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The solid state aggregation of two gold(I) nitrate complexes†

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(Trimethylphosphine)gold(I) nitrate was prepared from the reaction of $(Me_3P)AuCl$ and $AgNO_3$ in MeOH–CH_2Cl_2. Single crystals from CH_2Cl_2–pentane contain trimers $[(Me_3P)Au(ONO_2)]_3$ as sub-units of polymeric chains. The organization is based on short aurophilic Au–Au contacts. A discussion considering all other known $(Me_3P)AuX$ structures leads to the conclusion that small, electronegative anions X favour aurophilic multi-coordination with longer Au · · · Au contacts, while less electronegative, bulky groups X induce dimerization with short Au · · · Au contacts. In all cases neighbouring molecules are arranged with their principal axes roughly perpendicular (staggered). Crystals of $(^tBuNC)Au(ONO_2)$ grown from CH_2Cl_2–pentane at −25 °C were shown to be a 2 : 1 dichloromethane solvate with a new meander-type structure, which is stable only at low temperature and under the standard pressure of a dichloromethane atmosphere. The structure is based on aurophilic interactions of a similar nature as in the solvent-free phase (obtained at 5 °C) as judged from the bond distance parameters, but the solvent molecules are accommodated in cavities formed through a different puckering of the chains. A comparison with other structures of (RNC)AuX molecules suggests that the parallel (eclipsed) head-to-tail alignment of the molecules is the preferred organization in the absence of other structure-determining effects.

Introduction

Supramolecular chemistry investigates the aggregation of molecules through forces other than conventional covalent, ionic or metallic bonding. Donor–acceptor and hydrogen bonding are the most commonly recognized modes of interactions and much of the contemporary synthetic strategies in crystal engineering and self-assembly design are based on these two fundamental types of intermolecular bonding.[1] Owing to the rather low inherent bond energies, supramolecular structures can undergo facile restructuring and rearrangements in response to changes in experimental conditions such as temperature, pressure, concentration and solvation.[2] This is particularly true for hydrogen-bonded structures as amply shown by the enormous flexibility of most biochemical systems.

Recent synthetic and structural studies have shown that the chemistry of the heavy late transition elements features another unique type of intermolecular interaction, also associated with low bond energies and therefore showing flexible response to minor changes in the molecular environment. These “metallophilic contacts” are based on what may be summarized as “closed-shell interactions” because they occur between metal centres with non-deficit electronic configurations. Although there are several scattered examples for this phenomenon in the chemistry of palladium, platinum, copper, silver and mercury, it is the chemistry of gold in particular where the effect is ubiquitous.[3,4] Knowledge about the structural chemistry of gold has advanced to a state, where “aurophilic” closed-shell interactions are predictable and may be taken as a dependable element of design of supramolecular structures.[5]

The most common types of interactions occur perpendicular to the principal axis of two-coordinate gold(I) complexes of the types L–Au–X, $[X–Au–X]^-$, $[L–Au–L]^+$ or mixtures of these units.[4a,6] Standard bonding distances range from 2.7 to 3.5 Å and are associated with bond energies of between 7.5 and as much as 12.5 kcal mol^{-1}. These parameters have been reproduced and confirmed in state-of-the-art theoretical treatments, the bonding being interpreted as strong correlation effects in the electron-rich heavy late transition elements, enhanced by particularly strong relativistic effects which reach a local maximum in the Periodic Table at gold.[7,8]

The metal–metal interaction is expected to be dependent on the nature of the ligands L and X^-, but to date the sequence derived from *ab initio* calculations has not always been in agreement with the experimental findings.[8] Strongly electronegative groups have been predicted to reduce the energy of the closed-shell interactions. This theoretical finding is supported by the solid state dimers of $(Me_2PhP)AuX$ (X = Cl, Br, I).[9] However, the complexes $(^tBuNC)AuX$ ($X = NO_3$, Cl, Br, CN) which all crystallise as polymeric zigzag chains, contradict this general theory with the nitrato complex exhibiting the shortest interactions.[10]

It is important to note that the interaction of two naked (closed-shell) Au^+ cations is repulsive making a species $[Au_2]^{2+}$ unstable at all inter-ionic distances.[11] The same approach of two ligand-bonded Au^+ centres such as $[LAuL]^+$, however, is attractive. The effect is even more common for polynuclear cationic species such as $[RS(AuL)_2]^+$ or $[O(AuL)_3]^+$, *etc.*[12]

Weak aurophilic contacts, not unlike hydrogen bonds, are influenced by steric effects and also must compete with other intra- or inter-molecular interactions. This can lead to a delicate balance between alternative structural motifs. In an effort to further delineate scope and limitations of aurophilic bonding, the present study examines two gold complexes where the Au^+ centres bear highly electronegative nitrate ligands and are not strongly impeded by steric shielding (using the smallest tertiary phosphine PMe_3 and a “slim” isocyanide).

