Silver and Gold Trinuclear Complexes Based on 3-Substituted or 3,5-Disubstituted Pyrazolato Ligands. X-Ray Crystal Structure of *cyclo*-Tris{μ-[3,5-bis(4-phenoxyphenyl)-1*H*-pyrazolato-$\kappa N^1:\kappa N^2$]}trigold Dichloromethane ($[Au(\mu\text{-}pz^{pp_2})]_3 \cdot CH_2Cl_2$)

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Ten new silver and gold trimeric complexes of the type $[M_3(\mu\text{-}pz')_3]$ (M = Au, Ag), where pz′ indicate pyrazolato ligands derived from mesogenic 3,5-disubstituted 1*H*-pyrazoles Hpz^{R_2} or non-mesogenic 3-substituted 1*H*-pyrazoles Hpz^R ($R = C_6H_4OC_nH_{2n+1}$), were synthesized and characterized. The gold and silver complexes **7**, **8**, **10**, and **11** containing symmetric pyrazolato ligands as bridging groups (pz^{R_2}; $R = C_6H_4OC_nH_{2n+1}$, $n = 4$ (pz^{bp_2}) and 8 (pz^{op_2})) exhibited a trigonal symmetric structure. The same results were obtained for the related silver derivatives **16**–**18** with 3-substituted pyrazolato ligands (pz^R; $R = C_6H_4OC_nH_{2n+1}$, $n = 4$ (pz^{bp}), 12 (pz^{ddp}), and 18 (pz^{odp})). By contrast the 3-substituted pyrazolato-gold compounds **13**–**15** adopted an asymmetric molecular structure related to the position of the substituents on the trinuclear core. The thermal behavior of these complexes was investigated by differential scanning calorimetry and polarized-light microscopy. The mesomorphism of the parent 3,5-disubstituted pyrazoles is avoided in their corresponding trinuclear complexes **7**, **8**, **10**, and **11**. However, the metal derivatives **14** and **17** containing the asymmetric 3-[4-(dodecyloxy)phenyl]pyrazolato ligand were found to have liquid-crystal properties. These compounds exhibited monotropic behavior with columnar mesophases that could be related to the disc-like shape of the molecular core and the appropriate length of the alkyloxy chain. For comparative purposes, the X-ray structure of the related gold complex $[Au_3(\mu\text{-}pz^{pp_2})_3]$ (**9**) having phenoxyphenyl substituents at the 3- and 5-positions of the pyrazolato ligand is also described. The molecular structure is formed by a non-planar $(Au-N-N)_3$ core, containing three Au-atoms bridged by three pyrazolato ligands. The molecular packing is described as a columnar organization, the shortest Au ··· Au distance being 4.639(1) Å between consecutive trimers.

1. Introduction. – Exobidentate *N*,*N*′-coordination of pyrazolato ligands has been extensively used on coordination oligomers and polymers [1–5]. Typical pyrazolato-silver or -gold(I) derivatives have commonly been found as dimers or trimers [1][2][6–8], the latter being proposed to have a cyclic structure [1][2][9–18] compatible with the sp^2-hybridized N-atoms of the pyrazolato ring, the usual sp-hybridization of the metal center, and the requirements of a nine-membered planar ring. Other values of oligomerization have also been established for related complexes. Thus, a cyclic hexanuclear structure has been described for $[Au_6(\mu\text{-}pz^{Ph_2})_6]$ (pz^{Ph_2} = 3,5-diphenylpyrazolato) [9][19], while bulky ligands such as 3,5-di(*t*-butyl)pyrazolato or the asymmetric 3-ethyl-4,5-dimethyl-pyrazolato have given rise to cyclic tetramers [10]. The latter structure has also been found for $[Ag_4(\mu\text{-}pz^{4\text{-i-}C_3F_7})_4]$ ($pz^{4\text{-i-}C_3F_7}$ = 4-(heptafluoroisopropyl)pyrazolato) [3].

Despite the fact that some of these pyrazolato complexes were synthesized a long time ago, little structural characterization is available. To the best of our knowledge, the X-ray structures of only some pyrazolato-gold trimers [9][11–14], one pyrazolato-silver trimer [9] and one pyrazolato-gold hexamer [9][19] have been reported. From these results, we observed that the nine-membered metallocyclic core of the trimetallic species was planar or slightly deviating from planarity depending on the substituents on the pyrazolato ligand. Besides, it was also interesting to note that the trimeric gold and silver derivatives containing 3,5-diphenylpyrazolato exhibited very different structures, *i.e.*, while the former was highly symmetric, the silver analogue presented a strong deviation from idealized geometry [9].

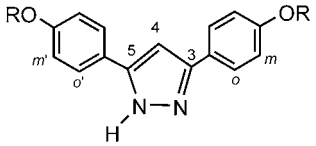
Recently it has been established that trigonal planar molecules with D_{3h} symmetry are specially prone to develop non-centrosymmetric packings, and they can be used as octupolar molecules with nonlinear optical (NLO) properties [20–22]. Therefore, the study of new trinuclear pyrazolato-metal complexes opens new vistas for designing the required trigonal molecules.

In addition, some trimetallic pyrazolato-gold(I) complexes of the type $[Au_3(\mu\text{-pz})_3]$ have been shown to have liquid-crystal (LC) properties exhibiting columnar mesophases [12][13][23]. Most of them carry from 12 to 18 side chains in the molecular periphery (4 to 6 for each pyrazolato group), configurating a discotic shape [12][23]. However, a new type of related complexes containing only three side chains from 4-substituted pyrazolato groups has also been found to behave as discotic metallomesogens [13]. These latter compounds exhibited a star-shaped dimeric structure formed by two alternated triangular molecules through Au ··· Au interactions, the dimers being considered disc-like molecules having six side chains [13].

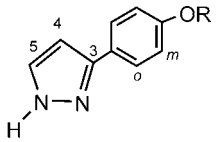
Following these considerations, we thought that, by using pyrazolato groups containing only one side chain at the 3-position, trigonal pyrazolato-metal molecules with only three arms could be obtained, which could be suitable to rearrange through supramolecular interactions in discotic six-arms molecules related to those mentioned above. With this idea in mind, we started to explore the incorporation of a family of 3-long-chain-substituted pyrazolato ligands (pz^R) into gold and silver centers. Related studies were also carried out with symmetrically 3,5-disubstituted pyrazolato groups (pz^{R_2}) derived from the corresponding mesogenic pyrazoles Hpz^{R_2} [24–26] to confirm the proposed behavior.

Our research group has a long-standing interest in the design of LC metal complexes based on long-chain-substituted pyrazole ligands [24][26–28]. We have reported the mesomorphic properties of some of those pyrazoles as well as the ability to generate mesogenic metal derivatives [24][26][27]. Therefore, we thought that these pyrazoles could be used as candidates to produce trinuclear $[M_3(\mu\text{-pz}')_3]$ (M = Ag, Au) compounds (pz′ = pyrazolato ligands derived from 3,5-disubstituted 1*H*-pyrazoles Hpz^{R_2} or 3-substituted 1*H*-pyrazoles Hpz^R), which could behave as discotic metallomesogens if they have the appropriate molecular shape. The analysis of the structural consequences of the substituents on the pyrazole ring should be a useful guide in the design of new trinuclear metal derivatives for potential LC and NLO molecular materials. In this work, new trinuclear metal complexes **7**–**18** derived from the pyrazole ligands **1**–**6** were studied.

