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Preparation and structural characterisation of isocyanide gold(I) nitrates, [Au(NO$_3$)(CNR)] (R = Et, Bu^t or C$_6$H$_3$Me$_2$-2,6); new auriophilic motifs†

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The first examples of isocyanide gold(I) nitrates, [Au(NO$_3$)(CNR)] (R = Et, Bu^t or C$_6$H$_3$Me$_2$-2,6) have been prepared from the corresponding chlorides and AgNO$_3$. Full characterisation included crystal structure determinations for each example. The structures of the analogous compounds [AuCl(CNR)] (R = Et or C$_6$H$_3$Me$_2$-2,6) were also determined for comparison. All species show Au···Au interactions in the solid state, but with different modes of aggregation; [AuCl(CNEt)] and [Au(NO$_3$)(CNBu^t)] have infinite zigzag chains, [AuCl(CNC$_6$H$_3$Me$_2$-2,6)] has a 'broken' chain of tetrameric units, [Au(NO$_3$)(CNEt)] has a linked chain of tetrameric units, while [Au(NO$_3$)(CNC$_6$H$_3$Me$_2$-2,6)] has a highly compressed chain. In each instance the Au···Au interactions for [Au(NO$_3$)(CNR)] are shorter than for the analogous [AuCl(CNR)], suggesting NO$_3^-$ enhances these secondary bonds. This is in direct contrast to previous theoretical predictions. The structure of the solvated ionic compound [Au(CNC$_6$H$_3$Me$_2$-2,6)$_2$]NO$_3$ has also been determined.

Introduction

Linear two-co-ordinate complexes are ubiquitous in gold(I) chemistry, and complexes of the type [AuX(L)] formed through the combination of a neutral ligand L and an anionic ligand X have been long known.[1] More recently, it has been recognised that the packing of these molecules in the solid state is often influenced by secondary Au···Au interactions (of similar energy to hydrogen-bonding forces) unless they are precluded for steric reasons.[2,3] This phenomenon has been termed[4] 'auriophilicity'. Several theoretical studies have examined the origin of these interactions which occur between Au^I and other closed-shell d^{10} metal ions, and have attributed them to correlation effects enhanced by relativistic effects.[5–7] The phenomenon is now sufficiently well established to be used in the design of specific solid state polymers.[8]

Gold(I) co-ordination chemistry is characterised by a strong preference for polarisable (soft) donor atoms,[2,3] so that for species [AuX(L)] the anion X is predominantly Cl$^-$, Br$^-$, I$^-$, CN$^-$ or SR$^-$. Compounds with Au^I–O bonds are relatively rare, and all the examples structurally characterised[9] have also incorporated stabilising phosphine ligands, usually PPh$_3$.

Haruta *et al.*[10] have shown that metallic gold particles supported on transition metal oxides, prepared from co-precipitated precursors, are very active catalysts for the oxidation of CO to CO$_2$ under ambient conditions. This is a process of significant technological interest. We are developing similar catalysts by deposition of organometallic precursors on metal oxide supports so needed gold complexes which would be readily absorbed onto surfaces and which could subsequently be thermally decomposed to Au^0 at moderate temperatures. Absence of halide or sulfide was also essential since these act as catalyst poisons.[10] We therefore explored the chemistry of previously unknown complexes of the general type [Au(NO$_3$)(CNR)] which appeared to fulfil our criteria, encouraged by parallel reports of the use of [Au(NO$_3$)(PPh$_3$)] for similar purposes.[11] The successful use of the new complexes for catalyst formation will be discussed in a future paper; herein we report the preparation and crystal structures of the novel compounds [Au(NO$_3$)(CNR)] [R = Et, Bu^t or xylyl (2,6-dimethylphenyl)], together with the structures of [AuCl(CNR)] (R = Et or xylyl) for comparison of the auriophilic interactions in the solid state. The ionic species [Au(CNC$_6$H$_3$Me$_2$-2,6)$_2$]NO$_3$ is also described. Aspects of this work have been communicated.[12]

Experimental

Preparations of gold nitrate complexes were carried out under an atmosphere of dry argon, in dried glassware which was wrapped in foil to minimise exposure to light. Solvents were routinely distilled under an inert atmosphere before use. Light petroleum spirit refers to a bp 60–80 °C fraction. The NMR spectra were recorded under standard conditions on a Bruker DRX400 spectrometer in CDCl$_3$ solutions, IR spectra as KBr discs on a Perkin-Elmer Model 1600 FTIR spectrometer. Differential thermal analysis was carried out on a Perkin-Elmer DSC6 differential scanning calorimeter, with a scan rate of 15 °C min^{-1}. Microanalyses were carried out at the Campbell Laboratory, University of Otago. The isocyanides RNC (R = Et, Bu^t or xylyl) were prepared following literature methods,[13] and the corresponding [AuCl(CNR)] compounds formed by displacement of tetrahydrothiophene from [AuCl(SC$_4$H$_8$)] in the standard manner,[14,15] and showed satisfactory microanalytical data. Melting points were [AuCl(CNEt)] 115 °C and [AuCl(CNC$_6$H$_3$Me$_2$-2,6)] 140 °C.

