Ligand Influences on the Supramolecular Chemistry of Simple Gold(I) Complexes: Mononuclear (Isonitrile)gold(I) Complexes

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Dedicated to Professor Max Herberhold on the occasion of his 60th birthday

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Gold(I) Complexes, Isonitrile Complexes, Auriophilicity, Crystal Structure

A series of (isonitrile)gold(I) complexes has been synthesized: (MeNC)AuX (X = Cl **1a**, I **1c**), (*t*-BuNC)AuBr **2b**, (PhNC)AuX (X = Cl **3a**, Br **3b**, I **3c**, SCN **3d**), (MesNC)AuCl **4a** [mes=mesityl], and (MeOC(O)CH$_2$NC)AuX (X = Cl **5a**, Br **5b**, I **5c**, SCN **5d**). The chlorides were prepared by the reaction of (Me$_2$S)AuCl with equimolar amounts (or with an excess) of the corresponding isonitrile. The bromides, iodides and thiocyanates were obtained from the reaction of (RNC)AuCl with K$^+$X$^-$ (X = Br, I, SCN) in the two-phase system H$_2$O/CH$_2$Cl$_2$. The molecular and crystal structures of **1a**, **2b**, **3a-c**, **4a**, and **5a-c** have been determined by X-ray diffraction methods. In the solid state the molecules are aggregated through short Au–Au contacts into dimers (**4a** and **5c**), chains (**1a**, **2b** and **3a-c**) or sheets (**5a** and **5b**). The influence of the isonitrile and halide ligands on the type and strength of the intermolecular Au–Au contacts is discussed.

Introduction

In recent years (isonitrile)gold(I) complexes have attracted increasing attention because of their use in new domains of applications. (Isonitrile)gold(I) alkyl complexes can be used as MOCVD precursors for the deposition of thin gold-films [1 - 3], and (isonitrile)gold(I) alkynyls and halides were shown to form a new type of liquid crystalline phases [4 - 9]. The ability of (isonitrile)gold(I) halides to give rise to liquid crystalline phases is thought to arise from the presence of weak gold–gold interactions in these systems [9], which can be compared in strength to hydrogen bonds [10 - 12]. Prior to these new areas of application, (isonitrile)gold(I) complexes were used as important starting materials for carbene complexes [13 - 25] and related compounds [26 - 34].

The structural data available for gold(I) complexes show that gold–gold interactions are ubiquitous in the solid phases of these compounds, and that they may even govern the supramolecular structure of the materials [35 - 41]. Classical theory of chemical bonding does not offer an explanation for this type of gold–gold interactions, and it was only recently that advanced studies including relativistic and correlation effects were able to account for the "auriophilicity" phenomenon [42 - 47].

Gold(I) complexes of the type L-Au-X (L = neutral donor ligand, X = halide or pseudohalide) can be aggregated into dimers, oligomers or polymers. The degree of oligomerization is clearly determined by a number of factors, among which the steric effect of the ligands is the most obvious. In order to learn more about other contributions to auriophilicity, a study of the structural chemistry of complexes with "slim" ligands was undertaken, which was thought to provide a better insight into the role of the nature of X and L. To date, only few (isonitrile)gold(I) complexes have been structurally characterized [48 - 54]. The small methyl group (**1**), the bulky *t*-butyl group (**2**), the flat phenyl (**3**) and mesityl groups (**4**), were chosen in this work as substituents for the neutral isonitrile ligands and Cl$^-$ (**a**), Br$^-$ (**b**), I$^-$ (**c**) and SCN$^-$ (**d**) as the anions X$^-$. The carboxymethylester derivatives (**5**) serve as models for functional isonitriles.

Results

The (isonitrile)gold(I) chlorides **1a**, **3a**, **4a** and **5a** were obtained in high yield (> 75%) following the

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Table I. Crystallographic data for (MeNC)AuCl (**1a**), (*t*-BuNC)AuBr (**2b**) and (PhNC)AuCl (**3a**).

Compound	**1a**	**2b**	**3a**
Empirical formula	C_2H_3AuClN	C_5H_9AuBrN	C_7H_5AuClN
Formula weight	273.47	360.01	335.54
Crystal system	monoclinic	orthorhombic	monoclinic
Space group (No.)	$P2_1$ (No.4)	Pnma (No.62)	$P2_1/c$ (No.14)
a [Å]	4.116 (1)	13.168(1)	10.935(2)
b [Å]	6.198 (1)	9.757(1)	6.458(1)
c [Å]	9.031 (1)	6.620(1)	12.253(2)
α [°]	90	90	90
β [°]	93.25 (1)	90	115.40(1)
γ [°]	90	90	90
V [Å^3]	230.02 (6)	850.5(1)	781.6
ρ_{calc} [gcm^{-3}]	3.948	2.85	2.871
Z	2	4	4
F(000) [e]	236	640	600
μ(Mo-K$_\alpha$) [cm^{-1}]	323.6	219.1	190.8
T [°C]	–56	–68	–68
Diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4	Enraf Nonius CAD4
Scan	Θ–Θ	Θ–Θ	Θ–Θ
hkl Range	$0 \leq h \leq 5, 0 \leq k \leq 8,$ $-11 \leq l \leq 11$	$0 \leq h \leq 16, 0 \leq k \leq 12,$ $-8 \leq l \leq 8$	$-13 \leq h \leq 13, 0 \leq k \leq 8$ $0 \leq l \leq 15$
Measured reflections	1136	1896	1920
Unique reflections	1108	960	1526
Observed reflections	1038	862	1301
R_{int}	0.1042	0.0134	0.0207
$F_o \geq$	$4\sigma(F_o)$	$4\sigma(F_o)$	$4\sigma(F_o)$
Refined parameters	25	217	111
H-Atoms (found/calcd)	– / 3	– / 9	5 / –
Absorption corr.:	empirical	empirical	no
T_{min} / T_{max}	0.1062 / 0.9982	0.4901 / 0.9954	
R *	0.0826	0.0240	0.0290
R_w **	0.0837	0.0235	0.0288
Weighting scheme ***	l = 1.0000 / k = 0.000391	l = 1.0000 / k = 0.000523	l = 1.0000 / k = 0.000117
ρ_{fin}(max/min) [eÅ^{-3}]	+ 18.50 / – 12.42	+ 1.13 / – 1.32	+ 1.26 / – 0.87

