

Effects of anions on the solid state structures of linear gold(I) complexes of the type (*o*-xylyl isocyanide)gold(I) (monoanion)

Holger Ecken,^a Marilyn M. Olmstead,^a Bruce C. Noll,^b Saeed Attar,^a Bruce Schlyer^a and Alan L. Balch^{*a}

^a Department of Chemistry, University of California, Davis, California 95616, USA.

E-mail: albalch@chem.ucdavis.edu

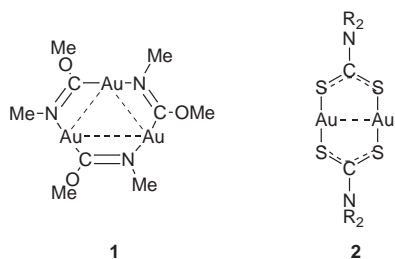
^b Department of Chemistry, University of Colorado, Boulder, Colorado 80309, USA

Received 2nd July 1998, Accepted 21st September 1998

The preparation, spectroscopic, and structural characterization of four gold(I) complexes, (*o*-xylylNC)AuX with X as I, Br, Cl or CN, are reported. Each crystallizes in a unique, solvent-free form with varying aurophilic interactions between the linear, two-coordinate molecules. Thus, (*o*-xylylNC)AuCl forms a simple dimer, while the bromo and iodo analogs form slightly kinked chains with extended Au...Au...Au... units. The bromo complex differs from the iodo complex due to the fact that an independent, non-interacting (*o*-xylylNC)AuBr unit lies off to the side of the linear chain. The structure of (*o*-xylylNC)AuCN consists of a complex grid which involves kinked chains of gold atoms cross linked by another aurophilically connected triad of gold centers. The complexes are all luminescent at room temperature in solution and in the solid state.

Introduction

Recent revelations concerning the luminescence properties of gold(I) complexes **1** and **2**, which undergo supramolecular aggregation *via* attractive intermolecular Au^I...Au^I interactions, suggest that the gold compounds capable of forming extended linear aggregates deserve further attention.^{1,2} Specifically, complex **1**, which forms trigonal prismatic columns through Au...Au interactions, displays solvoluminescence.¹ The colorless complex, after irradiation with near UV light, produces a yellow luminescence when brought into contact with organic solvents. Complex **2** is known to crystallize in colorless and orange forms.² The orange form contains linear arrays of the dimeric complex and displays luminescence at *ca.* 630 nm. Exposure of the colorless, solvate free crystals to organic vapors produces marked changes in both the absorption and emission spectra. Both phenomena, solvoluminescence and solvochromism, have potential for use as chemical sensors.



Two-coordinate Au(I) complexes with Au...Au separations less than 3.6 Å in the solid state are considered to experience attractive aurophilic interactions.³⁻⁶ Theoretical work has revealed that this weakly bonding interaction is the result of correlation effects which are enhanced by relativistic effects.⁷⁻¹⁰ The strength of this attractive interaction has been experimentally determined, on the basis of barriers to free rotation, to be *ca.* 7–11 kcal mol⁻¹.^{11,12} Such aurophilic interactions have been shown to be sufficiently strong to persist in solution and to play a role in guiding a chemical reaction.¹³ Theoretical studies by Pyykkö and co-workers^{7,8} predicted an increase in the strength of this aurophilic interaction for the H₃PAuX system in the series of anions (X) with F < CH₃ < H < Cl < CN < Br < I < SCH₃. In our laboratory this trend has been confirmed in

the compounds (Me₂PhP)AuX (X = Cl, Br, I) where the Au(I)...Au(I) contacts decrease in the order Cl > Br > I.¹⁴ A similar trend has been seen for the pair of complexes LAuX (L = 1,3,5-triaza-7-phosphaadamantane, X = Cl, Br).¹⁵ However, with phosphine ligands, bulky substituents on the phosphorus atoms can restrict association of molecules of the type (R₃P)AuX, but with smaller phosphines dimers, trimers and extended chains can form.^{14,16,17} Polymeric chains and networks of such dimers can form when diphosphines are used as ligands.^{18,19}

Here we report on the structural and spectroscopic properties of gold complexes of the type (*o*-xylylNC)AuX. The relatively flat nature of the isocyanide ligand was expected to provide an environment that would not inhibit self association of the complex, yet was a relatively easily handled and stored ligand. Moreover, isocyanides are precursors to **1** and analogous compounds,²⁰ and knowledge of the structural chemistry in this area is significant for further exploration of the chemistry of these trinuclear complexes. Earlier studies of (RNC)AuCl and related complexes revealed some tendency of these to associate through Au...Au contacts, but in many cases the separations between the gold centers were longer than 3.6 Å.²¹⁻²³ On the basis of our previous studies,¹⁴ we felt that the aurophilic attractions could be enhanced by alteration of the anions.

