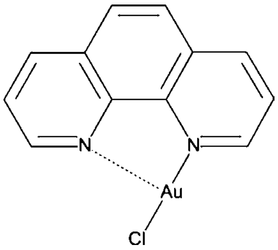


By contrast, the addition of tertiary amines R_3N reaches a much lower limit[12] and coordination at gold(I) does not generally exceed the 1:2 ratio in complexes $[R_3NAuNR_3]^+$ (**A**). This indicates a remarkable difference in the acceptor properties of the three coinage metals, of which the congeners copper(I) and silver(I) show a higher affinity to amines and ammonia with standard coordination numbers of 3 and even beyond.[13]

Presently, there is an increasing interest in gold-nitrogen chemistry[14,15] because the lability of the N-donor ligands at gold(I) centers allows access of even poorly coordinating substrates for activation. Representative examples have a mixed-ligand pattern [P−Au−N] combining a robust P-ligand with a labile N-ligand. The N-donors may include ammonia[16] and primary, secondary, or tertiary amines, but also imines −N═ and, in particular, cyanides RC≡N.[17] However, in all cases, again, the acceptor capacity of the gold(I) center is not exceeding the two-coordination. This is true even with potentially bidentate and rigid N-donors, such as phenanthroline, which has been shown to be unsymmetrically bound with a high preference for only one N-donor site (Scheme 2).[18]

To probe the acceptor capacity of gold(I) for ammonia as the smallest amine, we have now reinvestigated the reaction of anhydrous AuCl with a large excess of ammonia under very mild conditions, that is, in liquid ammonia. About a century ago, Biltz and Wein have shown that AuCl can be dissolved in anhydrous liquid ammonia.[19] From the results of tensimetric

Scheme 2. Unsymmetrical Bonding of Phenanthroline to AuCl



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and calorimetric studies, they have concluded that the AuCl-NH_3 system may contain no less than five discrete phases, $AuCl\cdot(NH_3)_n$ with $n = 12, 6, 4, 2$, and 1. The structures of these compositions were unknown, and the question has remained if any of these would contain a gold atom coordinated to more than two ammonia molecules.

The existence of the 1:2 complex in aqueous solution was confirmed in potentiometric studies by Skibstedt and Bjerrum, and its equilibrium constant and standard potential were determined.[20] Crystalline samples of compounds $[H_3N{-}Au{-}NH_3]^+X^-$ with X = Br, BF_4, and SbF_6 were obtained by Mingos et al. from the reaction of the precursors $[(PhCN){-}Au{-}(NCPh)]^+X^-$ with ammonia in acetonitrile, and the crystal structure of the bromide has been determined.[21] It was also claimed that AuCl would dissolve in *aqueous* ammonia as the complex $(H_3N)AuCl$, but no data have become available on this species.[22] It should be noted that the ionic formulation $[H_3N{-}Au{-}NH_3]^+[Cl{-}Au{-}Cl]^-$ is another plausible assumption. We were now able to isolate and characterize the 1:6 phase.

■ EXPERIMENTAL SECTION

Preparation. AuCl was synthesized according to the method published first by Biltz and Wein.[19] A flame-dried vessel was charged with 103.1 mg of this product (0.44 mmol) and the solid suspended in 10 mL of anhydrous liquid ammonia. The yellow suspension was kept at 233 K for 4 weeks. Colorless crystals separated from the mother liquor were isolated by decantation at 233 K in almost quantitative yield (140 mg, 96%). One suitable specimen was selected for X-ray structure analysis. The crystals lose ammonia rapidly upon warming to room temperature, and the sample left at 296 K is extremely sensitive to moisture. Therefore, no meaningful elemental analysis, IR spectrum, or powder X-ray diffraction pattern could be obtained.

Instrumentation. All work was carried out excluding moisture and air in an atmosphere of dried and purified argon (Westfalen AG) using high-vacuum glass lines. Liquid ammonia (Westfalen AG, 99.98%) was dried and stored over sodium in a special high-vacuum glass line. All crystals were handled in a perfluorinated ether under a nitrogen atmosphere at temperatures below −50 °C. The crystals were mounted on an Oxford Xcalibur3 system using the MiTeGen MicroLoop system. The diffraction data were reduced with the CrysAlisRed software, and an empirical absorption correction using spherical harmonics with SCALE3 ABSPACK was applied. The structure was solved using direct methods implemented in SHELX97 and refined on F^2. All non-hydrogen atoms were localized by Fourier cycling methods and refined anisotropically. Hydrogen atoms were located from the difference Fourier map and were refined isotropically. For crystallographic details, see Table 1.