$^*R = \sum(||F_o|-|F_c||)/\sum|F_o|$; $^{**}R_w = [\sum(w(|F_o|-|F_c|)^2)/\sum w(F_o^2)]^{1/2}$; $^{***}w = 1/[\sigma^2(F_o) + k\,F_o^2]$.

general synthetic route illustrated in eq. (1).

$$(Me_2S)AuCl + RNC \rightarrow (RNC)AuCl + Me_2S \quad (1)$$

The (isonitrile)gold(I) bromides **2b**, **3b** and **5b**, iodides **1c**, **3c** and **5c**, and thiocyanates **3d** and **5d** were prepared in virtually quantitative yield by stirring a solution of (RNC)AuCl in dichloromethane with a solution of K^+X^- (X = Br, I, SCN) in water for several hours at ambient temperature (eq.(2)).

$$(RNC)AuCl + KX \rightarrow (RNC)AuX + KCl \qquad (2)$$
$$(X = Br, I, SCN)$$

This method was first reported by Swan and coworkers, but had only been applied to (phosphane)gold(I) complexes [55, 56]. The products were isolated as colourless crystals from dichloromethane solutions by careful addition of pentane. The compounds are light- and airstable and can be stored at room temperature. Only the iodides and thiocyanates undergo slow decomposition after a period of several months, as indicated by the change in their colour. The solubility in dichloromethane increases in the sequence RNCAuCl < RNCAuBr ~ RNCAuSCN < RNCAuI, following the increasing covalent character of the Au-X bond. The compounds were identified by standard spectroscopic methods and elemental analysis. In the IR spectra, the CN stretching frequencies of the isocyanide ligands were monitored as listed together with the NMR data in the

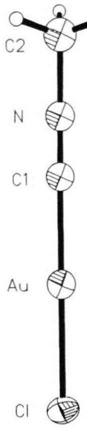

Fig. 1a. Molecular structure of (MeNC)AuCl (**1a**), with atomic numbering. Selected bond lengths (Å) and angles (°): Au-Cl 2.259(7), Au-C1 1.95(2), C1-N 1.10(3), N-C2 1.45(4), C1-Au-Cl 178.8(5), N-C1-Au 177(6), C2-N-C1 163(5).

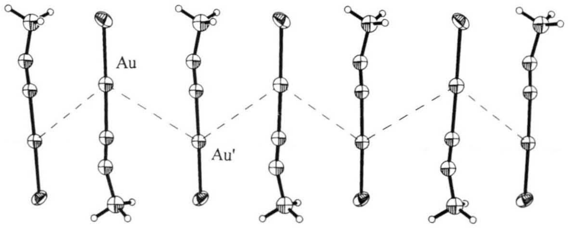

Fig. 1b. Supramolecular structure of **1a**. Polymeric zig zag chains with antiparallel arrangement of the molecules [Au-Au' 3.637(1) Å].

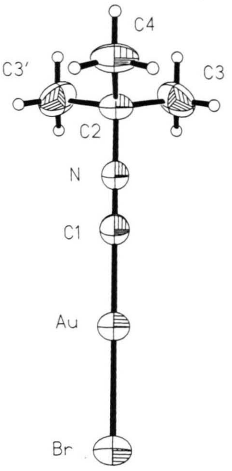

Fig. 2a. Molecular structure of (*t*-butylisonitrile)gold(I) bromide (**2b**), with atomic numbering. Selected bond lengths (Å) and angles (°): Au-Br 2.370(1), Au-C1 1.939(8), C1-N 1.13(1), N-C2 1.45(1), C1-Au-Br 177.2(3), N-C1-Au 177.5(8), C2-N-C1 177.9(8).

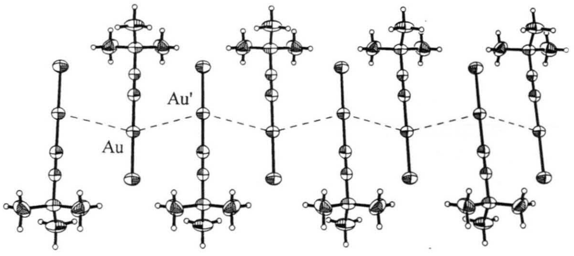

Fig. 2b. Supramolecular structure of **2b**. Polymeric zig zag chains with antiparallel arrangement of the molecules [Au-Au' 3.689(1)].

Experimental Part. The ^{1}H and ^{13}C NMR spectra show coupling of their nuclei with ^{14}N in most cases, a feature characteristic for many isonitriles and their complexes.

