Gold as intermolecular glue: a predicted planar triaurotriazine, $C_3Au_3N_3$, isomer of gold cyanide

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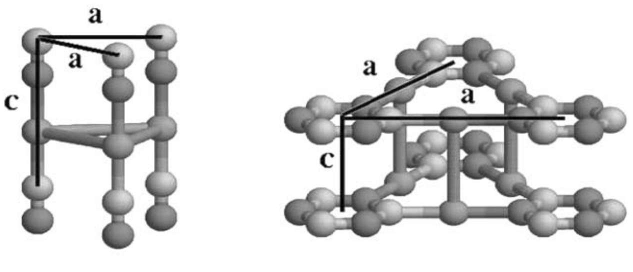
Received (in Cambridge, UK) 24th April 2006, Accepted 17th May 2006
First published as an Advance Article on the web 1st June 2006
DOI: 10.1039/b605757h

It is predicted that solid gold cyanide, AuCN, could have an alternative infinite trigonal-sheet crystal structure, of almost the same energy as the known hexagonally-packed infinite-chain structure.

Solid gold cyanide, AuCN, **1**, consists of a hexagonal packing of infinite, one-dimensional –CN–Au–CN–Au– chains. The cyanides can be disordered and the Au(I) ions of neighbouring chains are, remarkably, in the same perpendicular plane. This was an early example of 'aurophilic' or 'metallophilic' bonding.[1,2] The original AuCN crystal structure by Zhdanov and Shugam[3] is reproduced by Pauling in ref. 4.

Recently a number of compounds have been synthesized whose molecular constituents are held together by C–Au···N bonds (see *e.g.* refs. 5,6). It occurred to us that such interactions could lead to the formation of an infinite lattice, **2**, where triazine-like C_3N_3 rings are coupled to each other by such C–Au···N interactions, see Fig. 1. That structure could also be seen as one infinite example of the structures, combining metals and five- or six-membered nitrogen heterocycles.[7]

As gold cyanide is a commodity chemical, often providing the material for galvanic gold plating, such an alternative form could be of interest. Also the materials science aspects of such a potential new material are worthy of study. We therefore carried out a band-structure calculation, optimizing both structures, **1** and **2**.†



1 **2**

Fig. 1 The chain structure of gold cyanide, **1**, and the sheet structure of triaurotriazine, **2**. The lattice vectors are indicated.

Table 1 Bond lengths, lattice parameters *a* and *c* (picometers) and bond angles (degrees) for solid AuCN **1**, solid $C_3Au_3N_3$ **2**, molecular $C_3Au_3N_3$ **2′** and molecular triazine, $C_3H_3N_3$, **3**. For structure **2**, ⊥ (‖) denotes the inter- (intra-) planar distance. 'PW2' refers to the present molecular calculations

		Solid-state calc. (PW1)			Reference data		
Case	Parameter	LDA	GGA	GGA-PAW	Value	Ref.	Method
1	Au–C	192.6	194.6	194.2			
	Au–N	197.0	200.3	200.0			
	Av. Au–C/N	194.8	197.4	197.1	197.03(5)	[a]	Exp.
	C–N	115.8	116.4	116.7	114.99(2)	[a]	Exp.
	Au–Au (= *a*)	321.4	369.5	379.6	339.6(2)	[b]	Exp.
					340.5(4)	[c]	Exp.
	c	505.4	511.2	510.8	509.0(1)	[a]	Exp.
					509.2(2)	[b]	Exp.
					509.5(4)	[c]	Exp.
2	Au–C	197.1	200.0	199.5			
	Au–N	204.7	210.3	210.2			
	C–N	134.3	136.1	136.2			
	Au–Au ‖	335.3	341.3	341.2			
	Au–Au ⊥ (= *c*)	278.2	335.7	344.5			
	a	670.5	682.5	682.1			
	C–N–C	121.3	121.5	121.5			
2′	Au–C	194.9	199.4	198.3	197.9	PW2	BP86
	C–N	132.1	133.4	133.5	134.5	PW2	BP86
	C–N–C	115.5	115.0	114.8	114.2	PW2	BP86
3	C–N				133.68(1)	[d]	
	C–N–C				113.82	[d]	

[a] Ref. 8. [b] Ref. 9. [c] Ref. 26. [d] Ref. 27.

The calculated interatomic distances are shown in Table 1. The calculated total energies for the two solids are given in Table 2. Of the experimental distances, the neutron diffraction ones for **1** by Hibble *et al.*[8] take into account the directional disorder of the cyanides and are more accurate than those of Bowmaker *et al.*,[9] which do not. The percental deviations from experiment of Au–C/N and C–N distances for AuCN are 0.04% and 1.5%, respectively, at the GGA-PAW level. We find that for both **1** and **2** the Au–C/N and C–N distances are practically insensitive to the interchain or interplanar Au–Au distance. Even compared to isolated chains or sheets, the Au–C/N and C–N distances differ less than ~ 0.4% for GGA-PAW. The interchain Au–Au distances cannot be reliably described by DFT because they are dominated

Table 2 Calculated total energies per AuCN unit (eV)

	Method		
Case	LDA	GGA	GGA-PAW
1	−21.98	−19.57	−19.70
2	−22.53	−19.58	−19.70

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by dispersion interactions,[2,10] the deviations from experiment being of the order of 10% for **1** at the GGA-PAW level.

