Pyrazolato Ligands towards Gold(I) Derivatives with Aurophilic Interactions: X-Ray Structure of Bis[3,5-(dibutoxyphenyl)-1*H*-pyrazolato-κN^1]bis(triphenylphosphine)digold(Au $\cdots$ Au)([Au(pz^{R_2})(PPh_3)]$_2$; R=$C_4H_9-O-C_6H_4$)

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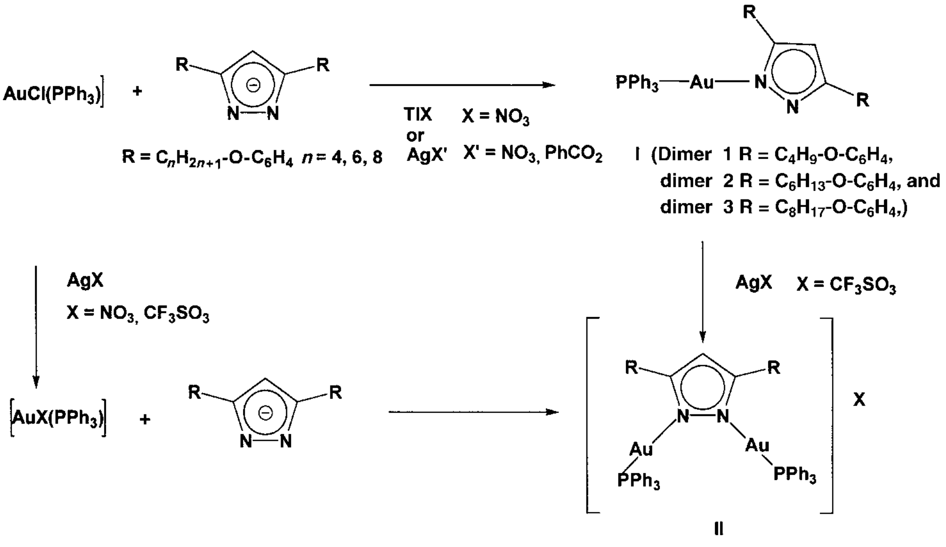
A crossed ‘torch’ structure and a short Au $\cdots$ Au contact was established by X-ray analysis for the dimeric complex [Au(pz^{R_2})(PPh_3)]$_2$ (pz^{R_2} = 3,5-disubstituted pyrazolato, R=$C_nH_{2n+1}-O-C_6H_4$, $n = 4$; **1**). The complex is a representative member of a new well-characterized family of derivatives containing the pyrazolato ligand in an uncommon monodentate coordination form. In addition, **1** is luminescent in the solid state at 77 K.

Pyrazolatogold(I) derivatives of the types [(PPh_3)Au(μ−pz)Au(PPh_3)]BF_4 and [Au(μ−pz)]$_n$ ($n = 3$, 6) [1–4] have been extensively described. By contrast, very few related compounds containing the pyrazolato group in a monodentate fashion are known [5]. In this context, it is remarkable to note that, in previous works, the complexes [Au(PPh_3)(pz)] (pz = 3,5-dimethylpyrazolato, 3,5-dimethyl-4-nitropyrazolato) were synthesized as part of a search for polymetallic derivatives [1][6][7]. More recently, [Au(pz)(PPh_3)] (pz = pyrazolato) has been described and structurally characterized [8]. The lack of data associated with the nature of monodentate pyrazolato-containing compounds encouraged us to investigate how to produce some of these Au^I derivatives.

