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# Synthesis and Solution- and Solid-State Characterization of Gold(I) Rings with Short Au···Au Interactions. Spontaneous Resolution of a Gold(I) Complex

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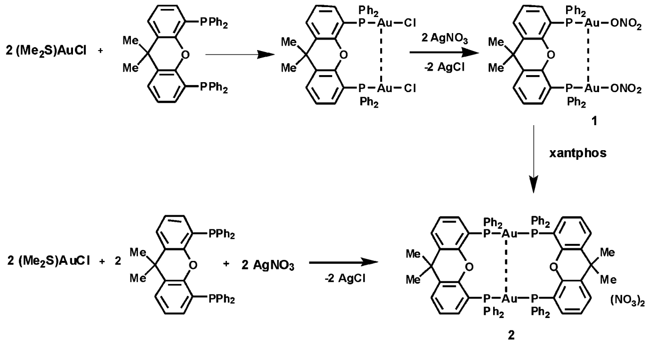
Within the field of supramolecular inorganic chemistry, the metal-assisted self-assembly of metallacycles, helicates, racks, ladders, grids, and cages represents an impressive achievement of molecular design and assembly.[1] The structure, conformation, and topology of these supramolecules should depend not only on the nature of the organic backbone, but also on the nature of the metal−ligand interaction; moreover, unique properties may result when metal−metal bonds are introduced.[2] The propensity of gold(I) for linear coordination geometry featuring Au···Au attractions in binuclear precursor molecules has been exploited in constructing macrocycles,[3a−f] catenanes,[3e−h] and polymers.[3i−n] The Au···Au interaction generally occurs perpendicular to the principal axis of the linearly two-coordinated Au(I) centers, and its typical length ranges from 2.75 to 3.40 Å.[4] Experimental and theoretical studies indicate that the strength of the aurophilic Au···Au attractions is comparable to that of hydrogen bonding.[5] The short aurophilic contacts observed in gold(I) supramolecules frequently induce intriguing spectroscopic and optoelectronic properties. Therefore, such complexes became ideal candidates for use in the development of molecular sensors and switches or energy storage devices.[3]

Eight- to eleven-membered rings in which two or more consecutive atoms are gold are relatively few, and macrocycles are even more rare.[6] Short Au···Au interactions have been observed in eight- and nine-membered gold(I) cyclic systems with $Ph_2P-(CH_2)_n-PPh_2$ diphosphine ligands; moreover, nine-membered gold(I) rings have been prepared using diphosphine ligands derived from rigid heteroatomic backbones.[7] Hence, it was of interest to see whether the self-assembly of diphosphine ligands derived from heteroatomic backbones with Au(I) ions would afford macrocycles showing short Au···Au interactions.

Herein, we report the synthesis and structural characterization of nine-membered and 16-membered gold(I) rings showing short 1,9-transannular Au···Au aurophilic interactions. They were prepared by reacting 9,9-dimethyl-4,5-bis(diphenylphosphino)-xanthene (xantphos) and $(Me_2S)AuCl$ in the presence of $AgNO_3$ (Scheme 1). The 2:1 stoichiometric combination of a dichloromethane solution of $(Me_2S)AuCl$ and xantphos produced the $[(AuCl)_2(\mu\text{-xantphos})]$ complex[7] which was further reacted with $AgNO_3$, and the resulting $[(AuNO_3)_2(\mu\text{-xantphos})]$ (**1**) was isolated. Likewise, the reaction of $(Me_2S)AuCl$ with xantphos and $AgNO_3$ in a molar ratio of 1:1:1 in dichloromethane yields $[Au_2(\mu\text{-xantphos})_2](NO_3)_2$ (**2**). Moreover, the reaction of **1** with xantphos also gave the complex **2**, indicating that **1** is a likely intermediate in the formation of **2**.

The structure determination of metallacycles in solution using X-ray diffraction is a very challenging problem with only a single report on platinum metallacycles.[8] The understanding of fluxionality of gold(I) metallacycles and their structure in solution is also limited.[9] Therefore, by use of solution X-ray diffraction and NMR methods we provide insight into the structure as well as the dynamics of gold(I) macrocycle **2**. Moreover, the photophysical properties of **1** and **2** were studied by UV−visible and luminescent spectroscopy.

***Scheme 1.*** Synthesis of Gold(I) Rings **1** and **2**



Diffraction-quality single crystals of both **1** and **2** were grown by diffusion of diethyl ether into a dichloromethane solution of each individual complex. The crystals **1** and **2** were isolated in Paratone-N cryoprotectant and successfully subjected to low-temperature X-ray diffraction study. The X-ray structure determination revealed the existence of disordered solvent molecules in each case. Figure 1 shows the skeleton of **1**, where the nitrate anions are coordinated to the gold centers bridged by the xantphos ligand, each having a linear coordination geometry and a short 1,9-transannular Au···Au distance to form a nine-membered ring. The ligand backbone is folded and twisted by 51.4(1)° about the Au···Au axis, most likely to accommodate the two Au(I) ions at a close distance of 2.950(1) Å. The nitrate groups are rotated by 59.1(1) and 50.7(1)° with respect to the least-squares plane of the nine-membered cycle, and they display a propeller-like arrangement with respect to one another. The crystal structure of the related $[(AuCl)_2(\mu\text{-xantphos})]$ has been reported.[7]