The literature has very few reports of gold(I) *nitrate* structures: (Tri*phenyl*phosphine)gold nitrate is a monomer in the solid state, clearly owing to the steric bulk of the PPh_3 ligand.[13] A series of (isonitrile)gold(I) nitrates $(RNC)Au(NO_3)$ investigated in a preceding study[10] has already illustrated the great variety of structures that can arise from changes in the nature of R. All gold(I) nitrates are promising candidates for the preparation of heterogeneous gold catalysts on supports.[14]

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Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b003523h/

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Table 1 Crystal data, data collection and structure refinement for $(Me_3P)Au(ONO_2)$ and $(Me_3CNC)Au(ONO_2)\cdot 0.5CH_2Cl_2$

	$(Me_3P)Au(ONO_2)$	$(^tBuNC)Au(ONO_2)\cdot 0.5CH_2Cl_2$
Empirical formula	$C_3H_9AuNO_3P$	$C_{5.5}H_{10}AuClN_2O_3$
M	335.05	384.57
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/Å	9.052(1)	26.743(1)
b/Å	10.436(2)	7.774(1)
c/Å	13.422(1)	10.513(1)
α/°	78.12(1)	90
β/°	75.62(1)	110.96(1)
γ/°	74.97(1)	90
U/Å^3	1172.6(3)	2041.2(1)
Z	6	8
μ(Mo-Kα)/cm^{-1}	189.7	146.7
T/K	163	163
Measured reflections	5398	3779
Unique reflections	5112 (R_{int} = 0.0184)	1986 (R_{int} = 0.0219)
Refined parameters	245	114
$R1$ [$I > 2\sigma(I)$]	0.0314	0.0575
$wR2$	0.0782	0.1440
Weighting scheme coefficients[a]	a = 0.0465 b = 8.70	a = 0.0967 b = 10.93

[a] $R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$; $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

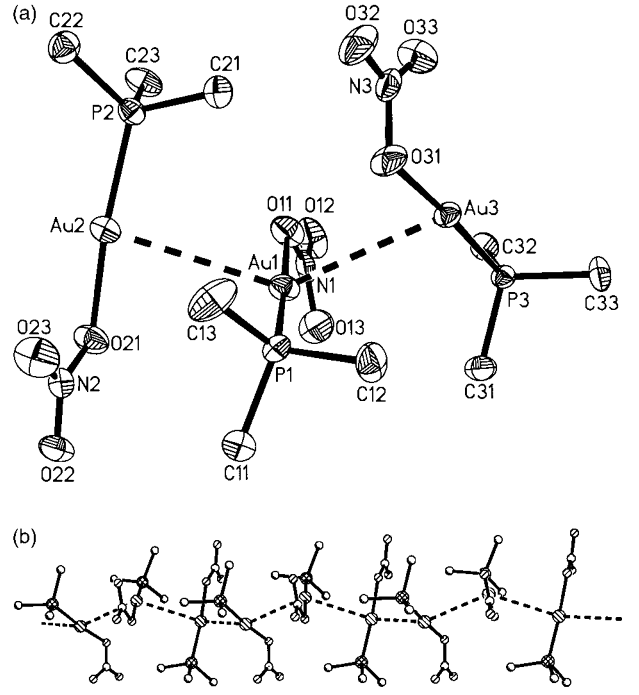

Fig. 1 (a) Trimeric unit $[(Me_3P)Au(ONO_2)]_3$ in the crystal structure of $[(Me_3P)Au(ONO_2)]_n$ with atomic numbering of the three crystallographically independent monomers. Selected bond lengths (Å) and angles (°): Au1···Au2 3.449(1), Au1···Au3 3.280(1), Au1–P1 2.216(2), Au1–O11 2.090(6), Au2–P2 2.219(2), Au2–O21 2.093(6), Au3–P3 2.216(2), Au3–O31 2.100(5); P1–Au1–O11 176.2(2), P2–Au2–O21 171.5(2), P3–Au3–O31 174.0(2). (b) Assembly of the trimers $[(Me_3P)Au(ONO_2)]_3$ into chains *via* Au···Au contacts [Au2···Au3′ 3.278(1)].