Syntheses

[Au(NO$_3$)(CNBu^t)]. A solution of AgNO$_3$ (0.30 g, 1.8 mmol) in MeOH (30 mL) was cooled to −45 °C. To this was added [AuCl(CNBu^t)] (0.45 g, 1.4 mmol) in CH$_2$Cl$_2$ (10 mL), maintaining the temperature at −45 °C. After stirring for 30 min the solvent was evaporated under vacuum and the solid residue immediately extracted with cold CH$_2$Cl$_2$ (5 mL). Light petrol-

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† Dedicated to Professor Warren Roper on the occasion of his 60th birthday.

eum was added to the filtered extract to precipitate the product as white microcrystals of $[Au(NO_3)(CNBu^t)]$ (0.32 g, 65%) (Found: C, 17.76; H, 2.47; N, 8.30. Calc. for $C_5H_9AuN_2O_3$: C, 17.55; H, 2.65; N, 8.19%). **CAUTION**: decomposes explosively without melting at 118 °C. IR (cm^{-1}): 2258 (CN), 1512, 1272, 977 (NO_3^-). NMR: ^1H, δ 1.60 (CH_3); ^{13}C, δ 29.7 (CH_3), 60.1 [$(CH_3)_3CN$] and 122.2 (N≡C).

$[Au(NO_3)(CNEt)]$. This complex was prepared in a directly analogous fashion from [AuCl(CNEt)] (0.103 g, 0.36 mmol) and $AgNO_3$ (0.076 g, 0.45 mmol) in mixed MeOH–CH_2Cl_2 solvent at −45 °C. Work-up as before gave $[Au(NO_3)(CNEt)]$ (0.076 g, 67%) (Found: C, 11.79; H, 1.59; N, 8.82. Calc. for $C_3H_5AuN_2O_3$: C, 11.47; H, 1.60; N, 8.92%). Decomposes without melting at 106 °C. IR (cm^{-1}): 2267, 1514, 1274 and 978. NMR: ^1H, δ 1.53 (CH_3), 3.75 (CH_2); ^{13}C, δ 13.9 (CH_3), 39.8 (CH_2) and 128.4 (N≡C).

$[Au(NO_3)(CNC_6H_3Me_2\text{-}2,6)]$. Similarly from $[AuCl(CNC_6H_3Me_2\text{-}2,6)]$ (0.137 g, 0.41 mmol) and $AgNO_3$ (0.075 g, 0.44 mmol) in mixed MeOH–CH_2Cl_2 solvent. Work-up as before gave $[Au(NO_3)(CNC_6H_3Me_2\text{-}2,6)]$ (0.114 g, 76%) (Found: C, 27.69; H, 2.04; N, 7.30. Calc. for $C_9H_9AuN_2O_3$: C, 27.71; H, 2.33; N, 7.17%). Decomposes without melting at 125 °C. IR (cm^{-1}): 2215, 1529, 1274 and 958. NMR: ^1H, δ 2.47 (CH_3), 7.19 (*meta* CH) and 7.37 (*para* CH); ^{13}C, δ 18.7 (CH_3), 124.1 (*ipso*-C), 128.6 (*meta*-C), 131.5 (*para*-C), 136.5 (*ortho*-C) and 134.9 (N≡C).

X-Ray crystallography

Single crystals were obtained from slow diffusion of pentane into a CH_2Cl_2 solution of [AuCl(CNR)] (R = Et or xylyl) at 20 °C, of $[Au(NO_3)(CNR)]$ (R = Et or Bu^t) at 4 °C and of $[Au(NO_3)(CNC_6H_3Me_2\text{-}2,6)]$ at −20 °C. The crystal of $[Au(CNC_6H_3Me_2\text{-}2,6)_2]NO_3$ used was formed during one recrystallisation of $[Au(NO_3)(CNC_6H_3Me_2\text{-}2,6)]$.

Unit cell dimensions and intensity data were obtained on a Siemens SMART CCD diffractometer, operating at 203 K, with monochromatic Mo-Kα radiation, λ 0.71073 Å. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal to detector distance was 5.0 cm. The data sets were corrected using SADABS.[16] For some of the structures this led to physically improbable values of $T_{max,min}$, but nevertheless gave what appeared to be the best data sets, based on R_{int} values and refinement behaviour. The values of T are therefore not strictly transmission factors in an absolute sense, rather they are correction factors for all of the anisotropic effects, and for variations during data collection. The SHELX 97 programs were used for all other calculations.[17]

The five structure determinations for [AuCl(CNR)] (R = Et, or xylyl) and $[Au(NO_3)(CNR)]$ (R = Et, Bu^t or xylyl) were routine, solved by automatic interpretation of Patterson maps and developed normally. In the final cycles of least-squares refinement based on F^2 against all data all non-hydrogen atoms were treated anisotropically and hydrogen atoms included in their calculated positions.

For the structure of $[Au(CNC_6H_3Me_2\text{-}2,6)_2]NO_3$ the data were consistent with the space groups *C*2, *Cm* or *C*2/*m*, with the latter being chosen for refinement. The gold atom was located on a site of 2/*m* symmetry, and a subsequent difference map located the remaining atoms of the cation. The remaining electron density was assigned as follows: a CH_2Cl_2 of crystallisation was found with site occupancy *ca.* 0.5, the two Cl atoms being well defined but the C atom was disordered over two symmetry equivalent sites. The nitrate anion was also disordered over two equivalent sites on a mirror plane, and appeared to be superimposed on a fragment which was consistent with a molecule of MeOH. It was assumed that this site of the crystal lattice was occupied equally by NO_3^- and MeOH (note that charge neutrality means that each of the sites can only contain half a NO_3^- ion). This model refined sensibly in *C*2/*m*. It was possible to refine the structure with non-disordered NO_3^- in the lower space groups, but there were clearly pseudo-symmetry problems and the refinement did not give significantly better agreement factors, so the disordered structure in the higher symmetry space group was preferred. For this structure H atoms were not included in the refinement.