Thus, we synthesized a new family of pyrazolato complexes of the type [Au(pz^{R_2})(PPh_3)] (pz^{R_2} = 3,5-disubstituted pyrazolato R = $C_nH_{2n+1}-O-C_6H_4$, $n = 4$, 6, 8) (**I**) *i.e.*, **1**–**3**. The compounds were produced by reaction of pyrazolato ligands, prepared *in situ*, and [AuCl(PPh_3)] followed by addition of $TlNO_3$. The thallium salt allowed us to obtain the complexes in a substantial yield after removal of TlCl. By contrast, when [AuX(PPh_3)] (X=NO_3, CF_3SO_3) were used as starting material, binuclear complexes of the type [(PPh_3)Au(μ−pz^{R_2})Au(PPh_3)]X (**II**) were isolated. Based on these results, [AuCl(PPh_3)] is proposed as the adequate parent compound to produce the pyrazolato-κN coordination to the AuPPh_3 fragment. Therefore, the nature of the AuX bond of the parent [AuX(PPh_3)] compounds appears to be responsible for the formation either type **I** or type **II** complexes. To confirm this suggestion, repeated reactions of [AuCl(PPh_3)] and pyrazolato ligands with subsequent addition of different silver salts like $AgNO_3$, Ag(CF_3SO_3), or Ag($PhCO_2$) were carried out. In all cases, the same final products of the type [Au(pz^{R_2})(PPh_3)] (**I**) were obtained in high yield (*Scheme*).

Scheme



The complex **1** is luminescent in the solid state, as a weak emission at 447 nm was observed at room temperature. But, at 77 K, **1** displays strong emissions at 415, 445, and 470 nm when excited at 320 nm.

Structural Studies. – All the analytical, IR, ^{1}H- and ^{31}P-NMR, and MS data for **1**–**3** agree with a complex of the monomeric type $[Au(pz^{R_2})(PPh_3)]$ (**I**). However, these results do not exclude the possible association of monomers in the solid state, as it was found for several [AuXL) complexes [9–12]. Available structural data for Au^I complexes show the presence of Au$\cdots$Au interactions as a general characteristic of the condensed phase, this feature being described as aurophilicity [13]. The aurophilicity phenomenon is responsible for complexes of the type [AuXL] (L = neutral ligand, X = halide or pseudohalide) to become aggregated as dimers, oligomers, or polymers [11].

By considering the flat core of the anionic pyrazolato ligands, the approach of two Au^I centers of molecules of the type $[Au(pz^{R_2})(PPh_3)]$ (**I**) should be possible without considerable steric hindrance. Looking for molecular aggregations through Au$\cdots$Au contacts, we determined the crystal structure of a single crystal of $[Au(pz^{R_2})(PPh_3)]_2$ (R = $C_4H_9-O-C_6H_4$; **1**). Crystals of **1** are monoclinic, space group $P2_1/n$, with four molecules in the unit cell. The molecular structure, as depicted in *Fig. 1*, shows the dimeric nature of the compound. The individual molecules present the metal centre bonded to a PPh_3 ligand and to a pyrazolato group in a monodentate form. Each pair of them shows a crossed 'torch' molecular structure with the ligands about the metal center connected in a staggered arrangement, the dihedral angle P(1)–Au(1)–Au(2)–P(2) being 83.1(2)°. The Au$\cdots$Au distance (3.029(1) Å) within the dimers is shorter than that observed in related dimers [10–12]. The individual molecule has a quasi-linear P(1)–Au(1)–N(1) atom sequence (169.8(3)°), but the N(2)–N(1)–Au(1) angle (124(1)°) deviating from the linearity of a 'torch' shape. The