■ RESULTS AND DISCUSSION

Crystals grown at 233 K from a solution of AuCl in strictly anhydrous liquid ammonia (eq 1) were investigated in order to determine their composition and structure. To this end, single crystals of the material were cooled to 123 K and found to be orthorhombic at this temperature, space group *Pbcn*.

$$\mathrm{AuCl} + 6\mathrm{NH_3} \rightarrow [\mathrm{Au(NH_3)_2}]^+\mathrm{Cl^-}\cdot 4\mathrm{NH_3} \qquad (1)$$

According to the results of the structure solution and refinement, the gold atom of the formula unit occupies the 4*a* Wyckoff position, where it is coordinated to two nitrogen atoms on 8*d* positions. The coordination is linear by symmetry with Au−N(1) bond lengths of 2.032(3) Å in the emerging $[H_3N{-}Au{-}NH_3]^+$ cation. The two coordinated ammonia molecules are in a staggered conformation to give the cation inversion symmetry. The cations are associated into chains via aurophilic contacts with a uniform distance $d(\mathrm{Au{-}{-}{-}Au}) = 3.1756(1)$ Å, which is half the *c* axis of the unit cell, a Au---Au---Au angle at 180°, and a dihedral angle N(1)−Au−Au−N(1) at 78.7(2)° (Figure 1, Table 2). The N(1)−Au(1)−Au(1) angles are found at 87.71(9)° and 92.29(9)°, so the $[H_3N{-}Au{-}NH_3]^+$ molecules are not parallel to the *ab* plane, but slightly tilted.

Table 1. Crystallographic Details of the Title Compound[a]

	$[Au(NH_3)_2]Cl\cdot 4NH_3$
empiric formula	$H_{18}AuClN_6$
color and habitus	colorless block
M [g/mol]	334.62
cryst syst	orthorhombic
space group	*Pbcn*
a [Å]	11.5614(2)
b [Å]	13.4841(3)
c [Å]	6.3512(1)
V [Å^3]	990.12(3)
Z	4
ρ_{calc} [Mg/m^3]	2.25
λ [Å]	0.71073
T [K]	123(2)
μ(Mo$K\alpha$) [mm^{-1}]	15.07
size [mm^3]	0.1·0.1·0.1
R_{int}, $R\sigma$	0.038, 0.014
$R(F)$ ($I > 2\sigma(I)$, all data)	0.014, 0.034
$wR(F^2)$ ($I > 2\sigma(I)$, all data)	0.037, 0.035
S (all data)	0.83
data, params, restraints	1510, 76, 5
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e·Å^{-3}]	1.08, −0.87

[a] Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), http://www.fiz-karlsruhe.de/icsd.html, on quoting the depository number CSD 425324, the name of the authors, and citation of the paper.

Apart from the two gold-coordinated ammonia molecules (2 × N(1)), there are four solvate ammonia molecules in the formula unit, also with pairwise symmetry equivalence (2 × N(2), 2 × N(3)). All six ammonia molecules are involved in various sorts of hydrogen bonding:

Two of the six hydrogen atoms in C_i symmetry-related positions of the $[H_3N{-}Au{-}NH_3]^+$ cation are each connected to a chloride anion Cl^- through a hydrogen bond [Cl···H(1B) 2.59(3) Å; N(1)···Cl 3.397(3) Å] (Table 3). The remaining four hydrogen atoms of the cation are hydrogen bonded to solvate ammonia molecules [N(1)···H(1C) 2.16(3) Å and N(3)···H(1A) 2.31(4) Å; N(1)···N(2) 2.964(5) Å and N(1)···N(3) 3.038(3) Å] (Scheme 3).

Each chloride anion (at the 4*c* Wyckoff position) functions as an acceptor for no less than 10 hydrogen bonds, 6 of which involve the different solvate ammonia molecules. Cl···H distances vary from 2.59(3) to 2.99(4) Å, and Cl···N distances from 3.397(3) to 3.731(4) Å. According to crystal symmetry, five different types of Cl···H−N hydrogen bonds can be distinguished (Figure 2, Table 3).

To characterize the environment of the gold atom, the following observations are important: (1) The shortest Au···Cl distance is 4.6114(8) Å, which places the Cl^- anion well "out of reach" of the gold atom. (2) All four solvate ammonia molecules are engaged in hydrogen bonding, either with the chloride anion or with the coordinated ammonia molecules of