Results

Synthetic and spectroscopic studies

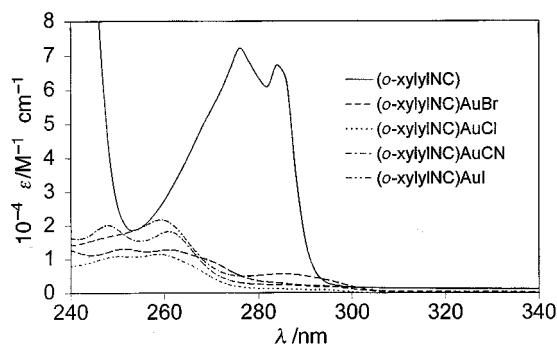
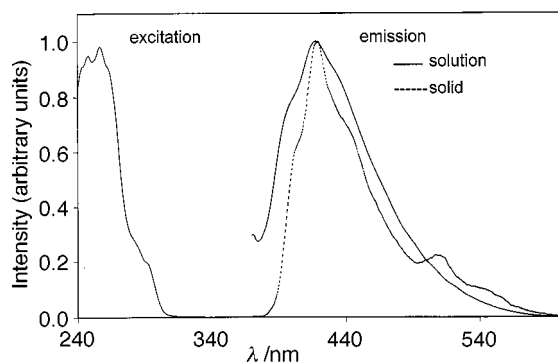
Treatment of a chloroform solution of (Ph₃As)AuCl with one equivalent of *o*-xylyl isocyanide results in the formation of (*o*-xylylNC)AuCl which has been obtained as a white crystalline solid. Colorless crystals of (*o*-xylylNC)AuBr and pale yellow crystals of (*o*-xylylNC)AuI were prepared similarly. Addition of *o*-xylyl isocyanide to a suspension of gold(I) cyanide in chloroform results in the formation of (*o*-xylylNC)AuCN also as white crystals. These complexes have good solubility in dichloromethane and chloroform but are insoluble in diethyl ether and methanol.

Attempts to prepare two-coordinate complexes of the type [(*o*-xylylNC)₂Au]⁺ or three-coordinate complexes of the types (*o*-xylylNC)₂AuX and [(*o*-xylylNC)₃Au]⁺ by treatment of (Ph₃As)AuX with up to a ten-fold excess of *o*-xylyl isocyanide

Table 1 Spectroscopic data

Compound	Infrared ^a $\nu(\text{N}\equiv\text{C})/\text{cm}^{-1}$	¹ H NMR ^b		Luminescence ^c $\lambda_{\text{max}}/\text{nm}$
		δ (ppm) C–H	δ (ppm) Me	
(<i>o</i> -xylylNC)	2117.5	7.12d, 7.19t	2.41s	415
(<i>o</i> -xylylNC)AuI	2198.4	7.18d, 7.37t	2.44s	420, 500
(<i>o</i> -xylylNC)AuBr	2204.2	7.19d, 7.37t	2.44s	420, 500
(<i>o</i> -xylylNC)AuCl	2215.8	7.20d, 7.32t	2.44s	420, 510
(<i>o</i> -xylylNC)AuCN	2156.0 (2223.5) ^d	7.21d, 7.39t	2.44s	430, 500

^a Taken as Fluorolube mulls between NaCl plates. ^b Taken in chloroform-*d* solutions with SiMe₄ as reference. ^c Solid state at 23 °C. ^d Vibration of the coordinated cyanide anion.

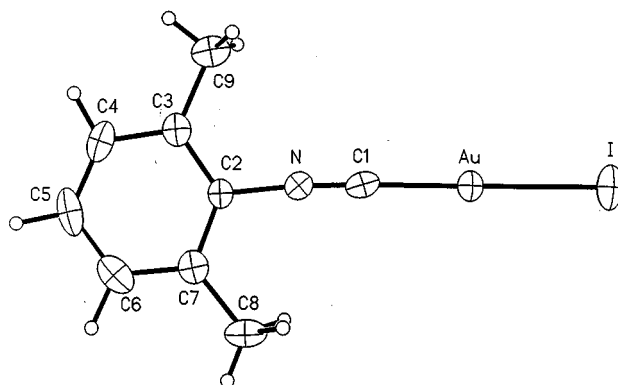
**Fig. 1** The electronic absorption spectra of dichloromethane solutions of (*o*-xylylNC)AuX and *o*-xylyl isocyanide.**Fig. 2** The emission and excitation spectra for a dichloromethane solution of (*o*-xylylNC)AuCl and the emission spectrum of solid (*o*-xylylNC)AuCl.

were unsuccessful. Only the neutral, two-coordinate complexes (*o*-xylylNC)AuX were isolated from the reaction medium.

Spectroscopic data for the new compounds are given in Table 1. The ¹H NMR spectra naturally resemble those of the parent free ligand, but in the complexes the doublet and triplet which are due to the *m*- and *p*-phenyl protons, respectively, are more widely separated in chemical shift. The infrared spectra of the complexes as Fluorolube mulls show that the isocyanide stretching frequencies decrease in energy in the order Cl > Br > I > CN in accord with expectations from backbonding. For (*o*-xylylNC)AuCN the band at 2156.0 cm⁻¹ is assigned to the isocyanide stretch while that at 2223.5 cm⁻¹ is assigned to the coordinated cyanide ion.