2. Results and Discussion. – 2.1. *Pyrazole Ligands.* The following two types of pyrazole derivatives were used for complexation to silver(I) and gold(I) centers: symmetric pyrazoles of type **A** containing (alkyloxy)phenyl or (aryloxy)phenyl substituents at the 3- and 5-positions of the pyrazol ring, *i.e.*, Hpz^{bp_2} (**1**), Hpz^{op_2} (**2**), and Hpz^{pp_2} (**3**), and asymmetric derivatives of type **B** carrying only one (alkyloxy)phenyl substituent at the 3-position with different length of the alkyl chain, *i.e.*, Hpz^{bp} (**4**), Hpz^{ddp} (**5**), and Hpz^{odp} (**6**). All the type-**A** and -**B** ligands, with the exception of **3**, have previously been described, and they were prepared by reported procedures [24][25][27][29]. The new ligand **3** was characterized by IR and ^{1}H-NMR spectroscopy and elemental analysis (see *Exper. Part*). The crystal structure of **3** was also determined (see below).



type A



type B

1 R= C_4H_9 (Hpz^{bp_2})
2 R= C_8H_{17} (Hpz^{op_2})
3 R= C_6H_5 (Hpz^{pp_2})

4 R= C_4H_9 (Hpz^{bp})
5 R= $C_{12}H_{25}$ (Hpz^{ddp})
6 R= $C_{18}H_{37}$ (Hpz^{odp})

Thermal studies by differential scanning microscopy (DSC) and polarized-light microscopy were carried out for all ligands. At variance with the LC behavior of the 3,5-disubstituted 1*H*-pyrazoles **1** and **2**, which exhibit smectic mesophases [24][25], the remaining 1*H*-pyrazoles (the new symmetric **3** and the asymmetric **4**–**6** [27][30]) did not show mesomorphic properties, the absence of those properties being associated with an inadequate length-to-width ratio of the molecules. This fact is basically produced by the shortening of the length of the molecule when only one long substituent was introduced at the 3-position.

2.2. *X-Ray Crystal Structure of 3,5-Bis(4-phenoxyphenyl)-1*H*-pyrazole* (Hpz^{pp_2}; **3**). An X-ray study of **3** was carried out. This pyrazole crystallizes in the $P2_1/c$ space group with four molecules per unit cell. Some representative bond distances and angles are listed in *Table 1*. *Fig. 1* depicts a perspective view of the molecule showing the atom-numbering scheme. As other pyrazoles [24][29][31], **3** shows the characteristic bond distances of a delocalized ring. The same feature is observed for the substituent benzene rings. At variance with the almost linear geometry found in related pyrazoles with (alkyloxy)phenyl substituents [24], this linearity is disrupted in **3** by the presence of the second benzene ring at each substituent. Thus, although the pyrazole ring and the directly bound benzene rings of the substituents are almost planar (dihedral angles of 9.11(6) and 8.12(6)°), the terminal benzene rings are strongly deviated as deduced from

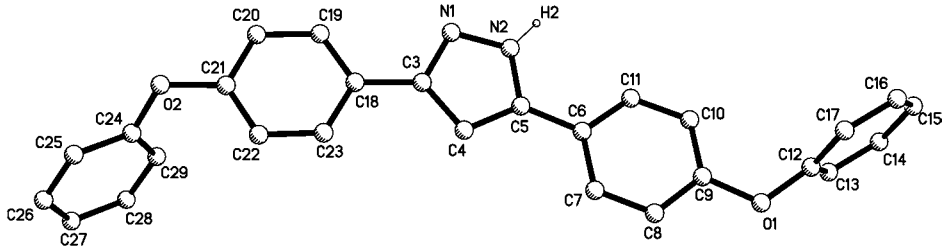


Fig. 1. *Molecular structure of* **3**. H-Atoms, except for H–N(2), have been omitted for clarity. Arbitratry numbering scheme.

Table 1. *Selected Bond Distances* [Å] *and Angles* [°] *for* Hpz^{pp_2} (**3**). For numbering, see *Fig. 1.*

N(1)–N(2)	1.354(2)	N(2)–C(5)	1.345(2)
N(1)–C(3)	1.342(2)	C(3)–C(4)	1.398(2)
C(5)–C(4)	1.385(2)	N(2)–H(2)	0.85
N(2) ··· N(1′)[a])	2.885(2)	N(1′) ··· H(2)[a])	2.16
N(1)–N(2)–C(5)	112.9(1)	C(3)–N(1)–N(2)	105.1(1)
N(2)–C(5)–C(4)	105.6(2)	N(1)–C(3)–C(4)	110.1(2)
C(3)–C(4)–C(5)	106.4(2)	N(2)–H(2) ··· N(1′)[a])	142.2

[a])′ means symmetry operation $1-x, -y, -z$.

the angle formed between the O(1)–O(2) line and the O(1)–C(16) and O(2)–C(27) lines of 49.95(5) and 66.42(4)°, respectively.

The most-interesting feature is related to the presence of a strong NH ··· N intermolecular H-bond between the NH group and the N-atom of neighboring molecules (*Fig. 2*). It suggests a dimeric structure, which has already been observed in other 1*H*-pyrazoles [24] [29]. The crystal packing can be viewed as columns of dimers in an eclipsed stacking along the *b* axis (*Fig. 2*).

2.3. *Pyrazolato-Silver or -Gold(I) Complexes.* The synthesis of tris(μ-pyrazolato-$\kappa N,\kappa N'$)trigold(I) or -silver(I) complexes $[M_3(\mu\text{-pz}')_3]$, *i.e.*, of **7**–**18**, is depicted in the *Scheme*. The compounds were isolated as white solids, soluble in polar solvents. Those derivatives containing symmetric ligands are moderately stable both in solution and in solid state. The remaining complexes are more unstable, exhibiting decomposition with deposition of free metal, and repeated purification procedures were required to allow their characterization. All complexes were studied by IR and ^{1}H-NMR spectroscopy, elemental analysis, and mass spectrometry (see *Exper. Part*). Because all attempts to get adequate crystals for X-ray crystal-structure determination of complexes containing (alkyloxy)phenyl substituents were unsuccessful, we prepared the related derivatives containing the 3,5-bis(4-phenoxyphenyl)pyrazolato ligand derived from **3**. The X-ray crystal structure of the gold complex $[Au_3(\mu\text{-}pz^{pp_2})_3]\cdot CH_2Cl_2$ (**9**) was used as reference for comparative purposes (see below).

The complexes **7** and **9** (Au) and **10** and **12** (Ag) based on **A**-type pyrazolato ligands exhibit the expected signals in their ^{1}H-NMR spectra, consistent with the formation of a trimetallic product containing three equivalent pyrazolato ligands, with a D_{3h}

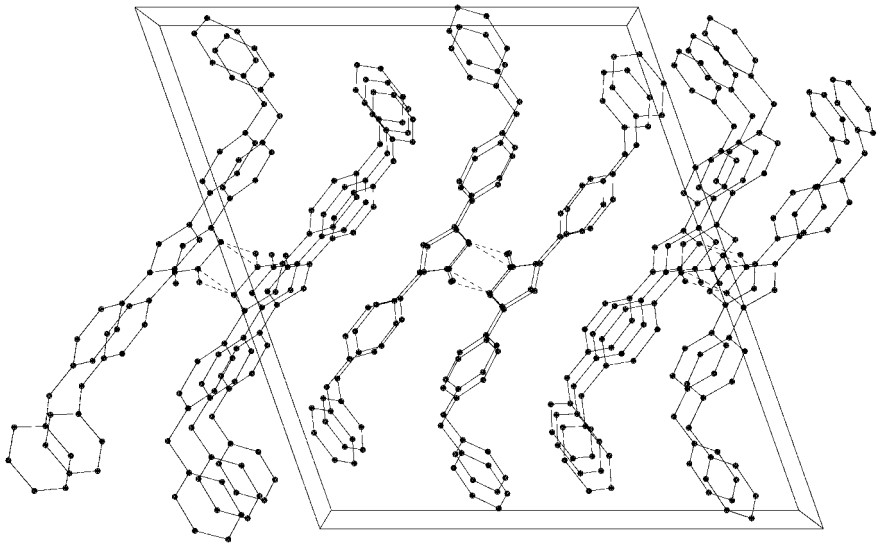
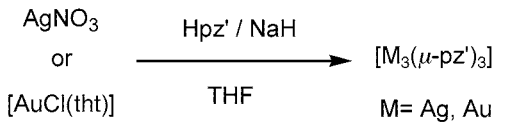


Fig. 2. *Molecular packing of* **3** *through the* b *axis*

Scheme



M= Au	M= Ag	pz'
7	**10**	pz^{bp_2}
8	**11**	pz^{op_2}
9	**12**	pz^{pp_2}
13	**16**	pz^{bp}
14	**17**	pz^{ddp}
15	**18**	pz^{odp}

symmetry, as a consequence of the rotation of the aromatic rings around the C(pyrazolato)-C(phenyl) bond in solution.