Results

(Trimethylphosphine)gold(I) nitrate

This complex was prepared from (trimethylphosphine)gold(I) chloride and silver nitrate in methanol–dichloromethane at −78 °C and crystallized from dichloromethane–pentane (77% yield, mp 121 °C). The product was identified by its elemental analysis and spectral data (Experimental section).

The crystals of $(Me_3P)Au(ONO_2)$ grown from CH_2Cl_2–pentane at −25 °C (triclinic, space group $P\bar{1}$, $Z = 6$) contain no solvent. The asymmetric unit comprises three independent molecules with very similar geometrical details (Table 1, Fig. 1). The nitrate anions are attached to their respective gold atoms by only one of the three oxygen atoms with Au–O distances of 2.090(6), 2.093(6) and 2.100(5) Å for Au1, Au2 and Au3, respectively. The geometries at the gold centres are close to linear [P–Au–O 176.2(2), 171.5(2), 174.0(2)° for Au1, Au2, Au3, respectively]. The configuration at the nitrogen atoms is planar with O–N–O bond angles in the range 116.8(7)–123.6(7)°. The N–O bonds connecting to the gold atoms are significantly longer than the non-ligated N–O bonds [1.294 (av.) *cf.* 1.227 Å (av.)], strongly indicative of covalent, coordinative Au–O bonding.

The $(Me_3P)Au(ONO_2)$ molecules are aggregated by two relatively short Au···Au contacts [Au1···Au3 3.2795(6), Au2···Au3′ 3.2783(6) Å] to form trimers, which are associated into chains *via* significantly longer Au···Au contacts [Au1··· Au2 3.449(1) Å] (Fig. 1). Neighbouring molecules are rotated into staggered conformations with torsion angles P–Au–Au–P of 112.7 and 114.4°.

The aurophilic motif of $(Me_3P)Au(ONO_2)$ is similar to those found for other $(Me_3P)AuX$ compounds (X = CN, Br, Cl, CF_3CO_2). The *chloride* and the *cyanide* analogues (X = Cl,[15] CN[16]) resemble the nitrate most closely, in that trimers are discernible with average Au···Au contacts of 3.338 and 3.289 Å, respectively, as compared to 3.336 Å for the nitrate. For the (trimethylphosphine)gold *bromide* (X = Br)[17] all of the Au··· Au contacts are relatively long with an average of as much as 3.725 Å, suggesting much weaker interactions. For the trifluoroacetate (X = CF_3CO_2)[18] the chains are clearly broken into trimers with intra-trimer Au–Au distances of 3.314(1) and 3.333(1) Å and an inter-trimer Au–Au distance of 4.322(6) Å, which is already close to the sum of the van der Waals radii of two gold atoms. In contrast the iodide (X = I)[19] was found to form independent dimers with one short Au–Au contact [3.168(1) Å] and a dihedral angle P–Au–Au′–I′ of *ca.* 70°. In this staggered conformation the two iodine atoms are on opposite sides and no intra-dimer I–I interaction can be invoked. The methyl sulfide (X = MeS)[20] also exists as a dimer in the solid state with a short Au–Au contact of 3.158(1) Å.

This short summary of the structural chemistry of (Me_3P)-AuX compounds suggests that soft ligands of low electronegativity lead to the formation of dimers (X = I, MeS), while small and hard ligands (X = Cl, Br, CN, CF_3CO_2, NO_3) give