Table 1 The ^{13}C NMR shifts for the N≡C carbon atom of isocyanide gold complexes

	δ		
R	CNR	[AuCl(CNR)]	$[Au(NO_3)(CNR)]$
Et	155.0	134.0	128.4
Bu^t	152.8	132.2	122.2
$C_6H_3Me_2\text{-}2,6$	167.9	144.9	134.9

Details concerning the crystal structures are given in Table 2, and selected structural parameters in Table 3.

CCDC reference number 186/1250.

See http://www.rsc.org/suppdata/dt/1999/201/ for crystallographic files in .cif format.

Results and discussion

Synthesis

The isocyanide gold(I) nitrate complexes were prepared in reasonable yields according to eqn. (1). The reactions were best

$$[AuCl(CNR)] + AgNO_3 \longrightarrow [Au(NO_3)(CNR)] + AgCl \quad (1)$$

carried out in a mixed MeOH–CH_2Cl_2 solution at −45 °C with exclusion of light. Straightforward work-up gave the pure complexes, the first examples of C,O-bonded gold(I) species. Samples can be stored indefinitely at −20 °C, and deteriorate only slowly at room temperature in the absence of light, so stability is reasonable. However on attempting to record melting points it was noted that $[Au(NO_3)(CNBu^t)]$ in particular reproducibly decomposed violently without melting. Differential thermal analysis of the $[Au(NO_3)(CNR)]$ complexes showed that all of them exhibited exothermic decomposition peaks centred around 139 (R = Et), 106 (R = Bu^t) or 125 °C (R = xylyl).

The novel compounds were characterised by microanalysis and by IR spectra which showed bands readily assigned to C≡N and monodentate NO_3^- group vibrations.[18] The NMR data were also consistent with the proposed formulae, and need little discussion, except perhaps for the ^{13}C signals for the ligated isocyanide carbon atom which have not been previously reported for C,O-bonded gold(I) complexes. The data are listed in Table 1 for the ‘free’ ligands and for the chloro and nitrate complexes. There is a consistent shift to higher field of about 20 ppm going from the ‘free’ ligand to the [AuCl(CNR)] complexes, and a further shift of 6–10 ppm for the $[Au(NO_3)(CNR)]$ complexes. This presumably reflects the higher electronegativity of the *trans* ligand for nitrate compared with softer chloride.

Structure determinations

(i) Molecular structures. The structures of the two chloro complexes [AuCl(CNR)] (R = Et or xylyl) were determined for comparison with the corresponding nitrates, and to add to the recent series with R = Me, Bu^t, Ph, Mes (2,4,6-trimethylphenyl) and $CH_2C(O)OMe$ reported by Schmidbaur and co-workers,[14] following an earlier report for the R = Bu^t example.[19] Individual

Table 2 Details for the X-ray crystallography determinations

	[AuCl(EtCN)]	[AuCl(CNC$_6$H$_3$Me$_2$-2,6)]	[Au(NO$_3$)(CNEt)]	[Au(NO$_3$)(CNBu^t)]	[Au(NO$_3$)(CNC$_6$H$_3$Me$_2$-2,6)]	[Au(CNC$_6$H$_3$Me$_2$-2,6)$_2$]NO$_3$·MeOH·0.5CH$_2$Cl$_2$
Formula	C_3H_5AuClN	C_9H_9AuClN	$C_3H_5AuN_2O_3$	$C_5H_9AuN_2O_3$	$C_9H_9AuN_2O_3$	$C_{19.5}H_{22.5}AuClN_3O_4$
M_r	287.50	363.59	314.06	342.11	390.15	595.32
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/m$
a/Å	4.4626(5)	10.6513(3)	8.1005(1)	6.2642(1)	15.1075(6)	20.7234(7)
b/Å	6.3014(7)	17.3099(4)	7.8684(1)	13.5595(3)	3.7802(2)	6.7276(1)
c/Å	10.0629(11)	11.0902(2)	20.3639(1)	10.6118(1)	8.0762(6)	8.3385(3)
β/°	96.100(2)	97.846(1)	96.987(1)	102.18	103.76(1)	107.925(2)
V/Å^3	281.37(5)	2025.59(8)	1288.31(3)	881.07(3)	1002.69(7)	1106.11(5)
Z	2	8	8	4	4	2
D_c/g cm^{-3}	3.393	2.385	3.238	2.579	2.584	1.781
μ(Mo-Kα)/mm^{-1}	26.5	14.7	22.7	16.7	14.7	6.8
$T_{max,min}$	0.912, 0.058	0.367, 0.174	0.041, 0.003	0.102, 0.023	0.527, 0.047	0.618, 0.407
F(000)	252	1328	1120	624	720	577
Crystal size/mm	0.18 × 0.15 × 0.05	0.60 × 0.11 × 0.10	0.45 × 0.39 × 0.29	0.43 × 0.34 × 0.23	0.54 × 0.11 × 0.05	0.22 × 0.11 × 0.05
θ Range/°	2 to 28	2 to 28	2 to 25	3 to 28	2 to 25	2 to 26
Total data	1742	11807	7434	4105	5881	6203
Unique data	680	4511	2267	1921	1774	1237
R_{int}	0.051	0.040	0.048	0.055	0.058	0.023
$R1$ [2σ(I) data]	0.0549	0.0402	0.0470	0.0536	0.0649	0.0420
(all data)	0.0562	0.0610	0.0544	0.0631	0.0762	0.0499
$wR2$	0.1385	0.0970	0.1370	0.1443	0.1652	0.1165
Goodness of fit	1.055	1.013	1.036	1.012	1.005	1.035
Final Δe/e Å^{-3}	4.26, −4.26	3.37, −1.48	2.29, −3.56	2.32, −3.12	7.12, −4.28	0.892, −1.737