The complexes **8** (Au) and **11** (Ag) containing eight C-atoms in the chain substituents could not be isolated as solid products. They were formed as an oil from which a quasi-liquid or waxy material was isolated after repeated attempts. However, the ^{1}H-NMR spectra are analogous to those of the above-mentioned compounds, suggesting the same type of trimetallic complexes. The presence of the long-chain substituents at the 3- and 5-positions of the pyrazole ring appears to be responsible for the non-solid nature of the compounds.

On the other hand, complexes **13**–**18** containing the **B**-type asymmetrically substituted pyrazolato ligands, display different patterns in their ^{1}H-NMR spectra

depending on the metal center. Thus, the gold derivatives **13**–**15** exhibit three H–C(4) and three H–C(5) pyrazolato signals in a 1:1:1 ratio. In some of these cases, the H–C(5) signals have almost identical chemical shifts, giving rise to two 2 *d* in a 2:1 ratio. Similar behavior is observed for the aromatic and the CH_2O protons of the substituents which appear as two H_o and two H_m *d*s ($J \approx 8$ Hz) and two *t*, respectively, in a 4:2 ratio. These results agree with the presence of a asymmetric compound of the type depicted in *Fig. 3*,*a*, which contains three nonequivalent pyrazolato ligands. By contrast, all the silver derivatives **16**–**18** exhibit a simpler ^{1}H-NMR spectrum showing single signals for the H–C(4) and H–C(5) protons as well as those required for the aromatic and alkyl protons of the substituent. Thus, we can deduce that these compounds belong to a family of trimetallic derivatives containing a symmetric C_{3h} structure (*Fig. 3*,*b*).

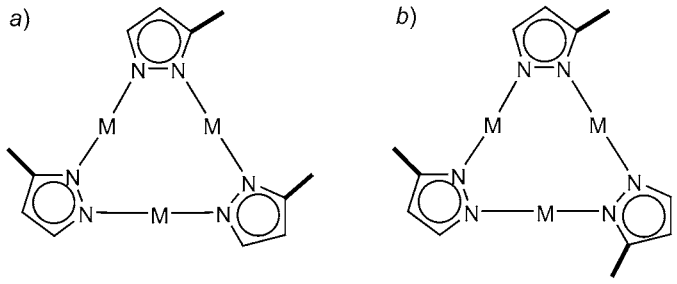


Fig. 3. a) *Asymmetric and* b) *symmetric isomers of* $[M_3(\mu\text{-pz}')_3]$

In the mass spectra (FAB-MS or ESI-MS (positive mode)) of the new complexes, the parent ions of a trimer $[M_3(\mu\text{-pz}')_3]$ are observed in most cases, in agreement with the proposed structure for metallocyclic derivatives. In complexes **12** and **18**, the highest mass fragment observed corresponds to the loss of a pyrazolato ligand. Other fragments from association reactions with the molecular ion were also produced in some of the silver derivatives.

In summary, we have established the formation of cyclic trimers for all selected symmetrical and unsymmetric pyrazolato ligands. The silver complexes with 3-substituted pyrazolato ligands were isolated as symmetrical isomers, while the gold analogues adopted the asymmetric form (*Fig. 3*). The presence of a mixture of the two isomers (a symmetric and an asymmetric one, derived from the disposition of asymmetric substituents at the pyrazolato ligand) has already been reported for several pyrazolato-gold(I) complexes [10][12][14]. However, to the best of our knowledge, this is the first case in which different trinuclear isomers are formed depending on the metal center.

2.4. *Thermal Studies of Complexes* **7**–**18**. Thermal studies of complexes **7**–**18** were carried out by DSC as well as by polarized-light-microscopy observations (see *Exper. Part*). On heating, some of them decomposed, this fact avoiding to get precise results.

On the basis of our and other previous studies, the 3,5-disubstituted 1*H*-pyrazoles Hpz^{R_2} with chains containing from 4 to 18 C-atoms were shown to be calamitic materials [24–26]. By contrast, the 3-substituted 1*H*-pyrazoles Hpz^R did not exhibit

liquid-crystal properties for the same range of C-atoms in the chains [27][30]. However the latter ligands were able to induce mesomorphism on rod-like complexes of the type $[PdCl_2(Hpz^R)_2]$ [27]. Now we used both types of ligands in trinuclear $[M_3(\mu\text{-}pz')_3]$ complexes with an approximately disc-like shape.

At variance with the mesogenic parent Hpz^{R_2} ligands [24][25], none of their trinuclear gold or silver derivatives **7**, **8**, **10**, and **11** showed LC properties.

Quite interestingly, the coordination of the non-mesogenic Hpz^{ddp} as pyrazolato ligand to gold and silver (complexes **14** and **17**) results in the appearence of mesomorphic behavior. By contrast, the other related complexes with shorter ($n = 4$) or longer ($n = 18$) chains, *i.e.*, **13**, **15**, **16**, and **18**, behave as nonliquid-crystal materials. It appears that the increase to 18 C-atoms in the alkyl chains probably disrupts the ordering on the columnar arrangement in the mesophases. The same results could be attributed to the presence of substituent chains with only four C-atoms which does not appear to be long enough to induce mesomorphic properties.

The new complexes **14** and **17** exhibit a monotropic behavior. The observed textures are fan-like or pseudo-focal-conic, which are typical of columnar mesophases (*Fig. 4*). For the gold derivative **14**, the mesophase is observed on cooling at 83.5° only when the temperature is very slowly modified. The DSC thermogram shows a very broad peak between 100 and 80° for this process. By heating from the mesophase, the mesophase to isotropic transformation (clearing point) is observed at 90.5°. The mesophase texture remains when the crystallization begins to take place, which is detected by DSC at an onset temperature of 76.4°. The silver complex **17** exhibits a related mesomorphic behavior. Upon heating and subsequent cooling, a mesophase is detected by microscopy at 96°, but the darkness precludes to see clearly the fan-like texture. The crystallization process is observed at 86°. By DSC, only a broad peak on cooling is found at an onset temperature of 93.4°, and it is attributed to the overlapping of the isotropic-mesophase and crystallization processes. Comparing the thermal behavior of both the gold and silver complexes **14** and **17** reveals, remarkably, that the latter is

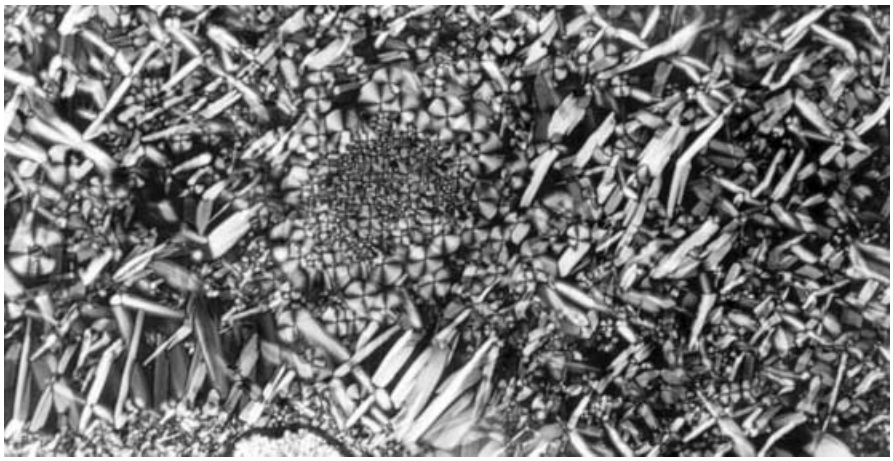


Fig. 4. *Photomicrograph of the texture of the mesophase of* $[Au_3(\mu\text{-}pz^{ddp})_3]$ **14** *at 81°* (on cooling)

associated to an increase in the melting and clearing points. This effect may be related to the differences on the molecular symmetry.