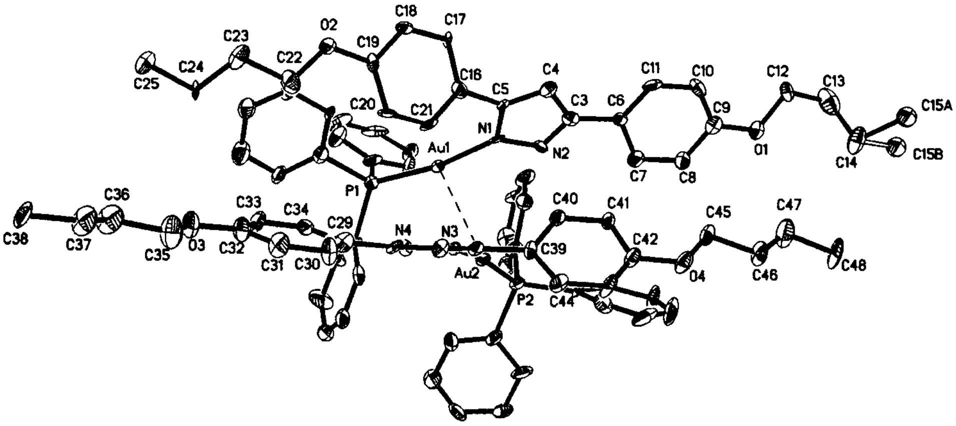


Fig. 1. *Perspective ORTEP plot of* $[Au(pz^{R_2})(PPh_3)]_2$ (R = C_4H_9–O–C_6H_4; **1**). H-Atoms and the solvent molecule are omitted for clarity. The thermal ellipsoids are at 30% probability level. Selected bond lengths [Å] and angles [°]: Au(1)–Au(2) 3.029(1), Au(1)–N(1) 2.02(1), Au(1)–P(1) 2.239(5), Au(2)–N(3) 2.04(2), Au(2)–P(2) 2.242(4), P(1)–Au(1)–N(1) 169.8(4), P(2)–Au(2)–N(3) 169.4(4), N(2)–N(1)–Au(1) 124(1).

average Au–N bond length (2.03(1) Å) is similar to those found for complexes like $[Au(\mu\text{–}pz)]_3$ or $[Au(Hpz^{3,5\text{-}Me_2})(PPh_3)]BF_4$ [4][14], this feature reflecting a similar back-bonding from gold to the pyrazole or pyrazolato groups. Further structural details are listed in the caption of *Fig. 1*.

The molecular shape of **1** suggests the examination of potential liquid-crystal properties of compounds **1**–**3**. In addition, it was hoped that $[Au(pz^{R_2})(PPh_3)]_2$ complexes have a solid-state structure appropriate to yield organized liquid phases. In this context, the molecular packing of **1** was also analysed. The crystal structure of **1** can be defined as having layer and columnar characteristics (*Fig. 2*, *a* and *b*). The layer is formed by columns of dimers, all of them with the same orientation, but opposite to that of neighboring layers. The columnar stacking arises from the periodic repetitions of dimeric unities along the crystallographic *a* axis. In each column, the dimers form chains with the individuals crossed in a head-to-head disposition, but the dimers are displaced with respect to each other in the plane perpendicular to the stacking axis giving rise to alternating Au···Au distances (3.029(1) Å) and (15.231(3) Å), corresponding to those in and between dimers, respectively.

Similar dimeric structures with monodentate pyrazolato ligands are suggested for **2** and **3** from the X-ray data obtained for **1**.

The thermal behavior of complexes **1**–**3** was also studied by light-polarized microscopy and differential scanning calorimetry. Unfortunately, in all cases, decomposition of the complexes with concomitant metal deposition was observed in the 150–190° range. This fact prevents the potential organization of phases in the fluid. New efforts will be required to achieve the desired supramolecular structure.