Table 3 Selected structural parameters (bond lengths in Å, angles in °) for isolated molecules [AuX(CNR)][a]

	[AuCl(CNEt)]	[AuCl(CNC$_6$H$_3$Me$_2$-2,6)][b]	[Au(NO$_3$)(CNEt)][b]	[Au(NO$_3$)(CNBu^t)]	[Au(NO$_3$)(CNC$_6$H$_3$Me$_2$-2,6)]
Au–Cl	2.277(5)	2.257(2)			
Au–C(1)	1.90(2)	1.94(1)	1.93(2)	1.92(1)	1.905(16)
C(1)≡N	1.20(2)	1.14(1)	1.12(2)	1.13(2)	1.15(2)
Au–O(1)			2.033(11)	2.062(9)	2.033(10)
O(1)–N(1)			1.32(2)	1.31(1)	1.33(2)
O(2/3)–N(1)			1.21(2)	1.22(1)	1.20(2)
Cl–Au–C(1)	177.9(6)	177.8(3)			
O(1)–Au–C(1)			177.0(5)	176.3(4)	174.8(5)
Au–O(1)–N(1)			115.0(7)	113.1(7)	110.7(8)

[a] Details of the auriophilic intermolecular interactions are given in the captions to the figures showing the structures. [b] Averaged for the two independent molecules.

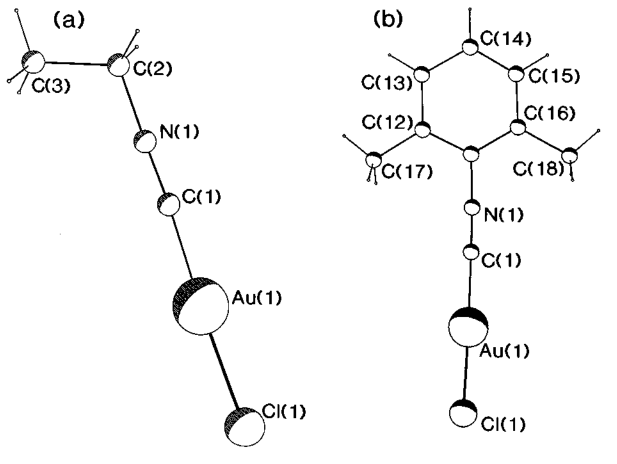

Fig. 1 The structures of isolated molecules of (a) [AuCl(CNEt)] and (b) [AuCl(CNC$_6$H$_3$Me$_2$-2,6)] showing atom numbering.

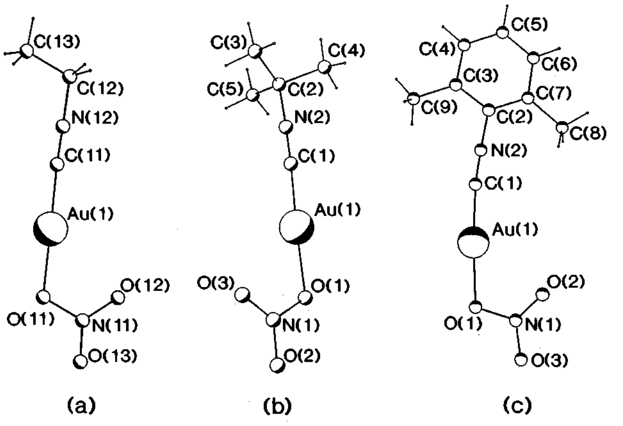

Fig. 2 The structures of individual molecules of (a) [Au(NO$_3$)(CNEt)], (b) [Au(NO$_3$)(CNBu^t)] and (c) [Au(NO$_3$)(CNC$_6$H$_3$Me$_2$-2,6)].

molecules are shown in Fig. 1, and require little discussion. For each, the co-ordination about the Au(1) atom is essentially linear (178° in each case). The bond distances within the molecules do not differ significantly from corresponding ones in related structures reported previously, although small variations would not be readily detected because of the difficulty in locating lighter atoms accurately in the presence of gold atoms. The crystal packing and auriophilic interactions are discussed later.

Individual molecules of the three [Au(NO$_3$)(CNR)] examples determined are shown in Fig. 2. They all consist of essentially linear (174–177°) Au^I co-ordinated to both the C of a normal isocyanide ligand and to one oxygen atom of a monodentate nitrate group. The Au–C distance does not differ significantly from those in the analogous chlorides, while the Au–O bond lengths of 2.03–2.06 Å appear to be slightly shorter than that in [Au(NO$_3$)(PPh$_3$)] of 2.074(8) Å, the only other gold(I) nitrate to have been structurally characterised.[20] As expected, the average N–O distance for the ligated oxygen atoms (1.32 Å) is longer than for the non-co-ordinated ones (1.21 Å). The Au–O–N angles are similar for all three examples in the range 111–115°.