The electronic spectra of the four complexes and of *o*-xylyl isocyanide itself are shown in Fig. 1. Significant absorption is seen for the complexes only in the region of ligand absorption. This is not surprising, since spectroscopic studies of complexes such as (EtNC)AuCN and [Au(CN)₂]⁺ have shown that metal-to-ligand charge transfer transitions appear at shorter wavelengths, generally below 250 nm.^{24–26} Coordination of the ligand by gold produces a marked perturbation of the ligand spectrum.

Each of the complexes is luminescent at room temperature, both in solution and in the solid state. Fig. 2 shows represent-

**Fig. 3** The molecular structure of (*o*-xylylNC)AuI with 50% thermal contours.

ative data for (*o*-xylylNC)AuCl. In solution a broad emission is seen with a maximum at 430 nm. The excitation profile for this emission parallels the absorption spectrum. For the solid, the emission spectrum also shows a strong emission at 430 nm along with new, weaker features at 520 and 540 nm. It is likely that the emission features arise from phenyl-localized $\pi\pi^*$ states. The free ligand itself is luminescent in dichloromethane solution where it shows a structureless emission with a maximum at 300 nm. Similar luminescence phenomena have been characterized in detail for gold complexes of phosphines with phenyl substituents.²⁷ The luminescence behavior of the other complexes is similar, as might be expected for processes that are localized on the *o*-xylyl isocyanide ligand. No unusual solvent effects on the luminescence behavior of these complexes in solution or in the solid state have been observed.

Crystallographic studies

Molecular structures. The molecular structures of all four complexes, (*o*-xylylNC)AuX where X is I, Br, Cl, or CN, are quite similar. The molecular structure of (*o*-xylylNC)AuI, which is representative of the group, is shown in Fig. 3. Structural parameters for the group are set out in Table 2 where bond lengths and distances can be compared. All complexes possess two-coordinate, nearly linear structures about gold and nearly linear Au–C–N portions. Thus, the C–Au–X angles fall in the narrow range from 175.5 to 180° and the Au–C–N angles fall in the range from 175.0(8) to 180°. Bond distances within each complex fall within normal ranges.

Despite the similarities in molecular structures, there are considerable variations in the intermolecular organization in the solid state. In particular, no two complexes in this group of four form isomorphous crystals. In view of the solvate dependent properties of **2**, it is significant to note that none of the complexes reported here crystallizes with solvent molecules incorporated into the solid.

Solid state molecular organization. Data regarding the intermolecular organization of the four new solids are given in

Table 2 Selected bond distances (Å) and angles (°) within molecules

	(<i>o</i> -xylylNC)AuI	(<i>o</i> -xylylNC)AuBr	(<i>o</i> -xylylNC)AuCl	(<i>o</i> -xylylNC)AuCN
Au(1)–C	1.947(9)	1.930(13)	1.933(13)	2.001(10)
Au(2)–C		1.919(14)	1.928(13)	1.945(10)
Au(3)–C		1.936(13)		1.940(13)
Au(1)–X	2.5288(6)	2.395(2)	2.258(3)	1.984(12)
Au(2)–X		2.3480(5)	2.256(3)	2.012(8)
Au(3)–X		2.369(2)		2.009(18)
C–Au(1)–X	179.9(2)	175.7(4)	178.3(4)	179.0(4)
C–Au(2)–X		178.8(4)	176.5(4)	178.4(5)
C–Au(3)–X		175.5(5)		180
Au(1)–C–N	178.5(7)	176.6(12)	179.1(11)	177.2(10)
Au(2)–C–N		178.1(13)	177.2(10)	175.0(8)
Au(3)–C–N		176.9(14)		180