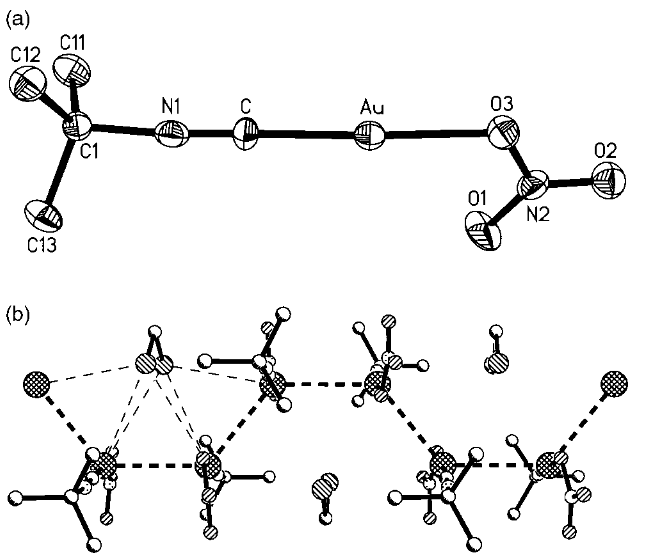

Fig. 2 (a) The monomeric unit in the crystal structure of $[(Me_3CNC)Au(ONO_2)]_2{\cdot}CH_2Cl_2$ with atomic numbering. Selected bond lengths (Å) and angles (°): Au–C 1.907(8), Au–O3 2.033(6), N1–C 1.142(11), N1–C1 1.477(11); C–Au–O3 177.6(3), Au–C–N1 178.7(8), C–N1–C1 175.2(8). (b) Meandering chain of $(Me_3CNC)Au(ONO_2)$ units with CH_2Cl_2 in trapezoid cavities. For clarity, Au···Cl contacts are shown for only one of the solvent molecules [Au···Au′ 3.249(1), Au···Au″ 3.231(1); Au′···Au···Au″ 128.3(1); Au···Cl 3.836 (av.)].

chains with discernible trimeric components. There is no correlation between anion electronegativity and the average Au–Au distance observed within the trimeric structures. The overall influence of the anions is probably a complicated blend of steric and electronic factors. In general terms, however, the small electronegative anions appear to favour multi-coordination (two Au···Au contacts for some or all of the gold atoms) whereas only one Au···Au contact per gold atom is observed for the less polar compounds (X = I, SMe).

(*tert*-Butyl isocyanide)gold(I) nitrate

This complex was prepared from (*tert*-butyl isocyanide)gold(I) chloride and silver nitrate in methanol–dichloromethane as previously described.[10] Crystals grown from dichloromethane–light petroleum at 5 °C (monoclinic, space group $P2_1/n$) were needles that contained no solvent. Their structure was determined and shown to contain zigzag chains of molecules with Au–Au contacts of 3.2963(8) and 3.3232(8) Å [Au–Au–Au 142.28(5)°] (Fig. 3).

It was noted now that crystals grown at −25 °C were square platelets which upon warming turned opaque and lost crystallinity. This low-temperature form was shown by X-ray crystallography to contain dichloromethane solvent in the molar ratio 2:1 and to have a different structure (monoclinic, $C2/c$, $Z = 8$): The monomeric units with their quasi-linear principal axis $(Me_3)C{-}N{-}C{-}Au{-}O(NO_2)$ are forming meandering instead of simple zigzag chains (Fig. 2). Neighbouring molecules are aligned head-to-tail. The underlying aurophilic contacts are only slightly shorter than those in the solvent-free form: Au–Au′ 3.2488(6), Au–Au″ 3.2312(5) Å [Au′–Au–Au″ 128.26(1)°].

The meandering sequence of gold atoms forms trapezoid cavities on both sides of the chain which are occupied by the solvent molecules. These solvent molecules are slightly tilted and shifted from the centre so every chlorine atom has contacts with three gold atoms (instead of four as expected for a fully symmetrical arrangement). Weak Au···Cl contacts (Au···Cl 3.822–3.849 Å) may be partially responsible for the CH_2Cl_2 positioning. Removal of the solvent leads to a collapse of the lattice and requires the set-up of a new more space-filling organization. The transformation of the zigzag chain in the solvent-free form (Fig. 3) into the meandering solvated form (Fig. 2) is associated mainly with an angle contraction (Au–Au–Au) from 142.28(5) to 128.26(1)° and a change in chain propagation motif from *cis*/*trans*/*cis*/*trans* to *cis*/*cis*/*trans*/*trans*.

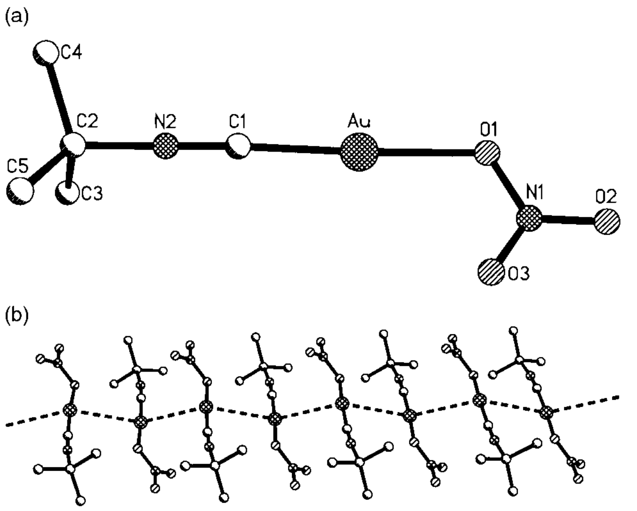

Fig. 3 (a) The monomeric unit in the crystal structure of $(Me_3CNC)Au(ONO_2)$ with atomic numbering. Selected bond lengths (Å) and angles (°):[10] Au–C1 1.92(1), Au–O1 2.062(9), N2–C1 1.13(2), N2–C2 1.47(2); C1–Au–O1 176.3(4), Au–C1–N2 176.5(9), C1–N2–C2 174.2(9). (b) Zigzag chain of $(Me_3CNC)Au(ONO_2)$[10] [Au···Au′ 3.324(1), Au···Au″ 3.295(1) Å; Au′···Au···Au″ 142.3(1)°].

