

# Ligand-unsupported Au(I) chains with short Au(I)⋯Au(I) contacts†

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A new series of solids with ligand-unsupported Au(I) chains with short Au⋯Au contacts were synthesized; as Ag compounds with the same structure are known, the new phases now allow unbiased comparison of Ag⋯Ag and Au⋯Au metallophilic bonds not supported by bridging ligands, which shows the latter to be consistently shorter by 0.03–0.04 Å.

Extensive attention has been focused on the attractive interactions existing between d<sup>10</sup> ‘closed-shell’ elements of group 11.<sup>1,2</sup> The term ‘aurophilicity’ has been coined to describe gold(I)–gold(I) bonding interactions evident in many molecular and solid state structures, which have been attributed to correlation and relativistic effects.<sup>3</sup> The strength of aurophilicity (30–50 kJ mol<sup>-1</sup>) is comparable to that of a typical hydrogen bond. It can be measured by experiment, and is strong enough to influence the overall supramolecular structure; on the other hand argentophilicity is relatively weak.<sup>4,5</sup> However, as pointed out by Pyykkö in 1997,<sup>2</sup> there are few examples that would permit a clean comparison of Ag⋯Ag and Au⋯Au metallophilic bonding. This may be attributed to the fact that the co-ordination abilities of the Au and Ag metal cores differ and that short Ag⋯Ag contacts typically occur in inorganic lattices,<sup>6</sup> compounds maintained by bridging ligands, and polymeric systems.<sup>2,7</sup> Compared with the widely investigated [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, which is quoted in textbooks as an example of linear coordination<sup>8</sup> and for which several structures are known,<sup>9–11</sup> up to the present only the structure of the bromide salt of [Au(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> has been reported.<sup>12</sup> It has been noted that in a series of analogous mononuclear systems, the Au(I) center is found to be smaller than Ag(I) by about 0.05–0.10 Å.<sup>13,14</sup> The first of these papers starts with the emphatic statement ‘gold is smaller than silver’. For two-coordinated diphosphane cations a difference between Ag and Au of 0.08 Å was reported.<sup>13</sup>

Although a number of studies on homologous ligand-bridged dinuclear coinage metal compounds<sup>15,16</sup> and polymeric systems<sup>17</sup> have shown a slightly shorter M⋯M distance in Au(I) compounds compared with the corresponding Ag(I) complexes, the structure analysis of unbridged [M(C<sub>6</sub>F<sub>5</sub>){N(H)=CPh<sub>2</sub>}]<sub>2</sub> (M = Ag, or Au)<sup>5</sup> shows a much longer M⋯M contact for Au [3.5884(7) Å] than for Ag [3.0668(4) Å] and shorter M–N/C distances (Table 1). Similarly, the 3.414(1) Å length of the closest M⋯M contact in [Au(NH<sub>3</sub>)<sub>2</sub>]Br, compared with an Ag⋯Ag contact of 3.131(2) Å in [Ag(NH<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>, (Fig. S1) is surprising, although shorter Au–N distances (Table 1) are found.<sup>12</sup> Does Au(I) usually make shorter intramolecular but longer intermolecular (*i.e.* ligand-unsupported

M⋯M, described as intermolecular by Pyykkö<sup>2</sup>) bonds? Unfortunately, the comparison is not straightforward. In [Au(C<sub>6</sub>F<sub>5</sub>){N(H)=CPh<sub>2</sub>}]<sub>2</sub> the M⋯M vector is bridged by N–H⋯F hydrogen bonds, which may dictate a longer Au⋯Au separation, whereas in the Ag(I) crystals the hydrogen bonds are directed towards neighboring dimers. The comparison of the ammonium compounds is affected by the different stacking modes and by the different counterions in the two salts (Fig. S1). As rigorous conclusions can only be drawn when comparing ligand-unsupported homologous compounds with identical structural arrangements, we have analyzed the structures of a number of new Au(I) salts for which the comparison can be made. This study is part of our work on ground-state and excited-state interactions between d<sup>10</sup> ‘closed-shell’ elements of group 11.<sup>18</sup>

The paucity of structural information on the [Au(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> ion is related to its limited stability compared with the corresponding phosphines.<sup>19</sup> However, as reported,<sup>20</sup> [Au(NH<sub>3</sub>)<sub>2</sub>]Cl is precipitated quantitatively by bubbling NH<sub>3</sub> through an acetone solution of [AuCl(tht)] (tht = tetrahydrothiophene), a powerful starting material in gold chemistry.<sup>21</sup> The perchlorate [Au(NH<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (**1**) and the nitrate [Au(NH<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> (**2**) were prepared by subsequent reaction in acetone of [Au(NH<sub>3</sub>)<sub>2</sub>]Cl with AgClO<sub>4</sub> and AgNO<sub>3</sub> respectively.<sup>20</sup> Colorless crystals were isolated by slow vapor-phase diffusion of diethyl ether into an acetone (**1**) or acetonitrile (**1'**, **2**) solution.