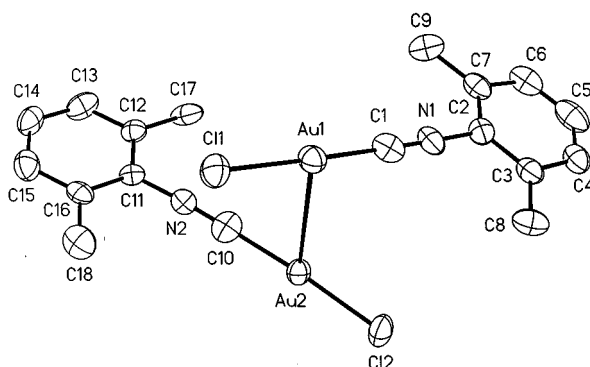
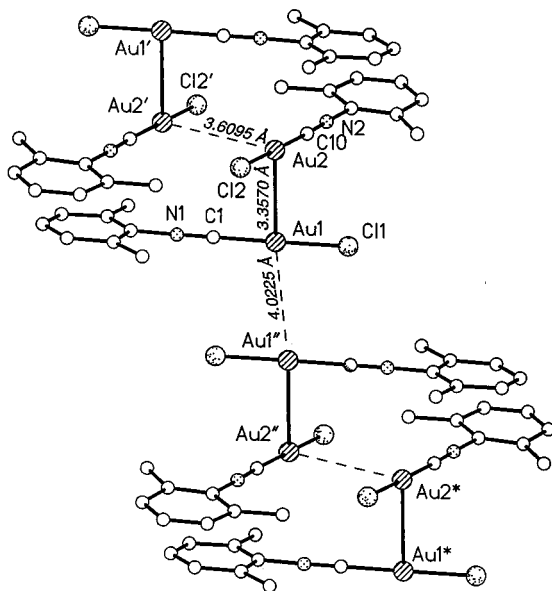
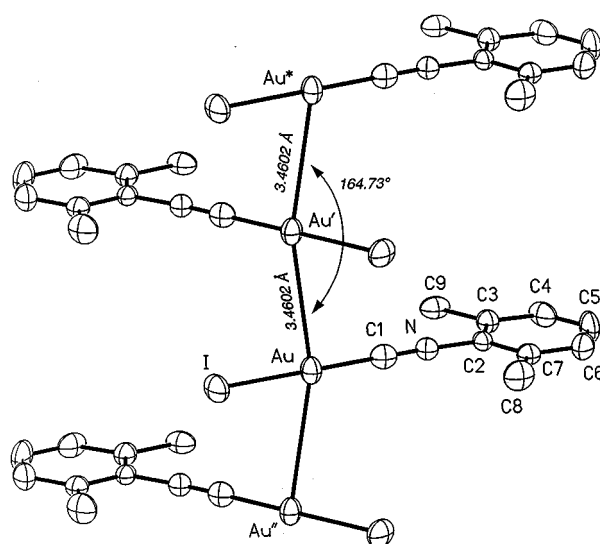
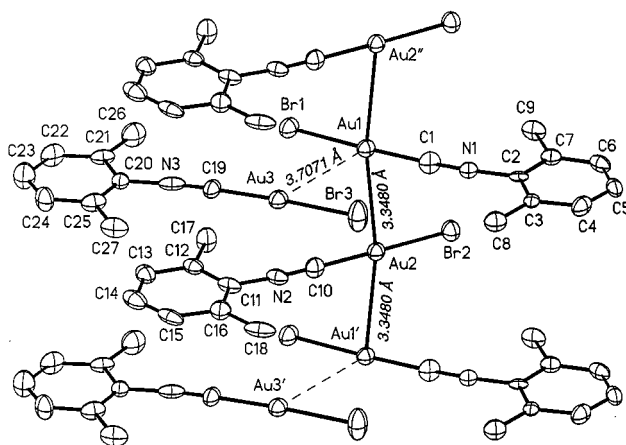
**Fig. 4** A view of the dimer of (*o*-xylylNC)AuCl with 50% thermal contours.**Fig. 5** A view of the organization of dimers of (*o*-xylylNC)AuCl into loose chains.

Table 3 while Figs. 4–9 show relevant drawings of the solid state structures.

1. (*o*-xylylNC)AuCl. There are two complete molecules of the molecular complex in the asymmetric unit and these form a dimer through a single close Au...Au contact of 3.3570(11) Å. A view of the dimer is shown in Fig. 4. These dimers are organized into loose chains as shown in Fig. 5. Within these chains of dimers, the additional contacts between gold centers exceed the distance where specific attractive interactions are present. The Au(2)...Au(2') separation is 3.6095(12) Å, while the Au(1)...Au(1') separation is even longer, 4.0225(12) Å.

2. (*o*-xylylNC)AuI. Although there is only one molecule in

**Fig. 6** A view of the molecular organization of chains within (*o*-xylylNC)AuI.**Fig. 7** A view of the molecular organization in (*o*-xylylNC)AuBr.

the asymmetric unit, the individual molecules are organized into chains through auriphilic interactions. A view of the chain is shown in Fig. 6. The Au...Au' distance within the chain is 3.4602(3) Å. The Au'...Au...Au'' angle along the chain is 164.73(2)°, so the chain is slightly kinked.