(ii) Crystal structures. The crystal packing of [AuCl(CNEt)] is shown in Fig. 3(a), and exhibits a zigzag chain of antiparallel molecules linked *via* Au···Au interactions (3.554 Å). Similar chains have been described[19] for [AuCl(CNBu^t)] where the Au···Au distance is 3.695 Å, and for [AuCl(CNMe)][14] with a Au···Au length of 3.637 Å. While the longer distance in the Bu^t example is expected for a bulkier ligand, the reason for the longer distance in the Me compound is less obvious. The stereoview of the packing for [AuCl(CNEt)] [Fig. 3(b)] shows the chain units stack so that the Au atoms of one layer lie between the C≡N groups of the neighbouring one.

For [AuCl(CNC$_6$H$_3$Me$_2$-2,6)] a unique "broken chain" packing was found. There are two independent molecules in the asymmetric unit, and these link across an inversion centre to give a tetrameric unit (Fig 4). The outer Au(1)···Au(2) interaction (3.355 Å) is of the crossed-dimer type, while the central one, Au(1)···Au(1′), 3.654 Å, is an antiparallel one. These distances follow the established pattern that distances are shorter between neighbouring molecules that lie orthogonal to each other, than between parallel or antiparallel ones. The closest Au···Au distance between separate tetrameric units is 4.071 Å, too long to be considered significant and is the "break" in the chain. This structure lies between those of the homologous species [AuCl(CNPh)] and [AuCl(CNMes)],[14] the former having an antiparallel chain structure (of the type described above for [AuCl(CNEt)]) with Au···Au 3.463 Å, and the latter forming separated dimer units with Au···Au 3.336 Å. An isolated tetrameric unit was also found for [Au(C≡CSiMe$_3$)(CNBu^t)] with a very short Au···Au distance of 3.124 Å, but this involved three molecular units aggregating about a single central one.[21]

The complex [Au(NO$_3$)(CNBu^t)] has the most straightforward supramolecular structure of the three nitrate complexes analysed. As shown in Fig. 5 it exhibits an antiparallel chain structure directly analogous to those of three other [AuX(CNBu^t)] complexes,[13] though the average Au···Au distance (3.31 Å) is markedly shorter than those of the X = CN (3.57 Å),[22] Cl (3.70 Å)[19] or Br (3.69 Å)[14] examples; this is *not* consistent with theoretical predictions that Au···Au interactions in [AuX(L)] should be enhanced as the softness of X increases.[5] However Pyykkö's calculations[5] were based on perpendicular dimers, where the electrostatic dipole–dipole interactions vanish. The nitrate group can orientate itself to provide a smaller steric interaction with adjacent groups compared with chloride, for example. In the common antiparallel stacking arrangement the X group is directly opposite the electron-rich

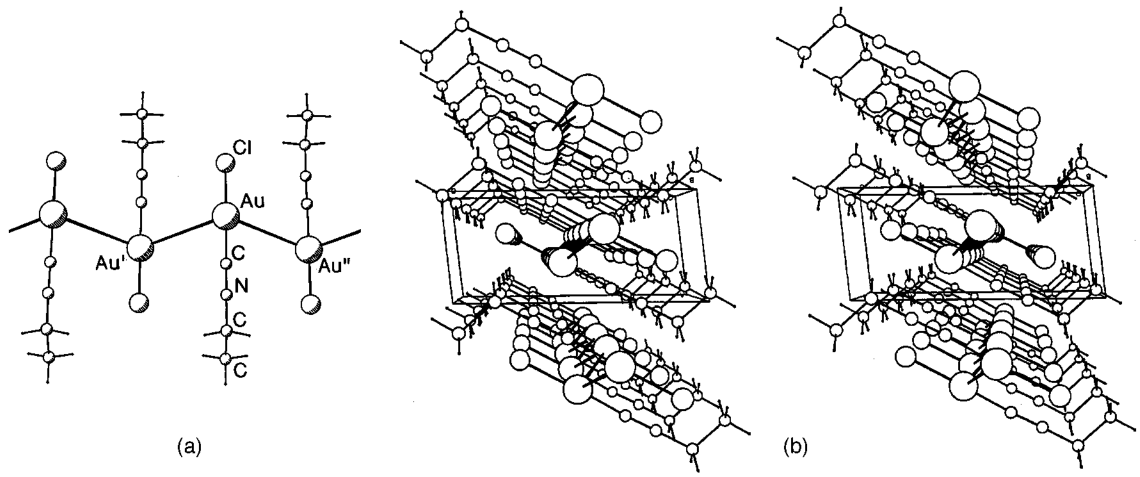

Fig. 3 (a) The packing of [AuCl(CNEt)] in the crystal showing the infinite zigzag chain [Au···Au 3.5536(6) Å; Au···Au···Au 124.90(1)°]. (b) A stereoview showing the packing of the chain units in the crystal.