2.5. *X-Ray Structure of* $[Au_3(pz^{pp_2})_3] \cdot CH_2Cl_2$ ($\mathbf{9} \cdot CH_2Cl_2$). As mentioned above, the bulky 3,5-bis(4-phenoxyphenyl)pyrazolato ligand was not used as organic ligand looking for mesogenic compounds but was employed to obtain insights into its influence on the oligomerized structure of its silver or gold derivatives.

We made different attempts to obtain crystals for all of the pyrazolato complexes prepared, but unfortunately, we only got adequate crystals for X-ray studies, although of poor quality, of $[Au_3(\mu\text{-}pz^{pp_2})_3] \cdot CH_2Cl_2$ ($\mathbf{9} \cdot CH_2Cl_2$). However, the analysis of its structure was considered of interest since it could establish the molecular nuclearity as well as the crystal packing.

The crystal structure of $\mathbf{9} \cdot CH_2Cl_2$ consists indeed of discrete trimeric molecules (see *Fig. 5* for a perspective view and the atom-numbering scheme). *Table 2* lists the most-relevant bond distances and angles. The complex crystallizes in the $P\bar{1}$ space group. The asymmetric unit consists of one indepedent trimeric molecule. There is also a CH_2Cl_2 molecule of crystallization bonded through a weak H-bonding interaction to the trimetallic unit (Cl(1) ··· H(27B) 2.96(1) Å, C(27) ··· Cl(1) 3.64(2) Å, C(27)–H(27B) ··· Cl(1) 131(1)°). This could be responsible for the decomposition of the crystals at room temperature and, therefore, the data collection was carried out at low temperature (see *Exper. Part*).

The nine-membered ring formed by three Au-atoms and six pyrazolato N-atoms is nonplanar and slightly nonregular and distorted. Similar features have been found for the reported complexes $[Au_3(\mu\text{-}pz^{R_2})_3]$ ($R = CF_3$, $MeOC_6H_4$) [11][12] and $[Ag_3(\mu\text{-}pz^{Ph_2})_3]$ [9], while the related $[Au_3(\mu\text{-}pz^{Ph_2})_3]$ showed a planar and symmetric nine-

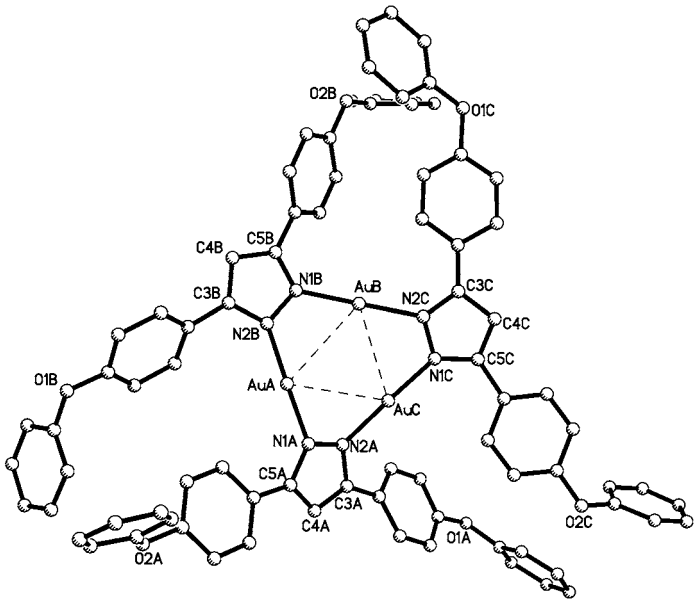


Fig. 5. *Molecular structure of* $\mathbf{9} \cdot CH_2Cl_2$. H-Atoms and solvent molecule have been omitted for clarity.

Table 2. *Selected Bond Distances* [Å] *and Angles* [°] *of* $[Au_3(\mu\text{-}pz^{pp_2})_3]\cdot Ch_2Cl_2$ ($\mathbf{9}\cdot CH_2Cl_2$)

Au(A) ··· Au(B)	3.347(1)	Au(B)–N(2C)	2.04(2)
Au(A) ··· Au(C)	3.358(1)	Au(C)–N(1C)	1.97(2)
Au(B) ··· Au(C)	3.224(1)	Au(C)–N(2A)	2.00(2)
Au(A)–N(2B)	1.96(2)	N(1A)–N(2A)	1.32(2)
Au(A)–N(1A)	2.09(2)	N(1B)–N(2B)	1.42(2)
Au(B)–N(1B)	2.00(2)	N(1C)–N(2C)	1.40(2)
N(2B)–Au(A)–N(1A)	174.2(6)	Au(B)–N(2C)–N(1C)	117(1)
Au(A)–N(1A)–N(2A)	115(1)	N(2A)–Au(C)–N(1C)	175.3(6)
Au(A)–N(1B)–N(2B)	117(1)	Au(C)–N(2A)–N(1A)	120(1)
N(1B)–Au(B)–N(2C)	178.6(7)	Au(C)–N(1C)–N(2C)	118(1)
Au(B)–N(1B)–N(2B)	118(1)		

membered ring [9]. A linear coordination at the Au^I atom is present in the trimer, the N–Au–N angles ranging between 174.2(6)° and 178.6(7)°. The Au–N lengths are in the 1.96–2.09(2) Å interval with a mean distance of 2.01(2) Å, these distances being very close to those complexes containing phenyl substituents (1.97–2.07 Å) [9][12][32][33]. The Au ··· Au distances in the trimers are 3.224(1), 3.347(1), and 3.358(1) Å (mean value of 3.310 Å), much longer than in metallic gold (2.884 Å) [34], and similar to those observed in other pyrazolato-gold(I) complexes (3.25–3.43 Å) [9][11–14]. A weak Au ··· Au intramolecular bonding interaction is suggested because all Au ··· Au distances are shorter than the calculated value for a planar nine-membered metallocycle (*ca.* 3.4 Å) [12].

The three pyrazole rings are not exactly coplanar among them, the dihedral angles ranging from 13.5(6) to 30.8(7)°. Additionally, these pyrazole rings and their own directly bound phenyl groups do not maintain the planarity observed in the free ligand (angles between 17.1(7) and 49.2(7)° in $\mathbf{9}\cdot CH_2Cl_2$ and *ca.* 9° in **3**). Besides, the terminal benzene rings are even more deviated from that planarity, and they are twisted from 55(1) to 88.3(7)° with respect to interior benzene rings. Despite these features, by assuming free rotation of the phenyl substituents, a trigonal symmetry could be defined for the whole molecule, a consequence of the bonds established between the metal and the pyrazolato ligands.