X-ray crystallography‡ shows that **1** crystallizes in the monoclinic space group *C2/m*. Data were collected at 170 K to allow comparison with the published Ag(I) structure.<sup>9</sup> There are two crystallographically independent but similar Au(I) atoms in a virtually linear coordination geometry, each being ligated by two ammonia molecules [Au–N 2.052(2) and 2.053(2) Å, N–Au–N 180°, Fig. 1]. Although **1** crystallizes in a different space group than the homologous Ag(I) compound (Table S1) as in the Ag(I) salt (Fig. S2), the [Au(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cations stack in a staggered conformation with N–Au⋯Au–N torsion angles of 83.7(2)°, resulting in ligand-unsupported Au(I) chains with short Au(I)⋯Au(I) contacts [2.990(1) Å]. The ammonia ligands are donors in hydrogen bonds to the oxygen atoms of the adjacent disordered perchlorate ions [N(H)⋯O 2.957(10)–3.413(5) (Fig. 1c)].

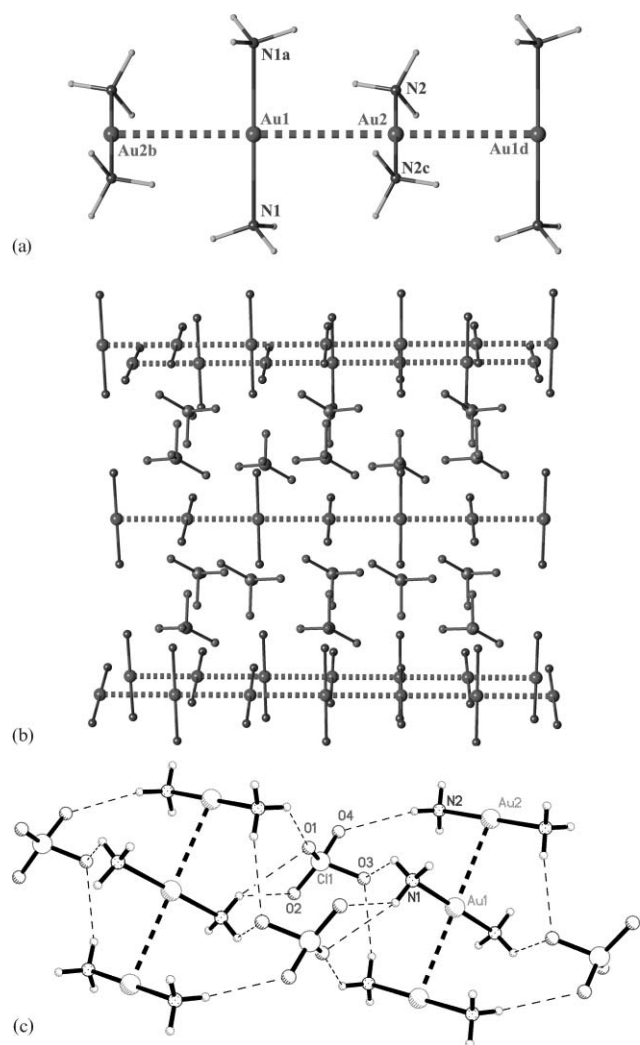
The result is confirmed by the structure of a polymorph of **1** (**1'**) which crystallizes in space group *P1*,<sup>22</sup> and similarly contains

**Table 1** The M–N and M⋯M distances in the [M(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> salts

	<i>T</i> /K	M⋯M/Å	M–N/Å
[Au(NH <sub>3</sub> ) <sub>2</sub> ]Br	RT	3.414(1)	2.01(2), 2.03(2)
[Ag(NH <sub>3</sub> ) <sub>2</sub> ]NO <sub>3</sub>	223	3.131(2)	2.116(10), 2.125(10)
[Au(NH <sub>3</sub> ) <sub>2</sub> ]NO <sub>3</sub>	170	3.091(1)	2.039(8), 2.052(10)
[Ag(NH <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub>	170	3.020(2)	2.129(11)–2.160(12)
[Au(NH <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub>	170	2.990(1)	2.052(2), 2.053(2)

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† Electronic supplementary information (ESI) available: Figures S1–S3 and Table S1. See DOI: 10.1039/b606999a