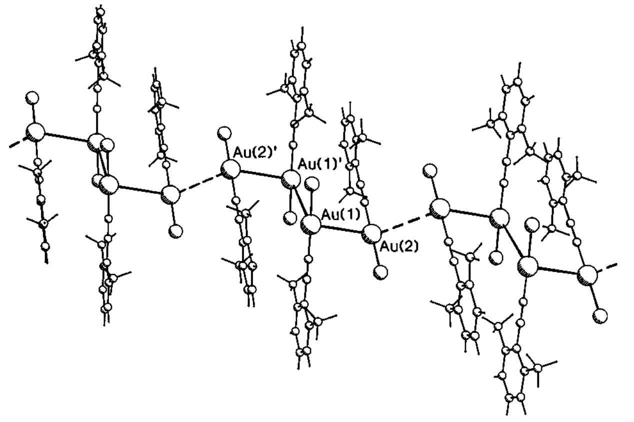

Fig. 4 The "broken chain" packing of the tetrameric units of [AuCl(CNC$_6$H$_3$Me$_2$-2,6)] in the crystal [Au(1)···Au(2) 3.3555(5); Au(1)···Au(1′) 3.6545(6) Å; Au(1′)···Au(1)···Au(2) 97.60(1)°].

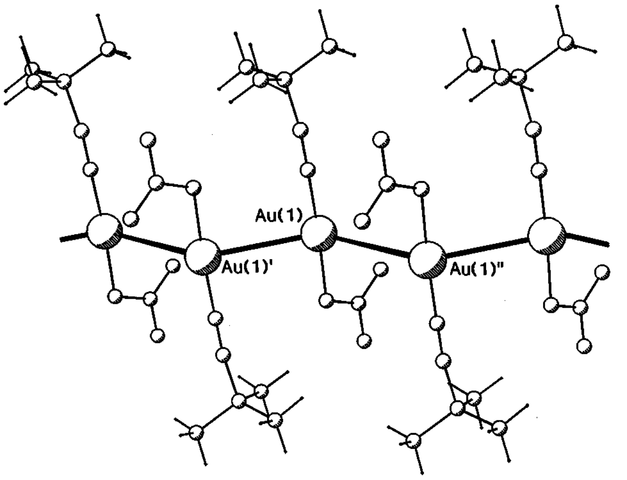

Fig. 5 The chain structure of [Au(NO$_3$)(CNBu^t)] in the crystal [Au(1)···Au(1′) 3.2963(8); Au(1)···Au(1″) 3.3232(8) Å; Au(1′)···Au(1)···Au(1″) 142.28(5)°].

C≡N of the isocyanide, which may lengthen the Au···Au distance by repulsion between the ligands when X is also electron-rich.

For [Au(NO$_3$)(CNEt)] the packing consists of a concertina'd chain, which gives tetrameric units linked together as shown in Fig. 6. Each Au is connected to three others but even so the Au···Au interactions are relatively short, with Au(1)···Au(1′) 3.194, Au(1′)···Au(2) 3.193, Au(2)···Au(1) 3.357 and Au(2)···Au(2′) 3.286 Å. The shorter distances are between

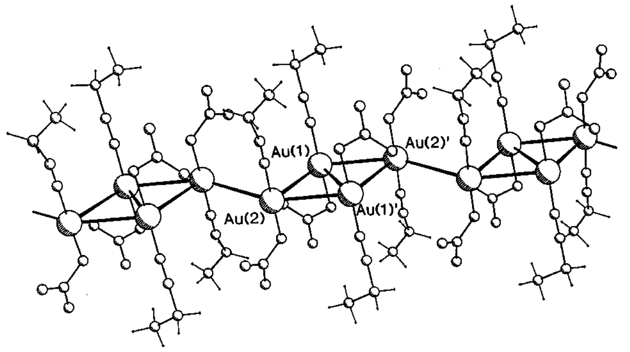

Fig. 6 The concertina'd chain structure for [Au(NO$_3$)(CNEt)] [Au(1′)···Au(2) 3.1932(7); Au(1)···Au(1′) 3.1941(10); Au(2)···Au(2′) 3.2856(11); Au(2)···Au(1) 3.3575(7) Å].

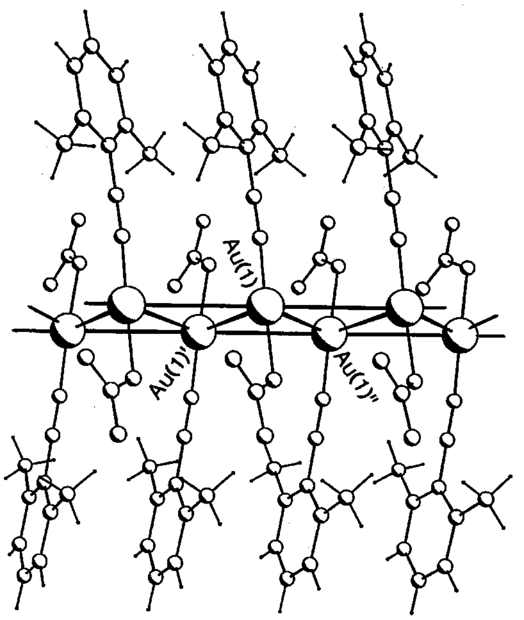

Fig. 7 The compressed chain structure of [Au(NO$_3$)(CNC$_6$H$_3$Me$_2$-2,6)] [Au(1)···Au(1′) 3.245(1); Au(1′)···Au(1″) 3.780(1) Å].