The molecular packing of the trimers corresponds to a columnar distribution. The columns are parallel to the crystallographic *a* axis, and they are formed by trimers that are stacked in an alternate disposition as depicted in *Fig. 6*. The Au_3 plane of trimers are not orthogonal to the *a* axis but deviated by 48.51(2)°. Therefore, the shortest Au ··· Au distance between consecutive trimers of 4.639(1) Å is derived for the orientation of the trimers along the columns. However the distance between the centroids of the Au_3 planes of consecutive trimers in the column is *ca.* 6.7 Å, longer than that reported for the related compound with methoxyphenyl as substituents (4.54 Å) [12] which is a typical intermolecular distance in LC materials with disc-like molecules [35]. This disposition in $\mathbf{9}\cdot CH_2Cl_2$ could be explained by the presence of the terminal phenyl group at the pyrazolato substituents, which must be responsible for the generation of a higher intermolecular separation.

Thus, we established that the intermolecular separation in the columns is the main difference of the structural features of $\mathbf{9}\cdot CH_2Cl_2$ as compared to other complexes also

Fig. 6. *Molecular packing of* **9** · CH_2Cl_2 *through the* b *axis.* The terminal benzene rings of the pyrazolato ligands have been omitted for clarity.

containing phenyl substituents at the pyrazolato ligands [9][12]. Therefore, columnar arrangements with shorter intermolecular separation should not be excluded as potential structures for the trimers with other (alkyloxy)phenyl substituents than the phenoxyphenyl groups.

Conclusions. – In this work, we showed that the coordination of different 3-substituted or 3,5-disubstituted pyrazolato ligands to gold or silver centers does not modify the formation of trinuclear cyclic complexes. As expected the 3,5-disubstituted pyrazolato complexes gave rise to a sole isomer consistent with a D_{3h} symmetry. By contrast, the 3-substituted pyrazolato derivatives yielded an Ag-symmetric or Au-asymmetric isomer. Of all investigated complexes, only those containing 3-[4-(dodecyloxy)phenyl] substituents $[M_3(\mu\text{-}pz^{ddp})_3]$ (M = Ag, Au) displayed mesomorphic properties associated with the presence of columnar mesophases. This organization is consistent with the columnar distribution of disc-like nonplanar trimers observed in the X-ray structure of the Au derivative containing the 3,5-bis(4-phenoxyphenyl)pyrazo-

lato ligand, which, in turn, behaves as a non-mesogenic material due to the absence of alkyl chains at the periphery.

On the other hand, although an increase in the number of alkyl chains at the bridging pyrazolato ligand should give rise to a higher-occupied surface favoring the disc-like structure, we found that, for the cyclic trinuclear compounds $[M_3(\mu\text{-pz}')_3]$, the presence of bridging 3-substituted pyrazolato ligands could be a sufficient requirement to get mesomorphic properties when an adequate chain is selected. New complexes will be prepared to assess these results.

We are grateful to the *DGI/MCyT of Spain* (Project No. PB98-0766) for financial support. We also thank the *Comunidad de Madrid* for a postdoctoral fellowship to *M. C. T.*

Experimental Part

General. The starting Au-complex [AuCl(tht)] (tht = tetrahydrothiophene) and the 3-substituted and 3,5-disubstituted [(alkyloxy)phenyl]-1*H*-pyrazoles were prepared by procedures described in [24][25][27][29][36]. The 1,3-bis(4-phenoxyphenyl)propane-1,3-dione was also prepared by a known method [37]. All commercial reagents were used as supplied. Phase studies: *Olympus BX50* microscope equipped with a *Linkam THMS-600* heating stage; temp. assignment on the basis of visual observations with polarized light. Differential scanning calorimetry (DSC): *Perkin-Elmer Pyris-1* calorimeter; sample (1–4 mg) hermetically sealed in aluminium pans; heating or cooling rate of 5–10°/min. IR Spectra: *FT-IR Nicolet Magna-550* spectrophotometer; KBr discs; 4000–350 cm^{-1} region; in cm^{-1}. ^{1}H- and $^{13}C\{^1H\}$-NMR Spectra: *Varian VXR-300*, *Bruker DPX-300*, or *Bruker AC-200* spectrophotometers; $CDCl_3$ solns.; chemical shifts δ in ppm rel. to $SiMe_4$, with the signal of the deuterated solvent as reference, J in Hz; δ(H) and δ(C) accurate to ± 0.01 and ± 0.1 ppm, respectively, J(H,H) to ± 0.3 Hz; atomic numbering as shown in **1**–**6**. MS: *VG AutoSpec* spectrometer (FAB), or *LC Squire* spectrometer (ESI); dry MeCN, $CHCl_3$, or MeOH as solvents; in m/z. Elemental analyses (C, H, N) were carried out by the Centre for Elemental Microanalysis of the Complutense University.

*3,5-Bis(4-phenoxyphenyl)-1*H*-pyrazole* (Hpz^{pp_2}; **3**). To a suspension of 1,3-bis(4-phenoxyphenyl)propane-1,3-dione (2 mmol) in EtOH (50 ml) was added an excess of hydrazine hydrate (2.2 mmol), and the mixture was refluxed for 3 h. Then, the soln. was allowed to cool at r.t. and kept overnight at 4°. The precipitated product was filtered and dried *in vacuo*; **3** (*ca*. 75%). M.p. 185°. IR (KBr): 3225 (NH), 1588 (CN). ^{1}H-NMR ($CDCl_3$): 10.90 (br. *s*, NH); 7.67 (*d*, J = 8.7, H_o); 7.36 (*t*, J = 7.8, $H_{m'}$); 7.13 (*t*, J = 7.5, $H_{p'}$); 7.05 (*d*, J = 8.6, H_m, $H_{o'}$); 6.74 (*s*, H–C(4)). ^{13}C-NMR ($CDCl_3$): 157.4; 156.8; 148.3; 129.8; 127.1; 126.2; 123.6; 119.2; 118.8; 99.5. FAB-MS: 405 ($[M+H]^+$). Anal. calc. for $C_{27}H_{20}N_2O_2$: C 80.2, H 5.0, N 6.9; found: C 79.9, H 5.2, N 6.7.

Preparation of [$M_3(\mu\text{-pz}')_3$] (M = Au, Ag) *Complexes* **7**–**18**. To a soln. of the corresponding 1*H*-pyrazole (26 mmol) in dry THF (25 ml) under N_2 an excess 60% NaH was added. After a few minutes of stirring, $AgNO_3$ or [AuCl(tht)] (26 mmol) was added. After 24 or 6 h for Ag or Au derivatives, resp., the formed solid was filtered and washed with THF. The soln. was evaporated and the oily solid obtained recrystallized in CH_2Cl_2/hexane.

cyclo-*Tris[μ-[3,5-bis(4-butoxyphenyl)-1*H*-pyrazolato-κN^1:κN^2]]trigold* ($[Au_3(\mu\text{-pz}^{bp_2})_3]$; **7**): M.p.: dec. from 160°, complete melting at 251°. IR (KBr): 1612 (CN). ^{1}H-NMR ($CDCl_3$): 7.71 (*d*, J = 7.8, H_o); 6.76 (*s*, H–C(4)); 6.65 (*d*, J = 7.8, H_m); 3.90 (*t*, J = 6.3, CH_2O); 1.78 (*quint.*, CH_2); 1.51 (*sext.*, CH_2); 1.00 (*t*, J = 7.3, Me). Anal. calc. for $C_{96}H_{81}Au_3N_6O_6$: C 48.7, H 4.8, N 4.9; found: C 49.0, H 4.9, N 5.0.