(MeNC)AuCl, **1a**, has been characterized previously, but the molecular and crystal structure had not been determined. Crystals of **1a** are monoclinic, space group $P2_1$, with 2 molecules in the unit cell. The individual molecule is rod-like with no crystallographically imposed symmetry. The Cl-Au-C angle is close to 180° [178.8(5)°], but the C-N-C-angle is smaller at 163(5)°. The Au-C bond distance [1.95(2) Å] is relatively short compared to the values of (phosphine)gold(I) alkyl complexes like $(Ph_3P)AuCH_3$ [Au-C 2.124(3) Å] [57]. This shortening may reflect a backbonding from gold to the isonitrile ligand, but is more likely associated with the sp-hybridization of the isonitrile carbon atom, similar to the situation in alkynyl complexes [53, 54, 58, 59]. Further details are listed in the caption of Fig. 1a and in Table I. An examination of the cell packing shows zig zag chains of molecules with the monomeric units arranged in an antiparallel fashion (Fig. 1b). The Au–Au contacts are surprisingly long [3.637(1) Å], probably due to the close antiparallel packing in layers, which forces the metal atoms into alternating position above and below the plane defining the center of the layer.

(*t*-BuNC)AuBr, **2b**, is isostructural to the known chloride analogue (*t*-BuNC)AuCl [49]. The structure of the bromide complex (**2b**) has been determined nevertheless because it allows for the first time the determination of an Au-Br bond distance in an (isonitrile)gold(I) complex. It was found

Table II. Crystallographic data for (PhNC)AuBr / I (**3b**, **3c**) and (MesNC)AuCl (**4a**).

Compound	**3b**	**3c**	**4a**
Empirical formula	C_7H_5AuBrN	C_7H_5AuIN	$C_{10}H_{11}AuNCl$
Formula weight	380.00	426.99	377.61
Crystal system	triclinic	triclinic	monoclinic
Space group (No.)	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)	$P2_1/c$ (No.14)
a [Å]	9.152 (1)	9.370 (1)	10.047 (1)
b [Å]	10.059 (1)	10.222 (1)	16.612 (2)
c [Å]	10.109 (1)	10.679 (1)	6.904 (1)
α [°]	102.68 (1)	103.43 (1)	90
β [°]	96.57 (1)	115.44 (1)	110.07 (1)
γ [°]	114.09 (1)	96.26 (1)	90
V [$Å^3$]	806.8 (2)	872.7 (1)	1082.3 (2)
ρ_{calc} [gcm^{-3}]	3.13	3.25	2.32
Z	4	4	4
F(000) [e]	672	744	696
μ(Mo-K_α) [cm^{-1}]	231.0	203.2	137.9
T [°C]	-62	-68	-68
Diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4	Enraf Nonius CAD4
Scan	ω	Θ	ω
hkl Range	$0 \leq h \leq 11, -12 \leq k \leq 12, -12 \leq l \leq 12$	$0 \leq h \leq +11, -13 \leq k \leq +13, -13 \leq l \leq +13$	$-8 \leq h \leq 8, 0 \leq k \leq 21, 0 \leq l \leq 12$
Measured reflections	3480	3776	2456
Unique reflections	3110	3494	2044
Observed reflections	2587	3054	1735
R_{int}	0.1042	0.0327	0.0207
$F_o \geq$	$4\sigma(F_o)$	$4\sigma(F_o)$	$4\sigma(F_o)$
Refined parameters	181	181	118
H-Atoms (found/calcd)	- / 5	- / 5	- / 11
Absorption corr.:	empirical	empirical	empirical
T_{min} / T_{max}	0.3319 / 0.9989	0.6006 / 0.9982	0.3222 / 0.9987
R *	0.0305	0.0272	0.0384
R_w **	0.0346	0.0298	0.0487
Weighting scheme ***	$l = 1.0000$ / $k = 0.000304$	unit weights	$l = 1.0000$ / $k = 0.006240$
ρ_{fin}(max/min) [$eÅ^{-3}$]	+ 1.46 / - 1.35	+ 0.72 / -0.96	+ 1.24 / -1.91

$^*R = \sum(||F_o|-|F_c||)/\sum|F_o|$; $^{**}R_w = [\sum(w(|F_o|-|F_c|)^2)/\sum w(F_o^2)]^{1/2}$; $^{***}w = 1/[\sigma^2(F_o) + k\,F_o^2]$.

[2.370(1) Å] to be comparable to the data for (phosphine)gold(I) complexes (average 2.40 Å) [60-63]. The C-Au-Br angle is virtually linear at 177.2(3)° (Fig. 2a). In the lattice the packing of the molecules is similar to that found in **1a** and in the chloride analogue [49]. The monomeric units form zig-zag chains with a sequence of anti-parallel arrangements. There are only very weak Au–Au interactions as suggested by long [Au-Au = 3.689(1) Å] distances (Fig. 2b).

The (phenylisonitrile)gold(I) halides **3a-c** are not isomorphous (Table I and II). In the chloride **3a** (Fig. 3a), all molecular units are crystallographically equivalent, with a C-Au-Cl angle of 178.5(3)° and a Au-Cl distance of 2.254(2) Å. The molecules are aggregated to form a zig-zaging chain with a sequence of the monomers in an antiparallel arrangement. The planes of the phenyl groups are parallel by symmetry on both sides of the chain. (Fig. 3b). The intra-chain gold-gold contacts [3.463(1) Å] are shorter by 0.174 Å as compared with **1a,** but still rather long.

The bromide **3b** crystallizes with two crystallographically independent molecules in the asymmetric unit. In the lattice there are puckered chains with an antiparallel arrangement of the neighbouring molecules (Fig. 4). The intra-chain gold-gold contacts are not equivalent [Au1-Au1' = 3.610(1) Å, Au2-Au2' = 3.507(1) Å, Au1-Au2 = 3.649(1) Å], with an average of 3.589 Å. This mean value

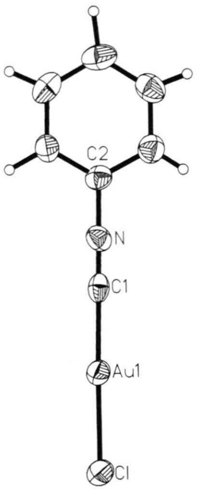

Fig. 3a. Molecular structure of (PhNC)AuCl (**3a**), with atomic numbering. Selected bond lengths (Å) and angles (°): Au-Cl 2.254(2), Au-C1 1.925(7), C1-N 1.142(9), N-C2 1.396(8), C1-Au-Cl 178.5(3), N-C1-Au 177.0(9), C2-N-C1 177(1).