3. (*o*-xylylNC)AuBr. There are three independent molecules within the asymmetric unit. The molecules involving Au(1) and Au(2) form slightly kinked chains through auriphilic interactions. These chains are shown in Fig. 7. They resemble the chains seen for (*o*-xylylNC)AuI, and the Au(1)...Au(2) distance within the chain is also similar, 3.3480(5) Å. The chains

Table 3 Intramolecular interactions (bond lengths in Å, angles in °) in gold complexes

(o-xylylNC)AuCl

Aurophilic interactions

Au(1)···Au(2) distance 3.3570(11)
Cl(1)–Au(1)···Au(2)–Cl(2) dihedral angle 124.42(12)
Cl(1)–Au(1)···Au(2)–C(10) dihedral angle 125.2(5)

Neighboring interactions

Au(2)···Au(2') separation 3.6095(12)
Cl(2)–Au(2)···Au(2')–Cl(2) dihedral angle 180
C(10)–Au(2)···Au(2')–C(10) dihedral angle 180
Au(1)···Au(2)···Au(2') angle 97.67(3)
Au(2)···Au(1)···Au(1'') angle 123.45(2)
Au(1)···Au(1'') separation 4.0225(12)
Cl(1)–Au(1)···Au(1'')–Cl(1'') dihedral angle 180
C(1)–Au(1)···Au(1'')–C(1'') dihedral angle 180
symmetry code: ' = -x, -y, -z; '' = -x, -y, 1 - z

(o-xylylNC)AuI

Aurophilic interactions

Au···Au' distance 3.4602(3)
Au'···Au···Au'' angle 164.73(2)
I–Au···Au'–I' dihedral angle 114.81(4)
C(1)–Au···Au'–C(1') dihedral angle 114.5(5)
symmetry code: ' = x - 0.5, y, 1.5 - z

(o-xylylNC)AuBr

Aurophilic interactions

Au(1)···Au(2) distance 3.3480(5)
Au(1)···Au(2)···Au(1') angle 170.29(2)
Au(2)···Au(1)···Au(2'') angle 170.29(2)
Br(1)–Au(1)···Au(2)–Br(2) dihedral angle 123.42(6)
C(1)–Au(1)···Au(2)–C(10) dihedral angle 129.00(6)

Neighboring interactions

Au(1)···Au(3) distance 3.7071(10)
Br(1)–Au(1)···Au(3)–Br(3) dihedral angle 180
C(1)–Au(1)···Au(3)–C(19) dihedral angle 180
symmetry code: ' = x, 1 + y, z; '' = x, y - 1, z

(o-xylylNC)AuCN

Aurophilic interactions

Au(1)···Au(2) distance 3.4220(6)
Au(1)···Au(2'') distance 3.4615(6)
Au(1)···Au(2)···Au(1*) angle 166.59(1)
Au(2)···Au(1)···Au(2'') angle 169.66(2)
C(1)–Au(1)···Au(2)–C(11) dihedral angle 160.6(4)
C(0)–Au(1)···Au(2)–C(20) dihedral angle 158.9(4)
Au(2)···Au(3) distance 3.1706(4)
Au(3)···Au(2)···Au(1) angle 92.38(2)
Au(3)···Au(2)···Au(1') angle 99.07(2)
Au(2)···Au(3)···Au(2') angle 164.97(3)
C(11)–Au(2)···Au(3)–C(21) dihedral angle 90.1(4)
C(20)–Au(2)···Au(3)–C(27) dihedral angle 88.6(4)
symmetry code: ' = -x, 1 - y, z; '' = 0.5 - x, y, z - 0.5, * = 0.5 - x, y, 0.5 + z

are slightly kinked with the Au(1)···Au(2)···Au(1') and Au(2)···Au(1)···Au(2'') angles both being 170.29(2)°.

The third molecule of *(o*-xylylNC)AuBr is set off to the side of Au(1) along the chain as seen in Fig. 7. The Au(3)···Au(1) distance is 3.7071(10) Å which is considerably longer than the Au(1)···Au(2) distance. Thus it is concluded that there is no aurophilic attraction between the chain and the isolated molecule that contains Au(3).

4. *(o*-xylylNC)AuCN. This structure also contains three independent molecules in the asymmetric unit, but unlike the case of the bromo complex, all three molecules are involved in aurophilic interactions. These interactions produce a complex grid that is shown in Fig. 8. Fig. 9 shows how the individual molecules interact within a portion of the grid. This grid lies in the *ac* plane and consists of chains comprised of alternating molecules containing Au(1) and Au(2). Along these chains there are two different Au···Au distances. The Au(1)···Au(2)

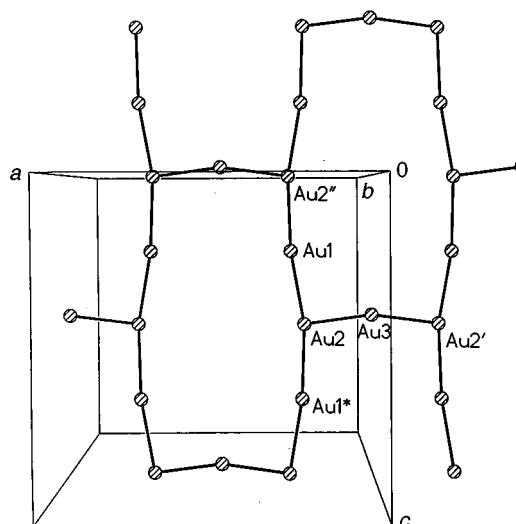


Fig. 8 A view of the grid of Au···Au interactions in *(o*-xylylNC)-Au(CN). Only the positions of the gold atoms are shown. This grid lies in the crystallographic *ac* plane.