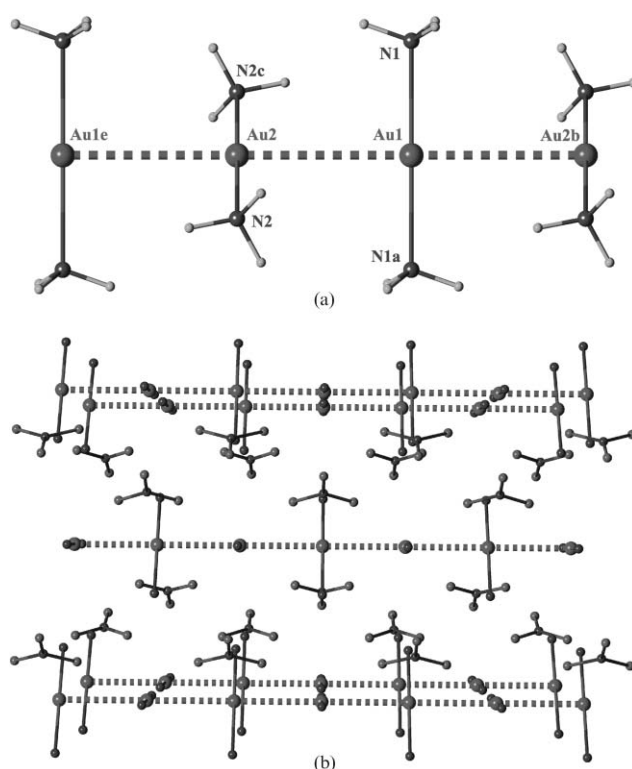


**Fig. 1** Perspective views of **1** showing a) the chain structure of  $[\text{Au}(\text{NH}_3)_2]^+$ , b) three-dimensional packing and c) the three-dimensional H-bond network. Disorder omitted.

ligand-unsupported  $[\text{Au}(\text{NH}_3)_2]^+$  chains (Fig. S3). The two independent  $\text{Au}\cdots\text{Au}$  contacts in **1'** of 2.976(5) and 2.9836(5) Å (90 K) are essentially identical to the  $\text{Au}\cdots\text{Au}$  distance in **1** at 90 K, which is 2.983(1) Å.

Like **1**, the nitrate salt **2** contains linearly coordinated  $[\text{Au}(\text{NH}_3)_2]^+$  cations [ $\text{Au}-\text{N}$  2.039(8) and 2.052(10) Å], stacked in a staggered conformation [ $\text{Au}\cdots\text{Au}$  3.091(1) Å;  $\text{N}-\text{Au}\cdots\text{Au}-\text{N}$  60.5(3)°] (Fig. 2). The ammonia ligands are donors in hydrogen bonds to the oxygen atoms of adjacent (disordered) nitrate ions [ $\text{N}(\text{H})\cdots\text{O}$  2.844(6)–3.210(4) Å].

Thus, in **1** and **2** the separation between adjacent  $\text{Au}(\text{I})\cdots\text{Au}(\text{I})$  cations is shorter by 0.03–0.04 Å than the  $\text{Ag}\cdots\text{Ag}$  separation in the corresponding  $\text{Ag}(\text{I})$  salts  $[\text{Ag}(\text{NH}_3)_2]\text{ClO}_4$  and  $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$  (Table 1), even though the  $\text{Au}-\text{N}$  distances are shorter than the  $\text{Ag}-\text{N}$  distances. Although the nearest-neighbor distances are equal in metallic Au and Ag (2.884–2.889 Å),<sup>23</sup> the van der Waals radii of Ag (1.72 Å) and Au (1.66 Å)<sup>24</sup> differ in the same direction. But unlike conclusions reached earlier on the basis of more limited structural information,<sup>2,12</sup> a shorter  $\text{M}\cdots\text{M}$  distance is not accompanied by a longer  $\text{M}-\text{N}$  distance. The earlier conclusion was based on comparison of  $\text{M}\cdots\text{M}$  in



**Fig. 2** Perspective views showing a) the structure of  $[\text{Au}(\text{NH}_3)_2]^+$  and b) the three-dimensional supramolecular array in **2**.

**Table 2** Unit cells of **1** and **2** at 90, 170 and 260 K

<i>T</i> /K	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	$\beta$ /°	<i>V</i> /Å <sup>3</sup>
<b>1</b>					
90	14.691(6)	5.966(2)	7.713(3)	115.485(18)	610.2(4)
170	14.769(3)	5.980(1)	7.756(2)	115.824(4)	616.6(2)
260	14.925(5)	6.030(2)	7.813(3)	116.591(16)	628.8(4)
<b>2</b>					
90	6.175(2)	10.969(4)	7.586(4)	90	513.8(4)
170	6.183(2)	10.976(4)	7.598(2)	90	515.6(3)
260	6.192(2)	10.992(6)	7.763(4)	90	528.4(4)

$[\text{Au}(\text{NH}_3)_2]\text{Br}$  and  $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$  which have different structural arrangements (Fig. S1) in the crystals.