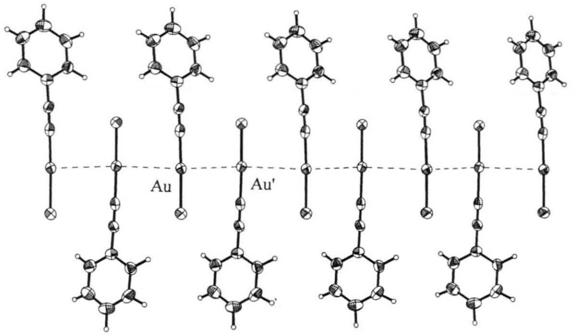

Fig. 3b. Supramolecular structure of **3a**. Polymeric zig zag chains with antiparallel arrangement of the molecules [Au-Au' 3.463(1) Å].

is thus larger than in the chloride homologue **3a** (above). However, unlike in **3a**, every second phenyl group on each side of the chain in **3b** is rotated by about 90°, bringing neighbouring phenyl groups in an approximately perpendicular arrangement. The two Au-Br distances have an average of 2.357 Å, very similar to the value found for **2b**.

The (phenylisonitrile)gold(I) iodide **3c** (Fig. 5) is isostructural to the bromide complex, **3b**, with the same sequential pattern in the chain structure. Interestingly, the intra-chain Au–Au contacts [3.640(1), 3.802(1) and 3.875(1) Å, average 3.772 Å] are longer than those in **3a** and **3b**, indicating

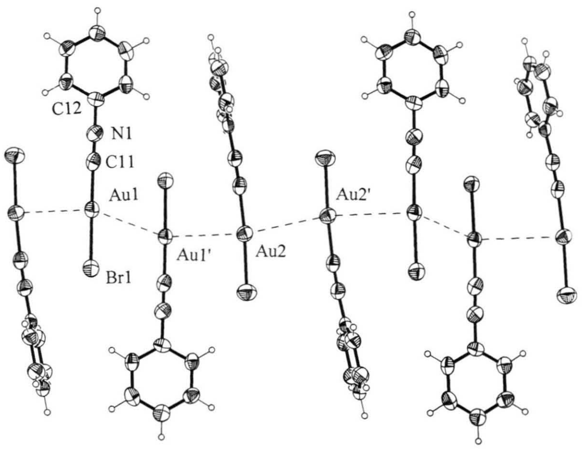

Fig. 4. Supramolecular structure of (PhNC)AuBr (**3b**). Unlike in **3a,** the phenyl groups are rotated by 90°. Selected bond lengths (Å) and angles (°): Intermolecular: Au1-Au1' 3.610(1), Au1'-Au2 3.649(1), Au2-Au2' 3.507(1); Intramolecular: Au1-Br1 2.360(1), Au1-C11 1.94(1), N1-C11 1.15(1), N1-C12 1.40(1), Au2-Br2 2.355(1), Au2-C21 1.94(1), N2-C21 1.13(1), N2-C22 1.40(1), C11-Au1-Br1 177.5(2), N1-C11-Au1 178.3(8), C12-N1-C11 179(1), C21-Au2-Br2 176.0(3), C22-N2-C21 176.4(8), N2-C21-Au2 176.5(9).

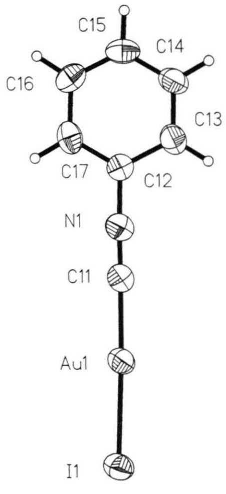

Fig. 5. Molecular structure of (PhNC)AuI (**3c**), with atomic numbering (only one of the two crystallographically independent molecules is shown). Selected bond lengths (Å) and angles (°): Au1-Au1' 3.875(1), Au2-Au2' 3.640(1), Au1-Au2 3.802(1), Au1-I1 2.524(1), Au1-C11 1.93(1), N1-C11 1.19(2), N1-C12 1.38(1), Au2-I2 2.523(1), Au2-C21 1.92(1), N2-C21 1.17(1), N2-C22 1.38(1), C11-Au1-Br1 177.1(3), C12-N1-C11 177(1), N1-C11-Au1 176.0(8), C21-Au2-Br2 175.3(4), C22-N2-C21 177.8(9), N2-C21-Au2 176.(1).

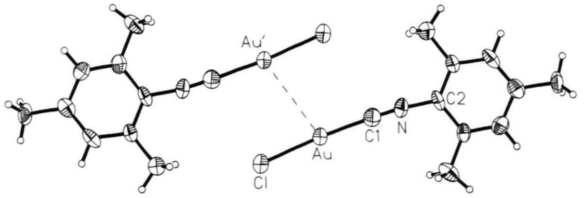

Fig. 6. Dimer of (MesNC)AuCl (**4a**), with an intermolecular Au-Au' distance of 3.336(1) Å. Selected bond lengths (Å) and angles (°) in the monomer: Au-Cl 2.262(3), Au-C1 1.98(1), C1-N 1.10(1), N-C2 1.35(1), C1-Au-Cl 175.0(4), N-C1-Au 176.0(8), C2-N-C1 174(1).

a weakening of the auriophilic bonding. The Au-I bond distances in **3c**, the first Au-I bond lengths determined for an (isonitrile)gold(I) complex, are 2.524(1) and 2.523(1) Å, which is somewhat shorter than found in monomeric Ph_3PAuI [2.556(1) Å] [61, 64] or polymeric Me_3PAuI [2.583(1) Å] [64].