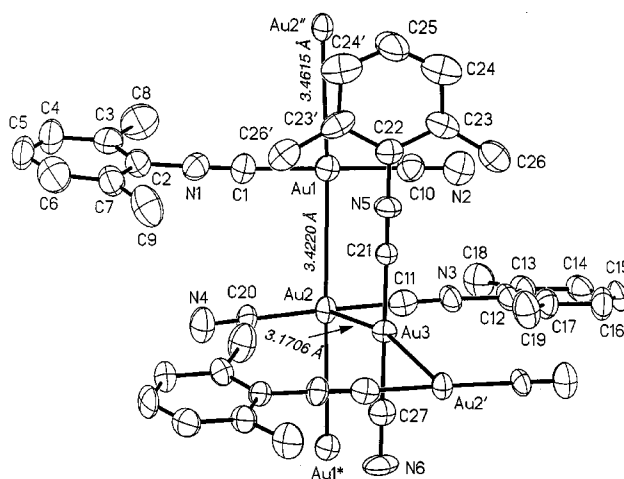


Fig. 9 A view of the structure of *(o*-xylylNC)Au(CN) which shows how the individual molecules interact.

distance is 3.4220(6) Å while the Au(1)···Au(2'') distance is 3.4615(6) Å. These chains are slightly kinked with Au(1)···Au(2)···Au(1*) and Au(2)···Au(1)···Au(2'') angles of 166.59(1) and 169.66(2)°, respectively. The chains of alternating molecules that involve Au(1) and Au(2) are connected by links through molecules that contain Au(3). Thus each Au(3) center interacts with two Au(2) centers. The Au(3)···Au(2) distance is 3.1706(4) Å and the Au(2)···Au(3)···Au(2') angle is 164.97(3)°. Thus within this solid, the gold centers, Au(1) and Au(2) are involved with aurophilic interactions with two other gold neighbors, while Au(3) is involved with aurophilic interactions with three neighboring gold centers.

Discussion

The results described here demonstrate that the solid state structures of the four gold(I) complexes display a marked variation in their intramolecular organization. The structures change with each anion, yet no remarkable feature in anionic environment is apparent within the structures, and there does not appear to be any evidence for secondary coordination of the anions to more than one gold center. The anions appear to be exerting an electronic effect on the gold centers to which they are bonded and thereby alter the ability of the gold centers to participate in aurophilic interactions. The general disparity among the four structures makes it difficult to compare the

Table 4 Crystal data and data collection parameters

	(<i>o</i> -xylylNC)AuI	(<i>o</i> -xylylNC)AuBr	(<i>o</i> -xylylNC)AuCl	(<i>o</i> -xylylNC)AuCN
Empirical formula	C ₉ H ₉ AuIN	C ₉ H ₉ AuBrN	C ₉ H ₉ AuClN	C ₁₀ H ₉ AuN ₂
<i>M</i>	455.04	408.05	363.59	354.16
Color, habit	Pale yellow, needles	Colorless, needles	Colorless, prism	Colorless, block
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>Cmca</i>	<i>Pnma</i>	<i>P2₁/n</i>	<i>Aba2</i>
<i>a</i> /Å	6.8591(6)	15.521(4)	10.614(3)	13.9609(2)
<i>b</i> /Å	20.3967(17)	6.6720(13)	17.216(4)	26.62590(10)
<i>c</i> /Å	15.5101(13)	29.135(6)	11.011(3)	13.63710(10)
β /°			97.93(2)	
<i>U</i> /Å ³	2169.9(3)	3017.1(11)	1992.8(9)	5069.20(8)
<i>Z</i>	8	12	8	20
<i>T</i> /K	169(2)	140(2)	130(2)	156(2)
ρ /g cm ⁻³	2.786	2.695	2.424	2.320
μ /mm ⁻¹	16.354	18.546	14.977	14.464
<i>R</i> 1 ^a (obsd data)	0.034	0.042	0.070	0.040
<i>wR</i> 2 ^b	0.069	0.096	0.051	0.134

^a $R1 = \sum |F_o - F_c| / \sum |F_o|$, ^b $wR2 = [\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2]$.

effects of the variation in the nature of the anions. Thus for example the Au...Au distances in (*o*-xylylNC)AuX decrease in the order I > Br > Cl, which differs from what is seen for the (Me₂PhP)AuX series of dimers¹⁴ or that predicted theoretically⁷ for such dimers. However, only (*o*-xylylNC)AuCl forms a simple dimer through Au...Au interactions, while (*o*-xylylNC)AuBr and (*o*-xylylNC)AuI form extended chains in which each gold atom participates in two rather than just one aurophilic interaction. Further work is needed to elucidate the structural effects of multiple aurophilic interactions.