The calculated distances in our **2** can also be compared with those in various $Au_3(NC_5H_4)_3$ structures[5] or $Au_3(MeN{=}COMe)_3$ (ref. 6). A typical Au···Au distance in them is 331 pm. The trinuclear pyrazolates $[Au(3,5\text{-}(CF_3)(C_3N_2H))]_3$ have 334 pm.[11]

For **2** the C–N distance of the central triazine ring is close to the experimental distances in related, isolated molecules. The other distances are also close to those in related molecules. The interlayer distances are much less certain. Anyway, taking the calculated GGA-PAW crystal densities for both **1** and **2**, the latter is only ~ 69% of the former. Therefore it is natural that the suggested new structure has not been observed in the high-pressure experiments on AuCN **1**.[12,13] No phase transitions were seen in them, but the electric conductivity increased by a factor of 10^5 between 10 and 50 kbar. The calculated GGA-PAW energy gap for a single sheet of **2** is about 1.7 eV.

We also show in Table 1 our calculated geometries for a single $C_3Au_3N_3$ monomer **2′**, calculated by both solid-state and molecular DFT methods, see Fig. 2. Both have C–N distances and C–N–C angles close to the experimental gas-phase geometry for s-triazine $C_3H_3N_3$ **3**. The Au–C distances are also closely similar to the calculated data for **2**.

The present structure **2** could possibly be synthesized from precursors of the triazine type. Another, brute-force approach could be to use the pyrolysis of the appropriate metal cyanide. Such experiments have, in fact, been reported for CuCN, AgCN and $Hg(CN)_2$. The resulting substances were described as a 'metal-containing paracyanogen'.[14] It is hoped that the present calculation will stimulate further experiments and a more stringent characterisation of the resultant products. A useful tool could be the calculated IR spectra. For the isolated molecule **2′** we obtain the three highest, in-plane ring deformations e' at 1395 (955), 1208 (616) and 739 (117) cm^{-1}, with the intensities in km/mol given in parentheses.

Concerning the faithfulness of the present DFT description, the main uncertainty comes from the aurophilic part of the energy. It is not impossible to calculate it also for solids, using localized-orbital-based methods, but that is a major undertaking already for relatively simple crystals like AgCl and AuCl.[15] A comparison of the two structures reveals here that in **1** each Au is experimentally surrounded by six equidistant Au atoms at 339.6 pm. In the calculated structure of **2** we find four intrasheet distances and two intersheet Au–Au distances, all of roughly similar order. Therefore, the DFT-induced errors may not drastically change the relative energies of **1** and **2**. Our best general estimate for the aurophilic attraction at R(Au–Au) = 340 pm is 12.6 kJ/mol (0.13 eV) per pair, using eqn. (3) of ref. 10.

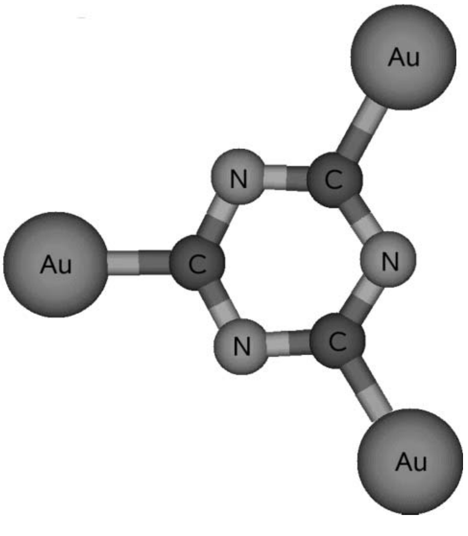

Fig. 2 The monomer structure of triaurotriazine, **2′**.

In conclusion, we predict the possible existence of a new crystalline isomer of AuCN. Similar structures could exist for AgCN and CuCN. It has not escaped our attention that the AuN groups could also be replaced by valence isoelectronic MC groups, where M is a divalent metal, such as Be or Zn–Hg. We invite the experimentalists to look for them in the pyrolysis experiments already carried out.[14]

We belong to the Finnish Center of Excellence in Computational Molecular Science (2006-2011). The grants 110571, 200903, 201291, 205967 and 206102 of The Academy of Finland are gratefully acknowledged. The work was also supported by the Research Funds of the University of Helsinki.

Notes and references

† Method of calculation: The bulk calculations for structures **1** and **2** were carried out using the plane-wave program VASP[16–18] within the density-functional theory (DFT). Ultrasoft (US) pseudopotentials[19,20] and projector augmented-wave (PAW) potentials[21,22] were employed with the generalized gradient approximation (GGA). The exchange–correlation functional by Perdew and Wang[23,24] was used. For comparison, a local-density approximation (LDA) calculation was also performed with US pseudopotentials. Standard values were used for the energy cutoffs for the plane-wave expansion. Supercell approximation was used, and a Γ-centered 6 × 6 × 6 grid for the k points was employed for the energetics. The unit cell has 3 and 9 atoms for structures **1** and **2**, respectively. Constant-volume calculations were performed to optimize the parameters a and c of the hexagonal lattice and the positions of the atoms in the unit cell.

Calculations were also performed for isolated 1-D chains of structure **1**, 2-D sheets of structure **2** and the molecule **2′** (separations about 9 Å, 12 Å and 16 Å, respectively). According to our tests the total energy differences between the systems can be expected to be accurate to ~ 0.05 eV or better per AuCN unit, whereas the interatomic distances (except the interplanar distance in **2**) are accurate to ~ 0.5% or better with the chosen computational parameters. The interplanar distance in **2** can be expected to be accurate to ~ 5%. For the in-plane distances in **2** there remained a small numerical noise component (less than 0.1%) in the calculated equivalent distances Au–C/N and C–N in the unit cell.

For reference, the molecular calculations on molecule **2′** were performed also using Gaussian03 at the BP86 level (19-VE Andrae pseudopotential, two f-functions of $\alpha = 0.2$ and 1.19[25]).

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