The mesitylisonitrile ligand in the chloride complex **4a** is much larger than the phenylisonitrile ligand in **3a-c** and was expected to exert steric effects. And indeed a new structure type is realized which comprises only dimers as shown in Fig. 6. The Au–Au distance [3.336(1) Å] within the dimers is shorter than that observed in the chains of any of the homologues (above). This phenomenon can also be observed in (phosphine)gold(I) complexes, where the Au–Au distances in dimers are generally shorter than in more extended oligomers. It should be noted that **4a** shows a relatively long Au-C bond [1.98(1) Å] as compared to other (isonitrile)gold(I) halides, probably also owing to steric effects.

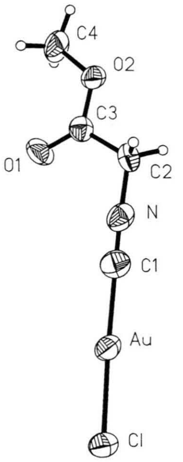

Fig. 7a. Molecular structure of $(MeOC(O)CH_2NC)AuCl$ (**5a**). Selected bond lengths (Å) and angles (°): Au-Cl 2.255(3), Au-C1 1.96(1), N-C1 1.11(2), N-C2 1.42(2), C1-Au-Cl 176.5(4), N-C1-Au 178(1), C2-N-C1 177(1).

The isonitrile derived from glycine methylester, $MeOC(O)CH_2NC$, was chosen as a ligand with a polar side group of limited steric influence. The usual synthetic pathways were followed to prepare the gold(I) complexes **5a-d** of this ligand.

The three halide complexes **5a-c** show two new structural motifs. The first one is represented by the chloride and bromide **5a**, **b** which form a novel isomorphous sheet structure, while the iodide **5c** appears in dimeric aggregates with a crossed orientation of the monomers. The individual molecules of **5a-c** are very similar in their configuration, characterized by a quasi-linear five atom sequence X-Au-C-N-CH_2, as well as in the conformation of the ester group, *i. e.* the syn orientation of the carbonyl oxygen atom and the nitrogen atom, and the syn orientation of the carbonyl oxygen atom and the ester methyl group (Fig. 7a, 9 and 10).

In the crystal of the chloride and bromide complexes, the monomers are surrounded by three other monomers and become members of corrugated sheets (Fig. 7b). These sheets contain a puckered layer of gold atoms in which each of the crystallographically equivalent metal atoms has contacts

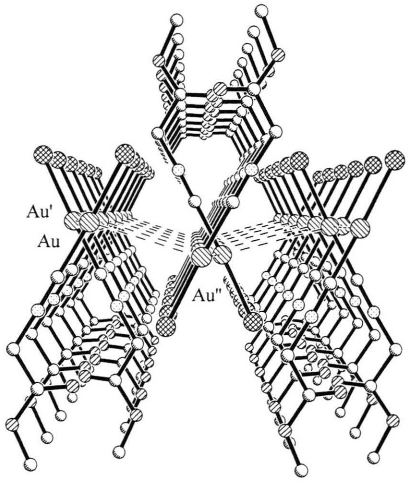

Fig. 7b. Supramolecular structure of $(MeOC(O)CH_2NC)AuCl$ (**5a**). The monomers form chains (perpendicular to the plane of the paper with neighbouring individuals "crossed"), which are associated into sheets with approaching monomers antiparallel head-to-tail. Intermolecular contacts Au-Au' 3.430(1), Au-Au'' 3.553(1) Å.

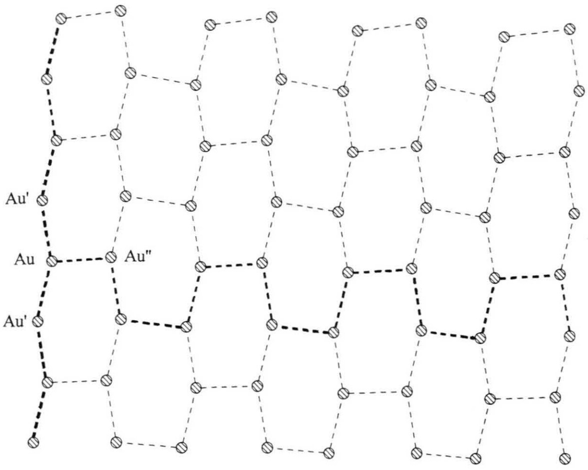

Fig. 8. Projection of the corrugated sheets of gold atoms in the isomorphous structures of (MeOC(O)CH$_2$NC)AuCl / Br (**5a**, **5b**). Each gold atom represents a monomer. The gold atoms form planar zig-zag chains (primary chain, running vertically), and meandering chains, running horizontally).

to three other metal atoms (Fig. 8). This connectivity leads to a quasi-hexagonal array of gold atoms, with each six-membered ring in a flat, distorted chair conformation. This structural motiv is reminiscent of the structure of black phosphorus. In another description each monomer is part of a zig-zag chain of molecules with their main axes "crossed like swords" in heraldic emblems. These chains, running vertical in Fig. 8 and perpendicular to the paper in Fig. 7b, are associated into sheets through a parallel head-to-tail approach of molecules of neighbouring chains. With the new contacts the gold atoms become part of new meandering chains running perpendicular to the primary chain as indicated in Fig. 8. There are two independent Au–Au distances of 3.430(1) and 3.553(1) Å in the primary and secondary chains of the chloro complex **5a**, respectively. The data for the bromide (**5b**) are similar: 3.441(1) and 3.622(1) Å.