Details of the structure of the (*tert*-butyl isocyanide)gold nitrate monomer in the dichloromethane-solvated phase are in good agreement with literature data for the solvent-free phase and for other compounds of the general formula (RNC)AuX.[21] The isostructural packing of the solvent-free monomers (^{t}BuNC)AuX ($X = NO_3$, Cl, Br and CN) is explained by the steric compatibility of the long rod-like isonitrile (with the *tert*-butyl group branching three atoms away from the metal), and relatively small anions which allows an efficient head-to-tail arrangement of parallel ligand molecules. This isostructural series has been broken using a sterically demanding anion in the complex (^{t}BuNC)Au($CCSiMe_3$) which crystallizes as a unique crossed-ligand tetramer.[22] In contrast, complexes of the type (XyNC)AuX (Xy = 2,6-dimethylphenyl; $X = NO_3$, Cl, Br, I, CN)[10,23] all crystallize with different aurophilic motifs.

In the $(Me_3P)AuX$ series the Me_3P ligand exhibits branching methyl groups much closer to the metal (as compared to the Me_3CNC ligand). Therefore aurophilic contacts require a rotation of the molecules from the parallel to the perpendicular conformation (eclipsed to staggered). In all cases, however, the aurophilic contacts are maintained as the principal element of assembly.

Conclusion

Aurophilicity has developed into an intriguing concept that combines aspects of supramolecular and theoretical chemistry with the general mystique that surrounds gold. The future challenge is to understand the individual factors that control the strength of the interactions, the orientation of the components, and the physical properties of the resulting materials.

Experimental

All experiments were routinely carried out in an atmosphere of dry, pure nitrogen. Solvents were dried and distilled under nitrogen, and glassware was oven-dried and filled with nitrogen. NMR: JEOL JNM-GX 400, $CDCl_3$ as a solvent at 25 °C, internal $SiMe_4$ and external H_3PO_4 as references. $(Me_3P)AuCl$[15] and ^{t}BuNC[24] were prepared following literature procedures.

(Trimethylphosphine)gold nitrate

A stirred solution of $AgNO_3$ (0.121 g, 0.72 mmol) in MeOH (5 mL) was cooled to −78 °C. To this was added dropwise a solution of $(Me_3P)AuCl$ (0.221 g, 0.72 mmol) in dichloromethane (10 mL) over a period of 2 h. The solvent was subsequently removed *in vacuo* and the residue extracted with 5 mL of CH_2Cl_2. Pentane was added to the filtered extract to precipitate, as a white microcrystalline powder, the product (0.184 g, 77% yield), mp 121 °C. Found: C, 10.77; H, 2.60; N, 3.83. Calc. for $C_3H_9AuPNO_3$ ($M = 384.57$): C, 10.75; H, 2.69; N, 4.18%. NMR: ^{1}H, δ 1.57 (d, $^2J_{PH} = 13.1$ Hz); $^{13}C\{^1H\}$, δ 17.5 (d, $^1J_{PC} = 70.7$ Hz); $^{31}P\{^1H\}$, δ −16.7 (s).

(*tert*-Butyl isocyanide)gold nitrate

The compound was prepared as described previously.[10] Crystals were grown by vapour diffusion of pentane into a solution of the complex in dichloromethane at −25 °C.

Crystallography

Specimens of suitable quality and size were fixed on glass capillaries and used for measurements of precise cell constants and intensity data collection (Mo-Kα radiation, λ(Mo-Kα) = 0.71073 Å). Intensity data of $(Me_3P)Au(ONO_2)$ were corrected for absorption effects (ψ-scans, $T_{min/max} = 0.503/0.997$), while the absorption correction of the data of $({}^tBuNC)Au(ONO_2)\cdot 0.5CH_2Cl_2$ could not be carried out due to crystal decomposition. Further information on crystal data, data collection and structure refinement is summarized in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions.

CCDC reference number 186/2027.

See http://www.rsc.org/suppdata/dt/b0/b003523h/ for crystallographic files in .cif format.

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