antiparallel monomers, while the longest distance is between head-to-head neighbours. If the Au(1)···Au(2) and Au(1′)···Au(2′) links in each tetrameric unit were stretched then a zigzag chain would result, providing a relationship between [Au(NO$_3$)(CNEt)] and the chain of [Au(NO$_3$)(CNBu^t)]. Averaging the four independent Au···Au distances for [Au(NO$_3$)(CNEt)] gives 3.25 Å, slightly shorter than the value for [Au(NO$_3$)(CN-

Bu^t)] (3.30 Å), presumably a steric effect. More significantly the average Au···Au distance is markedly shorter than that in [AuCl(CNEt)], indicating again that the nitrate group enhances auriophilic bonding compared to Cl in analogous compounds. The tetrameric units in this structure have some similarity to those in the ionic compound {[Au(Ph$_2$C=NH)$_2$][AuCl$_2$]}$_2$, which however are not further linked.[23] The complex [Au(pip)Cl] (pip = piperidine) has square Au$_4$ units in the crystal, again not further linked.[24]

The crystal packing for [Au(NO$_3$)(CNC$_6$H$_3$Me$_2$-2,6)] is different again, as shown in Fig. 7. It can be described as a compressed zigzag chain with primary Au···Au distances of 3.245 Å. There are additional, longer Au···Au interactions of 3.780 Å between every second gold atom. This leads to an acute Au···Au···Au angle of 71°, which compares with equivalent angles of 125–140° in the other chain structures discussed above. While the longer distance is at the outer limit of what is considered an auriophilic interaction, it is less than some of the Au···Au linkages found for [AuI(CNPh)] (>3.80 Å).[14] The reason for the compressed packing

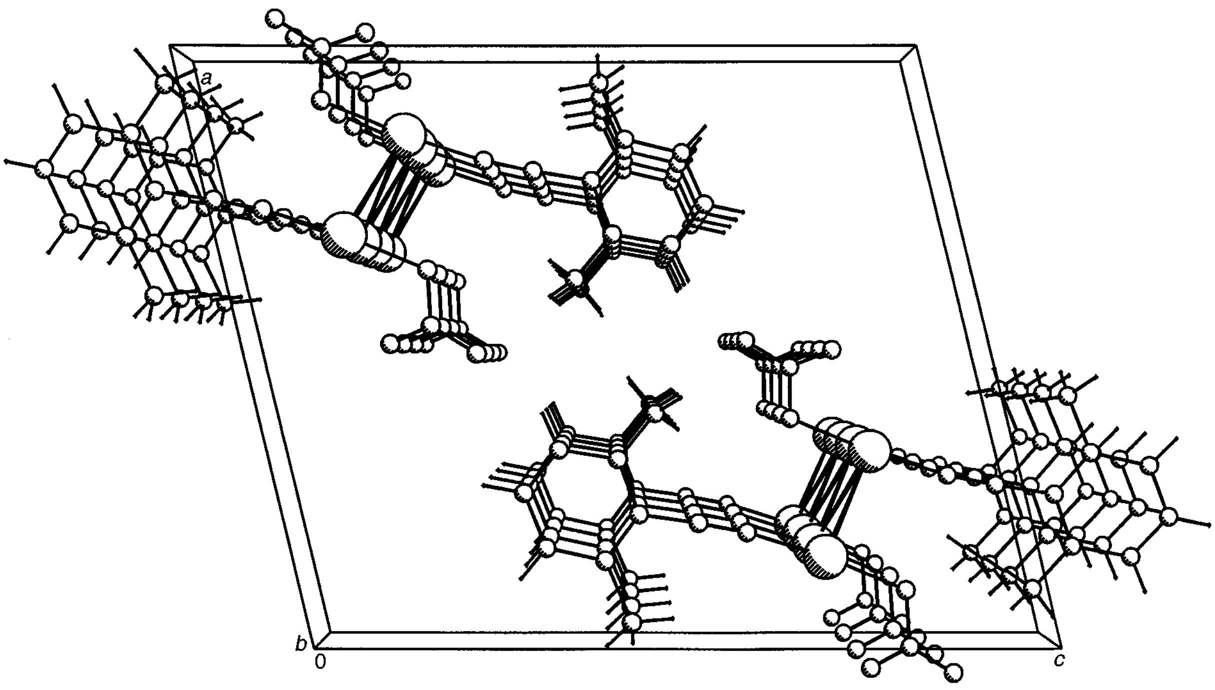

Fig. 8 An alternative view of the crystal packing for [Au(NO$_3$)(CNC$_6$H$_3$Me$_2$-2,6)], showing the π stacking of the arene rings.