The aurophilic interactions seen in the four complexes reported here are shorter and more extended than seen previously for most other complexes of the type (RNC)AuX. The compounds, (MeNC)AuCl, (*t*-BuNC)AuCl, (*t*-BuNC)AuBr, and (PhNC)AuBr, crystallize with the molecules arranged into zigzag chains with anti-parallel orientations of individual molecules.^{21,28} This anti-parallel orientation is that expected by simple consideration of dipolar effects. (In contrast, molecules that display strong aurophilic attraction have the individual molecules arranged in a staggered fashion with X-Au...Au-X dihedral angles that are close to 90°. ^{5,9,10}) The distance between gold centers in these chains falls in the range 3.6–3.7 Å, and attractive aurophilic interactions within these chains are expected to be weak. For (PhNC)AuCl a similar structure is formed, but the Au...Au distance is shorter, 3.463(1) Å, and significant aurophilic attractions may be present.²¹ (MesitylNC)AuCl forms a discrete dimer through an aurophilic attraction (Au...Au distance, 3.336(1) Å) that closely resembles that seen here for (*o*-xylylNC)AuCl.²¹ The complex (*t*-BuNC)-Au(NO₃) also forms a kinked chain with Au...Au distances of 3.2955(8) and 3.3243(8) Å,²² and (*t*-BuNC)Au(CN) forms a chain with an Au...Au distance of 3.695 Å.²⁹ (MeO-C(O)CH₂NC)AuX where X is Cl or Br forms a corrugated sheet structure that is somewhat related to that reported here for (*o*-xylylNC)Au(CN) but with longer distances between the gold centers.²¹

While the four new complexes reported here are luminescent in solution and in the solid state, it is likely that the emission comes from xylyl based, $\pi\pi^*$ states. The structural variation seen in the four complexes is not evident in the luminescence behavior.

Experimental

The precursor, (Ph₃As)AuCl, was prepared as described previously,³⁰ and the analogous bromo and iodo complexes were obtained by metathesis with sodium bromide or sodium iodide via the procedure described earlier for the preparation of (Ph₃As)Au(SCN).³⁰

Syntheses

(*o*-xylylNC)AuCl. A 256 mg (1.95 mmol) portion of *o*-xylyl isocyanide was added to a solution of 1 g (1.86 mmol) of (Ph₃As)AuCl in 20 mL of chloroform. The solution was stirred for 30 min. Diethyl ether (20 mL) was added, and the resulting solution was partially evaporated under reduced pressure until the white product crystallized. The product was collected by filtration, washed with diethyl ether, and dried under vacuum; yield 409 mg, 60%.

(*o*-xylylNC)AuBr. This was obtained as colorless crystals in 65% yield by the procedure described above but utilizing (Ph₃As)AuBr as starting material.

(*o*-xylylNC)AuI. This was obtained in 56% yield as pale yellow crystals by the procedure described above with (Ph₃As)-AuI as starting material.

(*o*-xylylNC)AuCN. A 67 mg (0.51 mmol) portion of *o*-xylyl isocyanide was added to a stirred suspension of 109 mg (0.49 mmol) of gold(i) cyanide in 20 mL of chloroform. The solution was stirred for 1 h during which the solid dissolved. The solution was filtered and a 50 mL portion of diethyl ether was added to the filtrate. The solution was partially evaporated under reduced pressure to produce the product as white crystals. These were collected by filtration, washed with diethyl ether, and dried under vacuum; yield, 141 mg, 82%.

Crystallography

X-Ray data collection. Crystals of all four complexes were obtained by direct diffusion of diethyl ether into a saturated solution of the complex in dichloromethane. All crystals were coated with a light hydrocarbon oil and mounted on a glass fiber in the cold dinitrogen stream of the diffractometer. Data for (*o*-xylylNC)AuBr and (*o*-xylylNC)AuCl were collected on a Siemens R3m/V diffractometer with graphite monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation, while data for (*o*-xylylNC)-AuI and (*o*-xylylNC)AuCN were collected on a Siemens SMART CCD with graphite-monochromated Mo-K α radiation. Lorentz and polarization corrections were applied. Check reflections were stable throughout data collection except for (*o*-xylylNC)AuCl which showed a 9.2% increase in intensity due to detector noise. This factor was corrected. Crystal data are given in Table 4.

Solution and structure refinement. Calculations for the structures were performed using SHELXS-97 and SHELXL-97. Tables of neutral atom scattering factors, f' and f'' , and absorp-

tion coefficients are from a standard source.³¹ The structures were all solved *via* direct methods. All atoms except hydrogen atoms were refined anisotropically. Hydrogen atoms were included through the use of a riding model. Three hydrogen atoms were affixed on each of the methyl carbon atoms to provide tetrahedral geometry about these carbon atoms. The positions of the hydrogen atoms were not refined since the structure is dominated by scattering from gold and other heavy atoms. For (*o*-xylyl)NC)AuBr and (*o*-xylyl)NC)AuCl an empirical absorption correction was used,³² while for (*o*-xylyl)NC)AuI and (*o*-xylyl)NC)AuCN a semi-empirical method utilizing equivalents was employed.³³

CCDC number 186/1170.