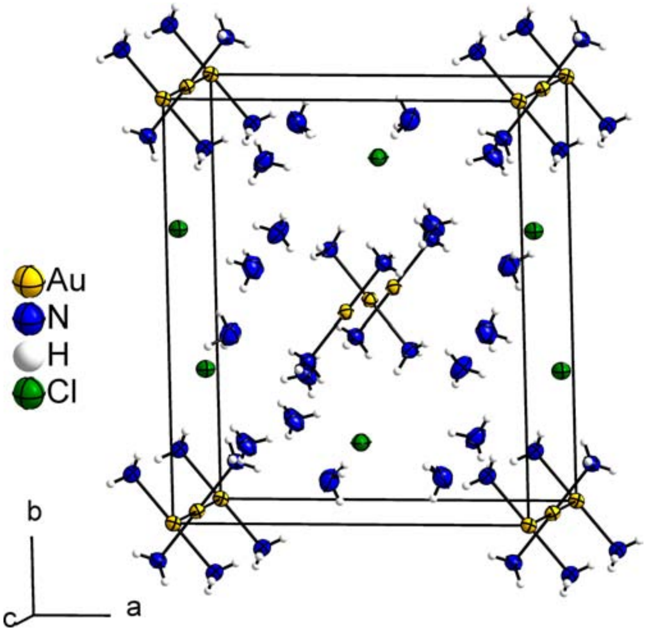


Figure 1. View of the unit cell of $[Au(NH_3)_2]Cl{\cdot}4NH_3$ at 123 K. Thermal ellipsoids are shown at the 70% level, hydrogen atoms isotropically.

the $[H_3N{-}Au{-}NH_3]^+$ cation. There is no evidence for an additional $H_3N \rightarrow Au$ coordination. (3) Only one of the N−H functions of a solvate ammonia molecule, N(2)−H(2A), is found near the gold atom with distances Au···H(2A) of 2.95(5) Å and Au···N(2) of 3.408(3) Å (Figure 3, Table 3). Given these distances, which are comparable to those determined for the N−H···Cl contacts in the same compound (above), the observed N−H···Au contacts may be considered as hydrogen bonds. A further specification in terms of conventional, unconventional, or nonconventional[23a] hydrogen bonds is not meaningful at this stage. The Au···H−N angle of 122(5)° is conspicuously small, but this is a consequence of the fact that the same hydrogen atom is involved in a N(2)−H(2A)···N(1) hydrogen bond, which also has a small angle of 138(7)°. Bonding of H(2A) with both N(1) and Au should, therefore, be almost comparable, and the latter cannot be neglected. (It should be noted that the terms "agostic", "pregostic", and "anagostic" interactions have been introduced specifically for M---H-*C* contacts and cannot be applied in the present context, but there are, of course, parallels with M---H-*N* contacts.[23b])

Experimental evidence for hydrogen bonding to gold in the condensed phase is generally very limited, with well-established examples only existing for gold atoms in the oxidation state −1, that is, in crystalline aurides,[24,25] where the anion Au^- resembles halide anions like I^-. Examples for Au···H−N hydrogen bonding involving Au^+ based on structural analyses in the solid state are still rare,[23,26] and all assignments are ambiguous because either packing forces in crystals or spatial preferences of ligands may induce conformations or arrays that force the N−H function into the vicinity of the metal atom. An interesting case in point is the structure of the bis(imidazolidine-2-thione)gold(I) chloride, where all N−H functions were found engaged in hydrogen bonding exclusively with the chloride anion and not with the gold atom.[27] The same preference is observed in the title compound. The results thus suggest that N−H···Au hydrogen bonds contribute only marginally to the stability of the systems concerned.

"Nonconventional" hydrogen bonding[23a,26] is meant to be distinguished from standard hydrogen bonding,[28−30] including "weak hydrogen bonds",[31,32] by considering, among other things, also metal atoms with closed-shell electronic configurations as hydrogen-bond acceptors to give rise to three center−four electron bonding. Of the late transition metals, gold is taken as the most prominent representative, and this is particularly true for the Au(−1) oxidation state.[23,26] By contrast, electron-deficient early transition metals are known to become involved most frequently in contacts that may be described by the three center−two electron bonding model, with borderline cases in between.[23b,33,34] Decisions based on this catalog are often arbitrary and unsatisfactory, and this is also true in the present case.

■ CONCLUSION

In this work, the existence of a hexaammoniate of AuCl with the composition $AuCl(NH_3)_6$, first detected by Biltz and Wein in tensimetric and calorimetric studies, has been confirmed. Its crystal structure has been determined at 123 K and shown to be composed of a $[H_3N{-}Au{-}NH_3]^+$ cation with C_i symmetry, a chloride anion, and four solvate ammonia molecules. All components participate in an extensive system of N−H···Cl and N−H···N hydrogen bonds. Only two ammonia molecules constitute the inner coordination environment of the gold atom. There are also two aurophilic contacts to neighboring gold atoms related by the inversion symmetry, further complemented by contacts with two N−H functions of ammonia molecules. The distances and the angle of the Au···H−N connections are not indicative of any major contribution from hydrogen bonding, but they cannot be fully ignored.[23,26]

In summary, the results have shown that gold(I) is not accepting more than two ammonia ligands as N-donors even at very low temperatures, with a large excess of ammonia and in the absence of any solvent (in liquid ammonia). Similar findings with tertiary amines documented in the literature suggest that gold(I) is indeed an extremely poor acceptor for nitrogen donors (**A**), in strong contrast to its affinity to phosphines, arsines, and even stibines (**B**−**D**). However, the gold(I) cation is not simply two-coordinate, but clearly involved in aurophilic bonding to become part of a chain of equidistant gold atoms, and possibly also a partner in some very weak hydrogen bonding.