The dimers present in the lattice of [MeOC(O)CH$_2$NC]AuI, **5c**, have the shortest intermolecular Au–Au distance [3.191(1) Å] observed in (isonitrile)gold(I) complexes. The Au-I bond distance of 2.538(1) Å is comparable to that found in **3c**. The monomers are in the "crossed" type of aggregation with the dihedral angle I-Au-Au-I approaching 90° (Fig. 10).

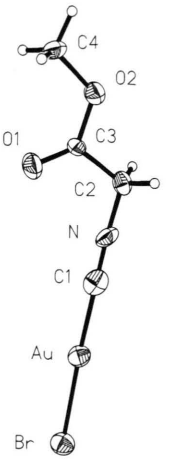

Fig. 9. The monomer in the sheet structure of (MeOC(O)CH$_2$NC)AuBr (**5b**), with atomic numbering. Selected bond lengths (Å) and angles (°): Au-Br 2.364(1), Au-C1 1.93(1), C1-N 1.16(2), C2-N 1.38(1), C1-Au-Br 177.8(4), N-C1-Au 178(1), C2-N-C1 177(1). The aggregation leads to intermolecular contacts Au-Au' = 3.441(1) (primary chain) and 3.622(2) (between primary chains, see text).

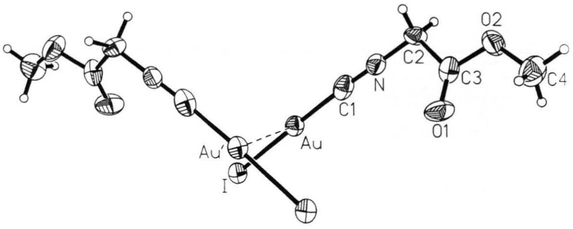

Fig. 10. The dimers of compound (MeOC(O)CH$_2$NC)AuI (**5c**). Selected bond lengths (Å) and angles (°): Au-Au' 3.191(1), Au-I 2.538(1), Au-C1 1.94(1), N-C1 1.17(2), N-C2 1.41(1), C1-Au-I 176.2(3), N-C1-Au 178(1), C2-N-C1 178(1).

Discussion

None of the (RNC)AuX complexes reported in this work is monomeric in the solid state. This behaviour is reminiscent of the molecularity of (phosphine)gold halide complexes with small phosphines. As also observed for these analogues, only two of the three possible types of aggregation A-C (Fig. 11) are realized. The parallel head-to-tail (A) and the crossed fashion (B) are the recurrent structural motifs, either seperately [A: **1a**, **2b**, **3a-c** and **4a**; B **5c**], or in a combination of both [**5a** and **5b**].

Table III. Crystallographic data for (MeOC(O)CH$_2$NC)AuCl / Br / I (**5a-c**).

Compound	**5a**	**5b**	**5c**
Empirical formula	$C_4H_5AuClNO_2$	$C_4H_5AuBrNO_2$	$C_4H_5AuINO_2$
Formula weight	331.51	375.97	422.98
Crystal system	monoclinic	monoclinic	monoclinic
Space group (No.)	$P2_1/c$ (No.14)	$P2_1/c$ (No.14)	C2/c (No.15)
a [Å]	13.291 (2)	13.427 (1)	25.559 (4)
b [Å]	8.259 (1)	8.307 (1)	4.655 (1)
c [Å]	6.705 (1)	6.758 (1)	13.866 (2)
α [°]	90	90	90
β [°]	102.74 (1)	101.91 (1)	100.44 (1)
γ [°]	90	90	90
V [Å^3]	717.9 (1)	737.6 (1)	1621.9 (5)
ρ_{calc} [gcm^{-3}]	3.09	3.38	3.47
Z	4	4	8
F(000) [e]	592	664	1472
μ(Mo-K$_\alpha$) [cm^{-1}]	209.3	252.9	218.8
T [°C]	22	–62	–62
Diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4	Enraf Nonius CAD4
Scan	$\Theta - 2\Theta$	$\Theta - \Theta$	ω
hkl Range	$0 \leq h \leq 16, 0 \leq k \leq 10, -8 \leq l \leq 8$	$-17 \leq h \leq 0, -10 \leq k \leq 0, -8 \leq l \leq 8$	$-32 \leq h \leq 32, -5 \leq k \leq 0$ $-17 \leq l \leq 17$
Measured reflections	1736	1696	2360
Unique reflections	1452	1529	1681
Observed reflections	1298	1406	1546
R_{int}	0.0425	0.2711	0.0323
$F_o \geq$	$4\sigma(F_o)$	$4\sigma(F_o)$	$4\sigma(F_o)$
Refined parameters	82	82	82
H-Atoms (found/calc.)	– / 5	– / 5	– / 5
Absorption corr.:	empirical	empirical	empirical
T_{min} / T_{max}	0.2298 / 0.9987	0.1324 / 0.9994	0.1953 / 0.9996
R *	0.0636	0.0567	0.0371
R_W **	0.0878	0.0598	0.0463
Weighting scheme ***	$l = 1.0000$ / $k = 0.034700$	$l = 1.0000$ / $k = 0.014337$	$l = 1.0000$ / $k = 0.008901$
ρ_{fin}(max/min) [eÅ^{-3}]	2.08 / – 2.87	4.47 / –3.98	2.49 / –1.96

$^*R = \sum(||F_o|-|F_c||)/\sum|F_o|$; $^{**}R_w = [\sum(w(|F_o|-|F_c|)^2)/\sum w(F_o^2)]^{1/2}$; $^{***}w = 1/[\sigma^2(F_o) + k\,F_o^2]$.