See <http://www.rsc.org/suppdata/dt/1998/3715/> for crystallographic files in .cif format.

Acknowledgements

We thank the US National Science Foundation (Grant CHE 9610507) for support and Johnson Matthey for a loan of chloroauric acid.

References

- 1 J. C. Vickery, M. M. Olmstead, E. Y. Fung and A. L. Balch, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1179; E. Y. Fung, M. M. Olmstead, J. C. Vickery and A. L. Balch, *Coord. Chem. Rev.*, 1998, **171**, 151.
- 2 M. A. Mansour, W. B. Connick, R. J. Lachicotte, H. J. Gysling and R. Eisenberg, *J. Am. Chem. Soc.*, 1998, **120**, 1329.
- 3 P. G. Jones, *Gold Bull.*, 1981, **14**, 102.
- 4 H. Schmidbaur, *Interdiscip. Sci. Rev.*, 1992, **17**, 213.
- 5 S. S. Pathaneni and G. R. Desiraju, *J. Chem. Soc., Dalton Trans.*, 1993, 319.
- 6 H. Schmidbaur, *Chem. Soc. Rev.*, 1995, 391.
- 7 P. Pyykkö, J. Li and N. Runeberg, *Chem. Phys. Lett.*, 1994, **218**, 133.
- 8 P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597.
- 9 P. Pyykkö, N. Runeberg and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1451.
- 10 P. Pyykkö and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1458.
- 11 H. Schmidbaur, W. Graf and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 417.
- 12 D. E. Harwell, M. D. Mortimer, C. B. Knobler, F. A. L. Anet and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1996, **118**, 2679.
- 13 A. L. Balch, E. Y. Fung and M. M. Olmstead, *J. Am. Chem. Soc.*, 1990, **112**, 5181.
- 14 D. V. Toronto, B. Weissbart, D. S. Tinti and A. L. Balch, *Inorg. Chem.*, 1996, **35**, 2484; B. Weissbart, D. V. Toronto, A. L. Balch and D. S. Tinti, *Inorg. Chem.*, 1996, **35**, 2490.
- 15 Z. Assefa, B. G. McBurnett, R. J. Staples, J. P. Fackler, Jr., B. Assmann, K. Angermaier and H. Schmidbaur, *Inorg. Chem.*, 1995, **34**, 75.
- 16 H. Schmidbaur, G. Weidenhiller, O. Steigelman and G. Müller, *Z. Naturforsch., Teil B*, 1990, **45**, 747.
- 17 K. Angermaier, A. Sladek and H. Schmidbaur, *Z. Naturforsch., Teil B*, 1996, **51**, 1671.
- 18 P. M. Van Calcar, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, 1997, **36**, 5231; P. M. Van Calcar, M. M. Olmstead and A. L. Balch, *J. Chem. Soc., Chem. Commun.*, 1995, 1773.
- 19 For a review on other gold-based polymers see: R. J. Puddephatt, *Chem. Commun.*, 1998, 1055.
- 20 J. E. Parks and A. L. Balch, *J. Organomet. Chem.*, 1974, **71**, 453.
- 21 W. Schneider, K. Angermaier, A. Sladek and H. Schmidbaur, *Z. Naturforsch., Teil B*, 1996, **51**, 790.
- 22 T. J. Mathieson, A. G. Langdon, N. B. Milestone and B. K. Nicholson, *Chem. Commun.*, 1998, 371.
- 23 W. Schneider, A. Sladek, A. Bauer, K. Angermaier and H. Schmidbaur, *Z. Naturforsch., Teil B*, 1997, **52**, 53.
- 24 S. K. Chastain and W. R. Mason, *Inorg. Chem.*, 1982, **21**, 3717.
- 25 W. R. Mason, *J. Am. Chem. Soc.*, 1976, **98**, 5182.
- 26 N. Nagasundaram, G. Roper, J. Biscoe, J. W. Chai, H. H. Patterson, N. Blom and A. Ludi, *Inorg. Chem.*, 1986, **25**, 2947.
- 27 L. J. Larson, E. M. McCauley, B. Weissbart and D. S. Tinti, *J. Phys. Chem.*, 1995, **99**, 7218.
- 28 D. S. Eggleton, D. F. Chodosh, R. L. Webb and L. L. Davis, *Acta Crystallogr., Sect. C*, 1986, **42**, 36.
- 29 C. M. Che, H. K. Yip, W. T. Wong and T. F. Lai, *Inorg. Chim. Acta*, 1992, **197**, 177.
- 30 N. J. DeStafuno and J. L. Burmeister, *Inorg. Chem.*, 1971, **10**, 998.
- 31 *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, vol. C.
- 32 S. Parkin, B. Moezzi and H. Hope, *J. Appl. Crystallogr.*, 1995, **28**, 53.
- 33 R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.

Paper 8/05086D