cyclo-*Tris{μ-[3,5-bis[4-(octyloxy)phenyl]-1*H*-pyrazolato-κN^1:κN^2]}trigold* ($[Au_3(\mu\text{-pz}^{op_2})_3]$; **8**): M.p. 85°. IR (KBr): 1613 (CN). ^{1}H-NMR ($CDCl_3$): 7.74 (*d*, J = 8.5, H_o); 6.84 (*d*, J = 8.5, H_m); 6.68 (*s*, H–C(4)); 3.95 (*t*, J = 6.4, CH_2O); 1.78 (*m*, CH_2); 1.6–1.2 (*m*, $(CH_2)_5$); 0.89 (*t*, J = 6.7, Me). ESI-MS: 2018 ($[Au_3pz_3+H]^+$), 1345 ($[Au_2pz_2]^+$). Anal. calc. for $C_{93}H_{129}Au_3N_6O_6$: C 55.4, H 6.4, N 4.2; found: C 55.6, H 6.5, N 4.2.

cyclo-*Tris{μ-[3,5-bis(4-phenoxyphenyl)-1H-pyrazolato-κN^1:κN^2]}trigold* ($[Au_3(\mu\text{-pz}^{pp_2})_3]$; **9**): M.p. 220° (dec.). IR (KBr): 1588 (CN). ^{1}H-NMR ($CDCl_3$): 7.71 (*d*, J = 8.4, H_o); 7.31 (*t*, J = 7.8, $H_{m'}$); 7.10 (*t*, J = 7.5, $H_{p'}$); 7.03 (*d*, J = 7.8, $H_{o'}$); 6.78 (*s*, H–C(4)); 6.77 (*d*, J = 8.4, H_m). FAB-MS: 1800 ($[Au_3pz_3]^+$), 1397 ($[Au_3pz_2]^+$), 1200 ($[Au_2pz_2]^+$). Anal. calc. for $C_{81}H_{57}Au_3N_6O_6$; C 54.0, H 3.2, N 4.7; found: C 53.8, H 3.2, N 4.7.

cyclo-*Tris{μ-[3,5-bis(4-butoxyphenyl)-1*H*-pyrazolato-κN^1:κN^2]}trisilver* ($[Ag_3(\mu\text{-pz}^{bp_2})_3]$; **10**): M.p. 219°. IR (KBr): 1612 (CN). ^{1}H-NMR ($CDCl_3$): 7.53 (*d*, J = 8.7, H_o); 6.67 (*d*, J = 8.7, H_m); 6.59 (*s*, H–C(4)); 3.86 (*t*, J = 6.6, CH_2O); 1.72 (*quint.*, CH_2); 1.48 (*sext.*, CH_2); 0.98 (*t*, J = 7.3, Me). ^{13}C-NMR ($CDCl_3$): 158.9; 153.5; 127.4;

127.3; 114.6; 100.0; 67.7; 31.4; 19.3; 14.0. FAB-MS: 1414 ($[Ag_3pz_3]^+$), 1050 ($[Ag_3pz_2]^+$), 944 ($[Ag_2pz_2]^+$), 471 ($[Agpz]^+$). Anal. calc. for $C_{69}H_{81}Ag_3N_6O_6$: C 58.6, H 5.8, N 5.9; found: C 58.7, H 5.8, N 5.9.

cyclo-*Tris{μ-[3,5-bis[4-(octyloxy)phenyl]-1*H*-pyrazolato-κN¹:κN²]}trisilver* ($[Ag_3(\mu\text{-}pz^{op_2})_3]$; **11**): M.p. 80–100° (onset at 93°). IR (KBr): 1613 (CN). ^{1}H-NMR ($CDCl_3$): 7.57 (*d*, *J* = 8.8, H_o); 6.68 (*d*, *J* = 8.8, H_m); 6.62 (*s*, H–C(4)); 3.88 (*t*, *J* = 6.6, CH_2O); 1.76 (*m*, CH_2); 1.6–1.2 (*m*, $(CH_2)_5$); 0.91 (*t*, *J* = 6.8, Me). ESI-MS: 1750 ($[Ag_3pz_3]^+$), 1273 ($[Ag_3pz_2]^+$), 1167 ($[Ag_2pz_2]^+$), 692 ($[Ag_2pz]^+$). Anal. calc. for $C_{93}H_{129}Ag_3N_6O_6$: C 63.8, H 7.4, N 4.8; found: C 64.0, H 7.5, N 4.9.

cyclo-*Tris{μ-[3,5-bis(4-phenoxyphenyl)-1*H*-pyrazolato-κN¹:κN²]}trisilver* ($[Ag_3(\mu\text{-}pz^{pp_2})_3]$; **12**): M.p. 155–180° (onset at 164°). IR (KBr): 1588 (CN). ^{1}H-NMR ($CDCl_3$): 7.61 (*d*, *J* = 8.0, H_o); 7.33 (*t*, *J* = 7.8, $H_{m'}$); 7.13 (*t*, *J* = 7.4, $H_{p'}$); 7.03 (*d*, *J* = 7.8, $H_{o'}$); 6.85 (*d*, *J* = 8.1, H_m); 6.70 (*s*, H–C(4)). ^{13}C-NMR ($CDCl_3$): 157.4; 156.5; 154.4; 128.8; 128.2; 127.7; 123.6; 119.5; 118.6; 101.0. FAB-MS: 1131 ($[Ag_3pz_2]^+$), 1022 ($[Ag_2pz_2]^+$), 510 ($[Agpz]^+$). Anal. calc. for $C_{81}H_{57}Ag_3N_6O_6$: C 63.4, H 3.8, N 5.5; found: C 63.1, H 3.6, N 5.4.

cyclo-*Tris{μ-[3-(4-butoxyphenyl)-1*H*-pyrazolato-κN¹:κN²]}trigold* ($[Au_3(\mu\text{-}pz^{bp})_3]$; **13**): IR (KBr): 1612 (CN). ^{1}H-NMR ($CDCl_3$): 7.91 (*d*, *J* = 8.8, H_o); 7.63 (*d*, *J* = 8.5, H_o); 7.44 (*d*, *J* = 2.3, H–C(5)); 7.33 (*d*, *J* = 2.3, H–C(5)); 6.96 (*d*, *J* = 8.8, H_m); 6.63 (*d*, *J* = 8.5, H_m); 6.61 (*d*, *J* = 2.3, H–C(4)); 6.56 (*d*, *J* = 2.3, H–C(4)); 6.54 (*d*, *J* = 2.0, H–C(4)); 4.02 (*t*, *J* = 6.5, CH_2O); 3.90 (*t*, *J* = 6.5, CH_2O); 1.78 (*m*, CH_2); 1.55 (*m*, CH_2); 1.00 (*t*, *J* = 7.3, Me). ESI-MS: 1236 ($[Au_3pz_3]^+$). Anal. calc. for $C_{39}H_{45}Au_3N_6O_3$: C 37.9, H 3.7, N 6.8; found: C 38.1, H 3.7, N 6.8.

cyclo-*Tris{μ-[3-[4-(dodecyloxy)phenyl]-1*H*-pyrazolato-κN¹:κN²]}trigold* ($[Au_3(\mu\text{-}pz^{ddp})_3]$; **14**): M.p. 103°. IR (KBr): 1609 (CN). ^{1}H-NMR ($CDCl_3$): 7.88 (*d*, *J* = 8.8, H_o); 7.57 (*d*, *J* = 8.5, H_o); 7.28 (*d*, *J* = 2.2, H–C(5)); 7.18 (*d*, *J* = 2.4, H–C(5)); 6.90 (*d*, *J* = 8.8, H_m); 6.58 (*d*, *J* = 8.5, H_m); 6.48 (*d*, *J* = 2.2, H–C(4)); 6.44 (*d*, *J* = 2.2, H–C(4)); 6.43 (*d*, *J* = 2.2, H–C(4)); 4.00 (*t*, *J* = 6.3, CH_2O); 3.88 (*t*, *J* = 6.1, CH_2O); 1.80 (*m*, CH_2); 1.6–1.2 (*m*, $(CH_2)_9$); 0.89 (*t*, *J* = 6.6, Me). ESI-MS: 1572 ($[Au_3pz_3]^+$). Anal. calc. for $C_{63}H_{93}Au_3N_6O_3$: C 48.1, H 6.0, N 5.3; found: C 48.1, H 5.8, N 5.4.