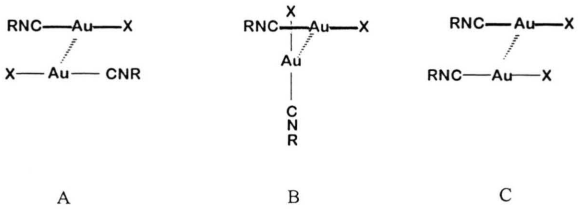

Fig. 11. The three principal modes of aggregation of complexes L-Au-X.

(MeNC)AuCN is the only example where, in a combination with mode A, mode C is also realized [48]. If the molecules are aggregated only into dimers (**4a** and **5c**), the Au–Au distances are the shortest, and the B-type iodide complex is associated most tightly as compared to the A-type chloride complex.

In the series of coordination polymers, the crossed contacts are also shorter than the parallel contacts, and it thus appears that this may be taken as a general feature. It is obvious from the models (A-C) that steric effects are a minimum for B, suggesting that the ligand repulsion is the decisive factor determining the association of the complexes.

The influence of the nature of the anion X is found to be smaller, and the variations for the same structure type are such that the larger halide leads to nearly equal (*e.g.* **2a** → **2b** and **3b** → **3c**) or to larger Au–Au contacts (**5a** → **5b**). This result is not in agreement with the predictions for isolated dimers from recent theoretical studies [65]. It is conceivable, however, that the consequences of electronic effects are overruled by steric effects arising from the incorporation of the dimers into polymers, and by packing forces.

Experimental Part

General: Conventional glass equipment was used throughout. Solvents (p.a. grade) were used as received and all experiments were carried out in air. *t*-BuNC was purchased, MeNC [66], PhNC [67], MesNC [68], MeOC(O)CH$_2$NC [69], (Me$_2$S)AuCl [70], (MeNC)AuCl **1a** [71, 72], (*t*-BuNC)AuCl **2a** [49]and (PhNC)AuCl **3a** [73, 74] were prepared according to literature methods.

Preparation of the (isonitrile)gold(I) chloride complexes

To a solution of (Me$_2$S)AuCl in dichloromethane an equimolar amount (or an excess) of the corresponding isonitrile ligand is added. After 1 h the solvent is removed in a vacuum and the colourless residue is crystallized from a dichloromethane/pentane mixture.

Chloride complex **4a**

From (Me$_2$S)AuCl (211 mg, 0.72 mmol) and 2,4,6-(Me)$_3$C$_6$H$_2$NC (104 mg, 0.72 mmol) in CH$_2$Cl$_2$ (20 mL); yield 284 mg (75%); m.p. 188°C; ^{1}H NMR (CDCl$_3$): δ = 2.4 ppm, s, *ortho*-CH$_3$ (6H); 2.3, s, *para*-CH$_3$ (3H); 7.0, s, *meta*-H (2H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 18.5 ppm, s, *ortho*-CH$_3$; 21.4, s, *para*-CH$_3$; 121.6, m, *ipso*-C; 129.2, s, *ortho*-C; 135.9, s, *meta*-C; 141.8, s, *para*-C; NCAu was not observed. IR (CH$_2$Cl$_2$): ν(CN) = 2214 cm^{-1}.

Analysis for C$_{10}$H$_{11}$AuClN (M = 377.61)
Calcd C 31.78 H 2.91 N 3.71%,
Found C 31.69 H 2.93 N 3.66%.

Chloride complex **5a**

From (Me$_2$S)AuCl (638 mg, 2.17 mmol) and MeOC(O)CH$_2$NC (215 mg, 2.17 mmol) in CH$_2$Cl$_2$ (60 mL); yield 582 mg (81%); decomposition temperature 198°C; ^{1}H NMR (CDCl$_3$): δ = 5.0 ppm, br. s, 2H; 3.8, s, 3H; ^{13}C{^{1}H} NMR was not recorded because of the low solubility of **5a**. IR (crystal): ν(CN) = 2273.1 cm^{-1}; ν(CO$_2$) = 1769.0 cm^{-1}.

Analysis for C$_4$H$_5$AuClNO$_2$ (M = 331.51)
Calcd C 14.48 H 1.51 N 4.22%,
Found C 14.45 H 1.51 N 4.20%.

Preparation of (isonitrile)gold(I) bromide, iodide and thiocyanate complexes

A solution of the corresponding (isonitrile)gold(I) chloride in dichloromethane (5 - 10 mL) is stirred with a solution of equimolar amounts of K$^+$X$^-$ (X = Br, I, SCN) in water (5 - 10 mL) for 4 h. After separation of the water phase, the dichloromethane solution is washed twice with small portions of water and the solvent is removed in a vacuum. The residue is crystallized from dichloromethane by layering the solution with pentane.

Iodide complex **1c**

From **1a** (89 mg, 0.33 mmol) and KI (81 mg, 0.49 mmol); yield 102 mg (85%); decomposition temperature 186°C; ^{1}H NMR (CDCl$_3$): δ = 3.5 ppm, br., Me; ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 29.7 ppm, s, Me; 144.2, t, ^1J(CN) = 25.7 Hz, NCAu. IR (CH$_2$Cl$_2$): ν(CN) = 2264 cm^{-1}.

Analysis for C$_2$H$_3$AuIN (M = 364.92)
Calcd C 6.58 H 0.83 N 3.84%,
Found C 6.90 H 0.85 N 3.90%.