Table 2. Selected Interatomic Distances and Angles of Compound[a]

atoms	distance [Å]	atoms	angle [deg]
Au(1)−N(1)	2.032(3)	N(1)−Au(1)−N(1)#2	180
Au(1)---Au(1)#1	3.1756(1)	N(1)−Au(1)−Au(1)#1	92.29(9)
Au(1)---Cl(1)	4.6114(8)	N(1)−Au(1)−Au(1)#1−N(1)#1	78.7(2)

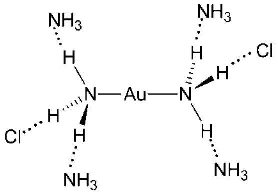
[a] Symmetry transformations for the generation of equivalent atoms: #1 $-x, y, -z - 0.5$; #2 $-x, -y, -z$.

Table 3. Relevant Interatomic Distances [Å] and Angles [deg] of N−H···Acceptor (A) Hydrogen Bonds in the Title Compound[a]

atoms N−H···A	N−H distance	H···A distance	N···A distance	N−H···A angle
N(1)−H(1A)···N(3)#4	0.76(3)	2.31(4)	3.038(4)	162(3)
N(1)−H(1B)···Cl(1)	0.81(3)	2.59(3)	3.397(3)	175(3)
N(1)−H(1C)···N(2)#1	0.85(3)	2.16(3)	2.964(5)	159(3)
N(2)−H(2A)···Au(1)	0.75(2)	2.95(5)	3.408(3)	122(5)
N(2)−H(2A)···N(1)#1	0.75(2)	2.36(5)	2.964(5)	138(7)
N(2)−H(2B)···Cl(1)#5	0.76(2)	2.89(2)	3.624(3)	161(3)
N(2)−H(2C)···Cl(1)	0.77(2)	2.98(2)	3.691(3)	155(3)
N(3)−H(3A)···Cl(1)#6	0.75(3)	2.99(4)	3.731(4)	172(4)
N(3)−H(3B)···Cl(1)#5	0.92(4)	2.68(4)	3.572(4)	166(3)
N(3)−H(3C)	0.84(3)			

[a] Symmetry transformations for the generation of equivalent atoms: #1 −*x*, *y*, −*z* − 0.5; #2 −*x*, −*y*, −*z*; #3 −*x*, *y*, −*z* − 0.5; #4 *x* − 1, *y*, *z*; #5 −*x* + 0.5, −*y* + 0.5, *z* − 0.5; #6 *x* + 0.5, *y* − 0.5, −*z* + 0.5.

Scheme 3. Hydrogen Bonds of the $[Au(NH_3)_2]^+$ Cation to Chloride Anions and Ammonia Molecules of Crystallization



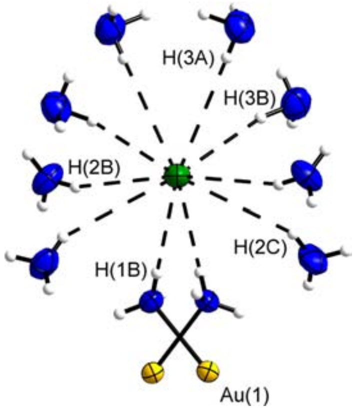


Figure 2. View (perpendicular to the 2-fold rotation axis) of the coordination sphere of the chloride anion in $[Au(NH_3)_2]Cl{\cdot}4NH_3$ at 123 K. Thermal ellipsoids are shown at the 70% level, hydrogen atoms isotropically.

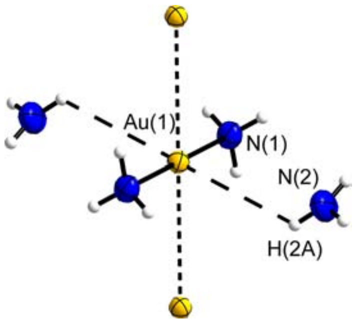


Figure 3. View of the coordination sphere of the Au(I) atom of $[Au(NH_3)_2]Cl{\cdot}4NH_3$ at 123 K. Thermal ellipsoids are shown at the 70% level, hydrogen atoms isotropically.

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Notes

The authors declare no competing financial interest.

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