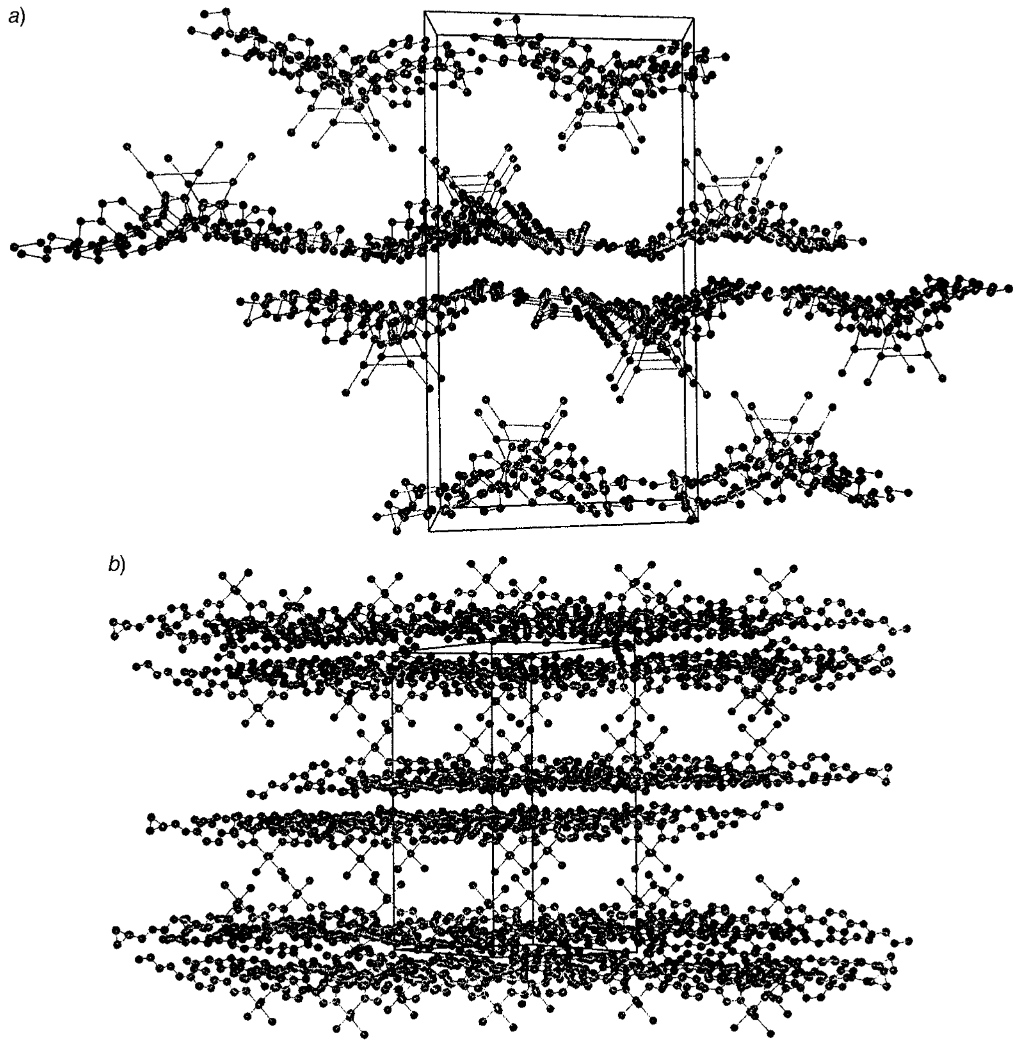


Fig. 2. *View of layer-like packing of the dimer* $[Au(pz^{R_2})(PPh_3)]_2$ ($R = C_4H_9-O-C_6H_4$; **1**) a) *along the* a-*axis and* b) *along the Au–Au axis.* The Ph substituents of the triphenylphosphine ligand are omitted for clarity.

Experimental Part

X-Ray-Diffraction Studies. The poor quality of the crystals necessitated repetition of the data collection and refinement with different crystals. Finally, a crystal gave good enough data to properly solve the structure.

*Crystal Data of Bis[(3,5-dibutoxyphenyl)-1*H*-pyrazolato-κ*N¹*]bis(triphenylphosphine)digold(Au···Au)-Dichloromethane* (**1** · CH_2Cl_2): $(C_{41}H_{42}N_2O_2PAu)_2 \cdot CH_2Cl_2$. M_r 1730.33, T 293(2) K; λ 0.71073 Å, *Bruker Smart-CCD* diffractometer; monoclinic, space group $P2_1/n$, $a = 15.231(3)$, $b = 30.804(5)$, $c = 17.154(3)$ Å, $\beta = 107.519(4)°$, $V = 7675(2)$ Å^3, $Z = 4$, $D_c = 1.497$ g cm^{-3}, μ [mm^{-1}] = 3.981. The structure was solved by direct methods and difference *Fourier* techniques and refined by full-matrix least-squares on F^2 [15]. Anisotropic thermal parameters were used in the last cycles of refinement for all non-H-atoms with some exceptions. The Me group C(15) of one butoxy chain (*Fig. 1*) and the CH_2Cl_2 molecule were found disordered in two positions and were assigned occupancy factors of 0.5. The H-atoms were calculated and refined as riding on a C-bonded atom with a common isotropic displacement parameter. The final R indices with $I > 2\sigma(I)$ was 0.0843 for 5410 observed reflections, while wR_2 for all data (13499 independent reflections) was 0.2108. The largest residual peak in the final difference map was 2.22 at 0.10 Å to the Au(2) atom. CCDC reference number is 174533.

Financial support from the *DGES* of Spain is gratefully acknowledged (Project no. PB98-0766). We also are grateful to Prof. *A. Laguna* and Dr. *M. Bardaji* for the luminescence measurements.

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Received January 24, 2002