Bromide complex **2b**

From **2a** (150 mg, 0.48 mmol) and KBr (57 mg, 0.48 mmol); yield 154 mg (89%); m.p. 161°C; ^{1}H NMR (CDCl$_3$): δ = 1.6 ppm, s, Me; ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 29.6 ppm, s, Me; 59.0, t, ^1J(CN) = 3.7 Hz, Me$_3$C; 135.9, t, ^1J(CN) = 23.0 Hz, NCAu. IR (CH$_2$Cl$_2$): ν(CN) = 2235.8 cm^{-1}.

Analysis for C$_5$H$_9$AuBrN (M = 360.01)
Calcd C 16.68 H 2.50 N 3.89%,
Found C 16.80 H 2.55 N 3.93%.

Bromide complex **3b**

From **3a** (104 mg, 0.31 mmol) and KBr (37 mg, 0.31 mmol); yield 105 mg (89%); m.p. 177°C; ^{1}H NMR (CDCl$_3$): δ = 7.5-7.6 ppm, m, Ph-H; ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 124.4 ppm, m, *ipso*-C; 126.9, s, *ortho*-C; 130.0, s, *meta*-C; 131.6, s, *para*-C; NCAu was not observed. IR (CH$_2$Cl$_2$): ν(CN) = 2222 cm^{-1}.

Analysis for C$_7$H$_5$AuBrN (M = 379.99)
Calcd C 22.13 H 1.33 N 3.69%,
Found C 22.62 H 1.44 N 3.80%.

Iodide complex **3c**

From **3a** (177 mg, 0.53 mmol) and KI (88 mg, 0.53 mmol); yield 182 mg (80%); m.p. 126°C; ^{1}H NMR (CDCl$_3$): δ = 7.5-7.6 ppm, m, Ph-H; ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 124.25 ppm, t, ^1J(CN) = 4.5 Hz, *ipso*-C; 126.8, s, *ortho*-C; 130.0, s, *meta*-C; 131.7, s, *para*-C; 151.0, t, ^1J(CN) = 23.2 Hz, NCAu. IR (CH$_2$Cl$_2$): ν(CN) = 2216 cm^{-1}.

Analysis for C$_7$H$_5$AuIN (M = 426.99)
Calcd C 19.69 H 1.18 N 3.28%,
Found C 19.62 H 1.16 N 3.35%.

Thiocyanate complex **3d**

From **3a** (120 mg, 0.36 mmol) and KSCN (35 mg, 0.36 mmol); yield 129 mg (100%); m.p. 135°C; ^{1}H NMR (CDCl$_3$): δ = 7.5-7.6 ppm, m, Ph-H; ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 123.95 ppm, m, *ipso*-C; 127.0, s, *ortho*-C; 130.2, s, *meta*-C; 132.15, s, *para*-C; NCAu and SCN

were not observed. IR (CH_2Cl_2): ν(CN) = 2228 cm^{-1}; ν(SCN) = 2133 cm^{-1}.
Analysis for $C_8H_5AuN_2S$ (M = 358.17)
Calcd C 26.83 H 1.41 N 7.82%,
Found C 26.79 H 1.40 N 7.76%.

Bromide complex **5b**

From **5a** (100 mg, 0.30 mmol) and KBr (36 mg, 0.30 mmol); yield 108 mg (95%); m.p. 194°C; ^{1}H NMR (d_6-acetone): δ = 3.85 ppm, s, Me; 5.0, br. s, CH_2; $^{13}C\{^1H\}$ NMR was not recorded because of the low solubility of **5b**. IR (crystal): ν(CN) = 2280 cm^{-1}; $\nu(CO_2)$ = 1765.5 cm^{-1}.
Analysis for $C_4H_5AuBrNO_2$ (M = 375.97)
Calcd C 12.77 H 1.34 N 3.72%,
Found C 12.98 H 1.31 N 3.58%.

Iodide complex **5c**

From **5a** (100 mg, 0.30 mmol) and KI (50 mg, 0.30 mmol); yield 110 mg (87%); m.p. 146°C; ^{1}H NMR (d_6-acetone): δ = 3.85 ppm, s, Me; 5.0, br. s, CH_2; $^{13}C\{^1H\}$ NMR (d_6-acetone): δ = 46.35 ppm, t, ^1J(CN) = 9.19 Hz, CH_2; 53.8, s, Me; 163.8, s, CO_2; NCAu was not observed. IR (crystal): ν(CN) = 2263.4 cm^{-1}; $\nu(CO_2)$ = 1749.5 cm^{-1}.
Analysis for $C_4H_5AuINO_2$ (M = 422.98)
Calcd C 11.35 H 1.19 N 3.31%,
Found C 11.18 H 1.13 N 3.06%.

Thiocyanate complex **5d**

From **5a** (100 mg, 0.30 mmol) and KSCN (29 mg, 0.30 mmol); yield 105 mg (89 %); m.p. 117°C; ^{1}H NMR ($CDCl_3$): δ = 3.9 ppm, s, Me; 4.6, br. s, CH_2; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 45.6 ppm, br. s, CH_2; 54.2, s, Me; 161.7, s, CO_2; NCAu and SCN were not observed. IR (crystal): ν(CN) = 2279.7 cm^{-1}; ν(SCN) = 2129.7 cm^{-1}; $\nu(CO_2)$ = 1759.7 cm^{-1}.
Analysis for $C_5H_5AuN_2O_2S$ (M = 354.13)
Calcd C 16.95 H 1.42 N 7.91%,
Found C 16.78 H 1.31 N 7.85%.

Crystal structure determination

Details of the X-ray structure determination of the compounds are summarized in the Tables. Further information on the structure determinations may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D–76344 Eggenstein-Leopoldshafen, Germany, on quoting the CSD number 59240.

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