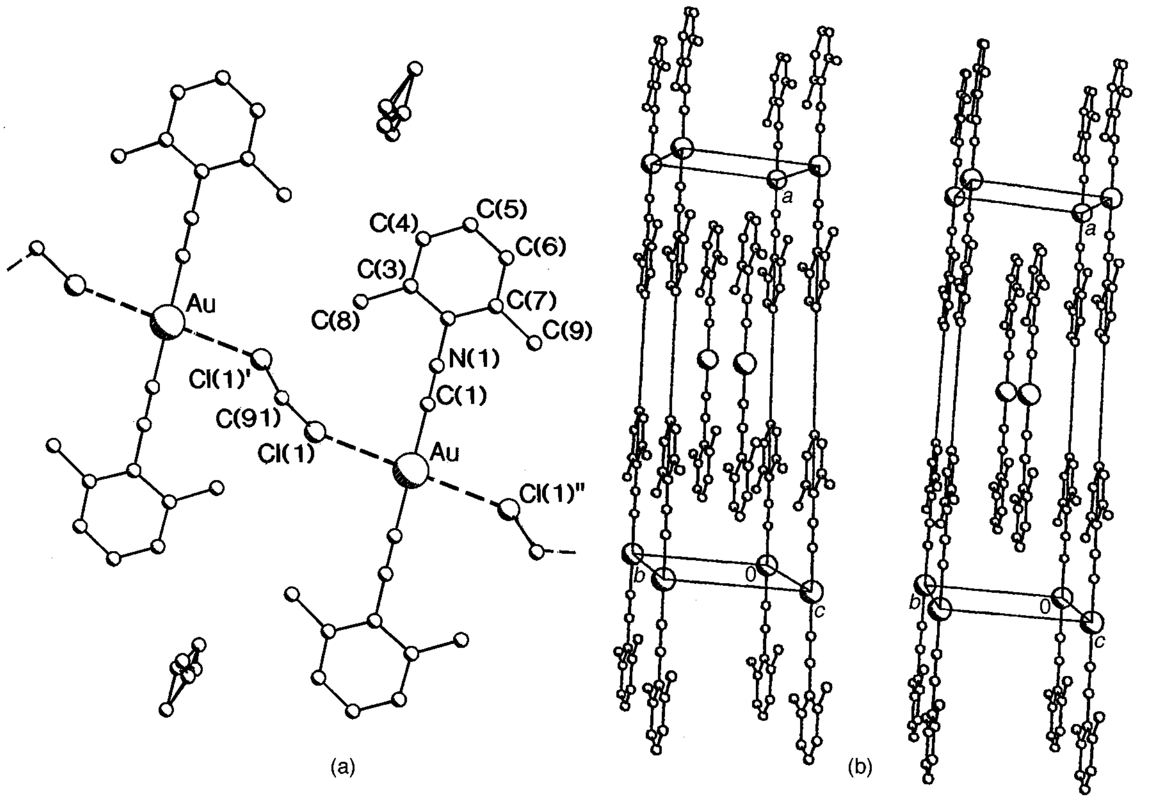

Fig. 9 (a) The arrangement of the ions and solvent molecules in the crystal of [Au(CNC$_6$H$_3$Me$_2$-2,6)$_2$]NO$_3$·MeOH·0.5CH$_2$Cl$_2$. Only one orientation of the disordered CH$_2$Cl$_2$ is shown, while the anion site contains superimposed NO$_3^-$ and MeOH species, with a 1 : 1 occupancy (see text). (b) A stereoview of the [Au(CNC$_6$H$_3$Me$_2$-2,6)$_2$]$^+$ cations only, showing the π stacking interactions.

may lie in the π stacking of the xylyl rings, Fig. 8, which are 3.780 Å apart; these could reinforce the additional Au···Au interactions.

(iii) The structure of [Au($CNC_6H_3Me_2$-2,6)$_2$]NO_3. In the initial attempt to determine the structure of [Au(NO_3)($CNC_6H_3Me_2$-2,6)] the crystal selected turned out to be a solvated ionic species [Au($CNC_6H_3Me_2$-2,6)$_2$]NO_3·MeOH·0.5CH_2Cl_2. This structure consisted of separated [Au($CNC_6H_3Me_2$-2,6)$_2$]$^+$ cations and NO_3^- anions, the former occupying a site of 2/*m* symmetry and the latter one of *m* symmetry. Charge neutrality requires that only half of the anion sites are occupied by NO_3^- ions, and it appears the otherwise empty sites have incorporated MeOH molecules. There are no auriophilic interactions in this crystal, the packing appearing to be determined by infinite π stacking of the xylyl groups of the cations in an interleaving fashion. The distance between the adjacent arene rings is 3.36 Å, essentially the same as between the layers of graphite (3.35 Å). In [Au(CCPh)($CNC_6H_3Me_2$-2,6)] there are isolated dimers held together by both Au···Au and π–π interactions of 3.33 Å.[25]

The packing in [Au($CNC_6H_3Me_2$-2,6)$_2$]NO_3 leaves space between adjacent gold centres for the gold cations to be linked together by weak Au···$ClCH_2Cl$···Au interactions (Au···Cl 2.99 Å) involving dichloromethane molecules in the lattice (Fig. 9). The structure can be compared with those of other [Au(CNR)$_2$]$^+$ salts (R = Ph or Mes) which have been described by Schmidbaur *et al.*[26] These, however, show neither Au···Au nor π-stacking interactions.

Conclusion

Isocyanide gold nitrates are less stable than other [AuX(CNR)] and [Au(NO_3)(PR_3)] species but are nevertheless readily synthesized. The combination of a sterically undemanding CNR ligand and a flat NO_3^- anion appears to favour short Au···Au auriophilic interactions in crystals, invariably more pronounced than in corresponding [AuCl(CNR)] compounds. Whether this should be attributed to the non-polarisable NO_3^- ion encouraging stronger Au···Au forces *per se*, which is contrary to expectations based on theoretical calculations,[5] or to lesser repulsion between adjacent ligands cannot be decided from the present examples. What is clear, however, is that the full range of structural motifs arising from secondary Au···Au interactions is still to be developed.

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