cyclo-*Tris{μ-[3-[4-(octadecyloxy)phenyl]-1*H*-pyrazolato-κN¹:κN²]}trigold* ($[Au_3(\mu\text{-}pz^{odp})_3]$; **15**): M.p. 87–92° (dec.). IR (KBr): 1613 (CN). ^{1}H-NMR ($CDCl_3$): 7.91 (*d*, *J* = 8.5, H_o); 7.62 (*d*, *J* = 8.8, H_o); 7.42 (*d*, *J* = 2.0, H–C(5)); 7.41 (*d*, *J* = 2.2, H–C(5)); 7.31 (*d*, *J* = 2.4, H–C(5)); 6.94 (*d*, *J* = 8.8, H_m); 6.62 (*d*, *J* = 8.5, H_m); 6.59 (*d*, *J* = 2.4, H–C(4)); 6.54 (*d*, *J* = 2.2, H–C(4)); 6.53 (*d*, *J* = 2.0, H–C(4)); 4.01 (*t*, *J* = 6.6, CH_2O), 3.89 (*t*, *J* = 6.8, CH_2O); 1.79 (*m*, CH_2); 1.6–1.2 (*m*, $(CH_2)_{15}$); 0.88 (*t*, *J* = 6.1, Me). ESI-MS: 1825 ($[Au_3pz_3 + H]^+$), 1216 ($[Au_2pz_2]^+$). Anal. calc. for $C_{81}H_{129}Au_3N_6O_3$: C 53.3, H 7.1, N 4.6; found: C 53.1, H 7.0, N 4.6.

cyclo-*Tris{μ-[3-(4-butoxyphenyl)-1*H*-pyrazolato-κN¹:κN²]}trisilver* ($[Ag_3(\mu\text{-}pz^{bp})_3]$; **16**): M.p. 162°. IR (KBr): 1613 (CN). ^{1}H-NMR ($CDCl_3$): 7.59 (*d*, *J* = 8.5, H_o); 7.50 (*d*, *J* = 2.0, H–C(5)); 6.81 (*d*, *J* = 8.3, H_m); 6.50 (*d*, *J* = 2.0, H–C(4)); 3.96 (*t*, *J* = 6.3, CH_2O); 1.80 (*quint.*, CH_2); 1.54 (*m*, CH_2); 1.01 (*t*, *J* = 7.3, Me). ESI-MS: 970 ($[Ag_3pz_3]^+$), 755 ($[Ag_3pz_2]^+$). Anal. calc. for $C_{39}H_{45}Ag_3N_6O_3$: C 48.3, H 4.7, N 8.7; found: C 48.5, H 4.5, N 8.5.

cyclo-*Tris{μ-[3-[4-(dodecyloxy)phenyl]-1*H*-pyrazolato-κN¹:κN²]}trisilver* ($[Ag_3(\mu\text{-}pz^{ddp})_3]$; **17**): M.p. 125°. IR (KBr): 1612 (CN). ^{1}H-NMR ($CDCl_3$): 7.59 (*d*, *J* = 8.3, H_o); 7.51 (*d*, *J* = 1.8, H–C(5)); 6.78 (*d*, *J* = 8.3, H_m); 6.50 (*d*, *J* = 2.0, H–C(4)); 3.94 (*t*, *J* = 6.3, CH_2O); 1.80 (*m*, CH_2); 1.6–1.2 (*m*, $(CH_2)_{15}$); 0.88 (*t*, *J* = 6.5, Me). ESI-MS: 1306 ($[Ag_3pz_3]^+$). Anal. calc. for $C_{63}H_{93}Ag_3N_6O_3$: C 57.9, H 7.2, N 6.4; found: C 58.0, H 7.1, N 6.3.

cyclo-*Tris{μ-[3-[4-(octadecycloxy)phenyl]-1*H*-pyrazolato-κN¹:κN²]}trisilver* ($[Ag_3(\mu\text{-}pz^{odp})_3]$; **18**): M.p. 108° (dec.). IR (KBr): 1611 (CN). ^{1}H-NMR ($CDCl_3$): 7.48 (*d*, *J* = 8.3, H_o); 7.32 (*d*, *J* = 1.8, H–C(5)); 6.73 (*d*, *J* = 8.3, H_m); 6.39 (*d*, *J* = 2.0, H–C(4)); 3.91 (*t*, *J* = 6.6, CH_2O); 1.80 (*m*, CH_2); 1.6–1.2 (*m*, $(CH_2)_9$); 0.89 (*t*, *J* = 6.9, Me). ESI-MS: 1147 ($[Ag_3pz_2]^+$), 519 ($[Agpz]^+$). Anal. calc. for $C_{81}H_{129}Ag_3N_6O_3$: C 62.4, H 8.3, N 5.4; found: C 62.0, H 8.3, N 5.4.

2.3. *X-Ray Structure Determination*. Colorless prismatic single crystals of Hpz^{pp_2} (**3**) were obtained by layering CH_2Cl_2 solns. with Et_2O. Light yellow crystals of $[Au_3(\mu\text{-}pz^{pp_2})_3] \cdot CH_2Cl_2$ (**9** · CH_2Cl_2) were obtained by layering CH_2Cl_2 solns. with hexane. The data were collected on a *Smart Bruker CCD* diffractometers. For data, see *Table 3*.

The structures were solved by direct methods and conventional *Fourier* techniques and refined by full-matrix least-squares treatment on F^2 [38]. Final mixed refinements were performed for the two compounds with the following differences. For **3**, all non-H-atoms were refined anisotropically. H-Atoms were calculated and refined as riding on the C-bonded atom, except for H–N(2) bonded to N(2), which was found as the first peak in a *Fourier* difference, included, and its coordinates fixed. The largest residual peak in the final difference map was 0.19 eÅ^{-3}.

Many attempts were made to obtain crystals of the trimetallic compounds of good quality. However only light yellow crystals of $[Au_3(\mu\text{-}pz^{pp_2})_3] \cdot CH_2Cl_2$ (**9** · CH_2Cl_2) could be obtained but of poor quality. In spite of this,

Table 3. *Crystal and Refinement Data for* Hpz^{pp_2} (**3**) *and* $[Au_3(\mu\text{-}pz^{pp_2})_3]\cdot Ch_2Cl_2$ (**9**·CH_2Cl_2)

	3	**9**
Formula	$C_{27}H_{20}N_2O_2$	$C_{82}H_{59}Au_3Cl_2N_6O_6$
M	404.45	1886.15
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P(-1)$
a/Å	20.7353(5)	13.343(1)
b/Å	5.6467(1)	15.207(1)
c/Å	18.8420(5)	17.755(1)
α/°		97.996(1)
β/°	109.521(1)	92.271(1)
γ/°		106.484(1)
U/Å^3	2079.32(8)	3408.9(4)
Z	4	2
$F(000)$	848	1824
D_c/g cm^{-3}	1.292	1.838
Temp./K	293(2)	173(2)
μ(Mo-$K\alpha$)/mm^{-1}	0.082	6.580
Crystal size/mm	$0.21\times0.21\times0.08$	$0.36\times0.10\times0.06$
Scan technique	θ and ω	θ and ω
Data collected	$(-24,-6,0)$ to (23,0,22)	$(-15,-13,-20)$ to (14,18,21)
θ/°	2.08–25.03	2.71–25.00
Refls. collected	3662	14673
Unique refls.	3662	11054 ($R_{int}=0.1819$)
Data, restraints, parameters	3662, 0, 281	11054, 0, 412
G.o.f (F^2)	1.025	1.030
$R(F)$ [$(F^2)>2\sigma(F^2)$][a])	0.047 (3662 refls.)	0.084 (7502 refls.)
$wR(F^2)$ (all data)[b])	0.137	0.242
Largest residual peak/e Å^{-3}	0.194	4.164