As listed in Table 2, only a slight change was found in the unit cells of **1** and **2** on changing the temperature from 90 to 260 K. As in both structures the Au(I) atoms are in a special position [(0,0,0) and (0,0.5,0) for **1**, (0,0,0) and (0.5,0,0) for **2**], this implies that the  $\text{Au}\cdots\text{Au}$  distances show very little temperature dependence [**1**: 2.983(1) Å at 90 K, 3.015(1) Å at 260 K; **2**: 3.088(1) Å at 90 K, 3.096(1) Å at 260 K].

The Mayer bond order<sup>25</sup> of  $\text{Au}(\text{I})\cdots\text{Au}(\text{I})$  in the geometry found in crystals of **1** is calculated to be 0.168,<sup>26</sup> showing the orbital interactions to be weakly attractive. However, the interaction energy of two closed-shell species having net charges of the same sign is repulsive due to electrostatic repulsion, which is the strongest component of the total interaction energy, as analyzed in detail by Novoa *et al.*<sup>27</sup> Our MP2 level calculation with BSSE correction employing the Gaussian03 suite of programs,<sup>28</sup> indicates the  $\text{Au}(\text{I})\cdots\text{Au}(\text{I})$  interaction to be repulsive by 274.8 kJ mol<sup>-1</sup>.<sup>29</sup> Thus, the anion $\cdots$ cation interactions with the adjacent  $\text{ClO}_4^-$  ions

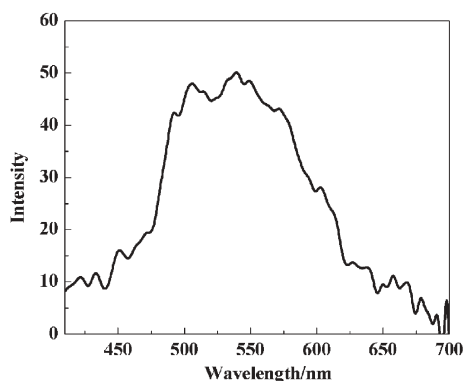


Fig. 3 The emission spectrum of a crystal of **1** at room temperature.

play an important role in the stabilization of the aggregates in the solid state.<sup>30</sup>

As shown in Fig. 3, under ambient conditions the crystal of **1** exhibits an intense orange emission in the 470–600 nm range upon 355 nm excitation, which can be assigned to an MMCT transition of the Au(I) cations.<sup>31</sup>

In summary, the newly determined structures of ligand-unsupported Au(I) chains with short Au...Au contacts offer the opportunity for unbiased comparison of Ag...Ag and Au...Au metallophilic bonding. They show the latter to be consistently shorter by 0.03–0.04 Å than the corresponding Ag...Ag distances, in contrast with earlier studies comparing similar but not structurally identical complexes.

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## Notes and references

‡ **Caution!** Perchlorate salts with organic cations may be explosive. Crystal data: Compound **1**:  $\text{H}_6\text{AuClN}_2\text{O}_4$ ;  $M_r = 330.48$ , monoclinic, space group  $C2/m$ ,  $a = 14.769(3)$ ,  $b = 5.9797(13)$ ,  $c = 7.7564(17)$  Å,  $\beta = 115.824(4)^\circ$ ,  $V = 616.6(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 3.560$  Mg/m<sup>3</sup>,  $\mu$  (Mo-K $\alpha$ ) = 24.231 mm<sup>-1</sup>,  $F(000) = 592$ ,  $GoF = 1.166$ . Among 5521 reflections, 1019 reflections are unique ( $R_{\text{int}} = 0.0264$ ). The final  $R_1$  and  $wR_2$  are 0.0180 and 0.0451, respectively, for 59 parameters and 953 reflections [ $I > 2\sigma(I)$ ]. Crystal data: Compound **2**:  $\text{H}_6\text{AuN}_2\text{O}_3$ ;  $M_r = 293.04$ , orthorhombic, space group  $Immm$ ,  $a = 6.1828(17)$ ,  $b = 10.976(4)$ ,  $c = 7.5983(15)$  Å,  $V = 515.6(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 3.775$  Mg/m<sup>3</sup>,  $\mu$  (Mo-K $\alpha$ ) = 28.439 mm<sup>-1</sup>,  $F(000) = 520$ ,  $GoF = 1.052$ . Among 4128 reflections, 855 reflections are unique ( $R_{\text{int}} = 0.0568$ ). The final  $R_1$  and  $wR_2$  are 0.0203 and 0.0593, respectively, for 69 parameters and 549 reflections [ $I > 2\sigma(I)$ ]. The data were collected on a Bruker APEX II CCD with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 170(2) K. Reflections were reduced by the SAINT program. The structures were solved by direct methods and refined by a full matrix least squares technique based on  $F^2$  using the SHELXL 97 program. CCDC 1: 607983, 2:607984, 1': 608549. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606999a

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