[a]) $\Sigma[|F_o|-|F_c|]/\Sigma|F_o|$. [b]) $\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

we considered it of interest to solve the structure to know the nuclearity degree and the molecular packing. Therefore, data collection and refinement of different crystals were carried out, at r.t. or at 173 K, obtaining better agreement factors at low temp. The different attempts carried out to solve the structure at r.t. gave rise to data decay. The weak H-bonding interaction between the CH_2Cl_2 molecule and a C-atom of one phenyl group observed could explain the decomposition observed at r.t. The compound crystallized in the triclinic system, and then the refinement was carried out in the centric ($P\bar{1}$) and acentric ($P1$) space groups. The acentric model led to poorer agreement factors, and, therefore, we proposed a structural model in the centric space group. The Au-atoms were refined anisotropically, while the remaining non-H-atoms were refined only isotropically because some thermal factors became negative. The H-atoms were calculated and refined as riding on the C-bonded atom with a common isotropic displacement parameter. All of these problems are reflected in the high R factors. The largest residual peaks in the final difference map were located in the vicinity of one Au-atom.

Supplementary crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* (CCDC deposition numbers 210429 and 210430 for **3** and **9**, resp.). These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the *Cambridge Crystallographic Data Center*, 12 Union Road, Cambridge CB2 EZ, UK; fax: +441223336033; e-mail: deposit@ccdc.cam.ac.uk).

REFERENCES

[1] G. La Monica, G. A. Ardizzoia, *Prog. Inorg. Chem.* **1997**, *46*, 151.
[2] S. Trofimenko, *Prog. Inorg. Chem.* **1986**, *34*, 115.
[3] S. Trofimenko, *Chem. Rev.* **1972**, *72*, 497.

[4] N. Masciocchi, M. Moret, P. Cariati, A. Sironi, G. A. Ardizzoia, G. La Monica, *J. Am. Chem. Soc.* **1994**, *116*, 7668.
[5] H. Okkersen, W. L. Groeneveld, J. Reedijk, *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 945.
[6] P. Ovejero, M. Cano, E. Pinilla, M. R. Torres, *Helv. Chim. Acta* **2002**, *85*, 1686, and refs. cit. therein.
[7] K. Nomiya, R. Noguchi, K. Ohsawa, K. Tsuda, M. Oda, *J. Inorg. Biochem.* **2000**, *78*, 363, and refs. cit. therein.
[8] H. Schmidbaur, *Nature (London)* **2001**, *413*, 31, and refs. cit. therein
[9] H. H. Murray, R. G. Raptis, J. P. Fackler Jr., *Inorg. Chem.* **1988**, *27*, 26.
[10] F. Bonati, A. Burini, B. R. Pietroni, R. Galassi, *Gazz. Chim. Ital.* **1993**, *123*, 691.
[11] B. Bovio, F. Bonati, G. Banditelli, *Inorg. Chim. Acta* **1984**, *87*, 25.
[12] J. Barberá, A. Elduque, R. Giménez, F. J. Lahoz, J. A. López, L. A. Oro, J. L. Serrano, *Inorg. Chem.* **1998**, *37*, 2960.
[13] S. J. Kim, S. H. Kang, K. M. Park, H. Kim, W. C. Zin, M. G. Choi, K. Kim, *Chem. Mater.* **1998**, *10*, 1889.
[14] G. Yang, R. G. Raptis, *Inorg. Chem.* **2003**, *42*, 261.
[15] M. Enomoto, A. Kishimura, T. Aida, *J. Am. Chem. Soc.* **2001**, *123*, 5608.
[16] G. Minghetti, G. Banditelli, F. Bonati, *Inorg. Chem.* **1979**, *18*, 658.
[17] N. Masciocchi, P. Cariati, A. Sironi, *Powder Diffr.* **1998**, *13*, 35.
[18] R. G. Raptis, J. P. Fackler Jr., *Inorg. Chem.* **1988**, *27*, 4179.
[19] R. G. Raptis, H. H. Murray, J. P. Fackler Jr., *J. Chem. Soc., Chem. Commun.* **1987**, 737.
[20] V. R. Thalladi, S. Brasselet, D. Blässer, R. Boese, J. Zyss, A. Nangia, G. R. Desiraju, *Chem. Commun.* **1997**, 1841.
[21] V. R. Thalladi, S. Brasselet, H. C. Weiss, D. Blässer, A. K. Katz, H. L. Carroll, R. Boese, J. Zyss, A. Nangia, G. R. Desiraju, *J. Am. Chem. Soc.* **1998**, *120*, 2563, and ref. cit. therein.
[22] H. Le Bozec, T. Renouard, *Eur. J. Inorg. Chem.* **2000**, 229, and ref. cit. therein.
[23] J. Barberá, A. Elduque, R. Giménez, L. A. Oro, J. L. Serrano, *Angew. Chem., Int. Ed.* **1996**, *35*, 2832.
[24] M. C. Torralba, M. Cano, J. A. Campo, J. V. Heras, E. Pinilla, M. R. Torres, *J. Organomet. Chem.* **2002**, *654*, 150.
[25] J. Barberá, C. Cativiela, J. L. Serrano, M. M. Zurbano, *Liq. Cryst.* **1992**, *11*, 887.
[26] M. C. Torralba, M. Cano, S. Gómez, J. A. Campo, J. V. Heras, J. Perles, C. Ruiz-Valero, *J. Organomet. Chem.* **2003**, *682*, 26.
[27] M. C. Torralba, M. Cano, J. A. Campo, J. V. Heras, E. Pinilla, M. R. Torres, *Inorg. Chem. Commun.* **2002**, *5*, 887.
[28] M. J. Mayoral, M. C. Torralba, M. Cano, J. A. Campo, J. V. Heras, *Inorg. Chem. Commun.* **2003**, *6*, 626.
[29] M. Cano, J. V. Heras, M. Maeso, M. Alvaro, R. Fernández, E. Pinilla, J. A. Campo, A. Monge, *J. Organomet. Chem.* **1997**, *534*, 159.
[30] M. C. Torralba, M. Cano, J. A. Campo, J. V. Heras, E. Pinilla, M. R. Torres, *J. Organomet. Chem.* **2001**, *633*, 91.
[31] F. Aguilar-Parrilla, C. Cativiela, M. D. Díaz de Villegas, J. Elguero, C. Foces-Foces, J. I. García-Laureiro, F. Hernández-Cano, H. H. Limbach, J. A. S. Smith, C. Toiron, *J. Chem. Soc., Perkin Trans. 2* **1992**, 1737.
[32] R. G. Raptis, H. H. Murray, J. P. Fackler Jr., *Acta Crystallogr. C* **1988**, *44*, 970.
[33] R. G. Raptis, J. P. Fackler Jr., *Inorg. Chem.* **1990**, *29*, 5003.
[34] P. G. Jones, *Gold Bull.* **1981**, *14*, 102.
[35] A. M. Levelut, *J. Chim. Phys.* **1983**, *80*, 149.
[36] R. Usón, A. Laguna, M. Laguna, *Inorg. Synth.* **1989**, *296*, 85.
[37] J. A. Campo, M. Cano, J. V. Heras, M. C. Lagunas, J. Perles, E. Pinilla, M. R. Torres, *Helv. Chim. Acta* **2001**, *84*, 2316.
[38] G. M. Sheldrick, 'SHELXL97, Program for Refinement of Crystal Structure', University of Göttingen, Göttingen, Germany, 1997.

Received August 5, 2003