Complex **1** crystallized in the noncentrosymmetric, monoclinic space group $P2_1$; thus the molecule is chiral, and the crystal contains only one of the two enantiomers, either right- or left-handed. Refinement of the Flack parameter led to a value of ∼0, which confirms the enantiomeric purity of the crystal. Although many double- and triple-helical metal complexes have been reported,[10] the simpler monohelical complexes have received much less attention.[11] This is perhaps because spontaneous resolution more likely occurs when strong, selective, and directional interactions, such as coordination and/or hydrogen bonding, extend the neighboring chiral molecules into multidimensional arrays.[12]

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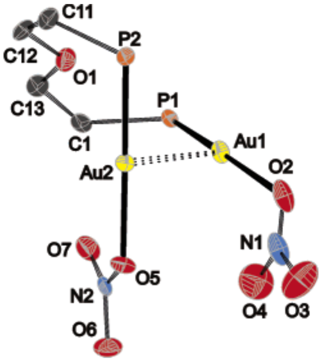

*Figure 1.* Ortep view of the skeleton of **1**, illustrating the nine-membered gold(I) ring and the coordinated nitrate anions with thermal ellipsoids at the 30% probability level. Selected distances (Å) and angles (deg): Au(1)$-$Au(2) 2.950(1); Au(1)$-$P(1) 2.224(3); Au(2)$-$P(2) 2.226(3); Au(1)$-$O(2) 2.199(9); Au(2)$-$O(5) 2.091(8); P(1)$-$Au(1)$-$O(2) 168.3(3); P(2)$-$Au(2)$-$O(5) 173.3(3).

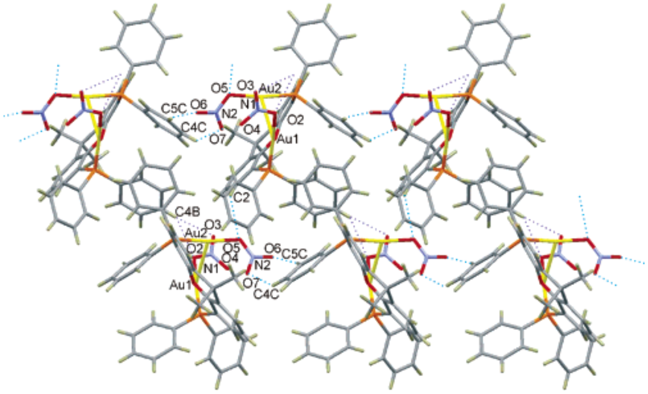

*Figure 2.* View illustrating the C$-$H$\cdots$O bonded homochiral helices of **1**, which are also interconnected by C$-$H$\cdots$O interactions to form an interhelical network.

As shown in Figure 2, the molecules of **1** are linked throughout via C$-$H$\cdots$O and Au$\cdots\pi$ interactions into a 2D array. This is achieved in such a way that one of the nitrate groups with its O(2) and O(3) atoms is involved as an acceptor in the C$-$H$\cdots$O hydrogen bonding. These C$-$H$\cdots$O and additional Au$\cdots\pi$ interactions link the molecules of **1** into homochiral helices, which are also interconnected with each other by C$-$H$\cdots$O contacts (Supporting Information, Table S1). Thus, all oxygen atoms of the second nitrate function are involved in C$-$H$\cdots$O interactions, which connect the C$-$H$\cdots$O and Au$\cdots\pi$ bonded helices into an interhelical meander-shaped network. The role of the nitrate anions played in the C$-$H$\cdots$O linking of the molecules is chirally discriminative and required that complex **1** exhibits the same absolute configuration. Therefore, the chirality is preserved and extended into the crystal. To the best of our knowledge this represents the first example of crystallization-induced spontaneous resolution of a binuclear gold(I) metallacycle. This chiral gold(I) complex has potential in absolute asymmetric (stereoselective) syntheses where optically active materials are prepared from achiral (or racemic) starting materials in the absence of optically active catalyst or reagents.

The X-ray structural data of **2** indicate that it consists of $[Au_2(xantphos)_2]^{2+}$ cations in which two strands of xantphos are folded relative to each other and held together by two Au(I) ions (Figure 3). In addition, the structure contains uncoordinated nitrate anions, as well as disordered solvent molecules. In this structure, the ligand backbone is folded and tilted by 72.2(1)° with respect to the Au$\cdots$Au axis, and the two xantphos ligands bridge the Au(I) ions to form a short aurophilic attraction. With this interaction taken into account, the molecule of **2** exists in a figure-eight conformation, where the 16-membered ring contains one short Au$\cdots$Au linkage (2.858(1) Å), as shown in Figure 3. This represents an example of a 16-membered ring with a 1,9-transannular Au$\cdots$Au interaction. This structure crystallized in centrosymmetric space group $C2/c$, thus both right- and left-handed molecules are present in the crystal.

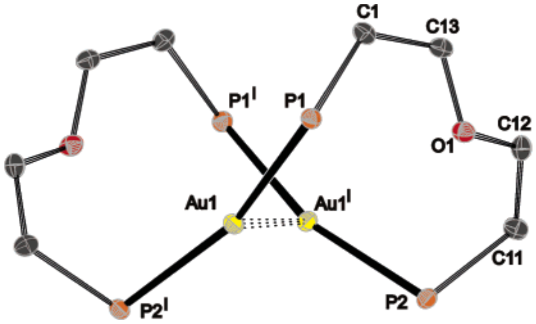

*Figure 3.* Ortep view of the cationic skeleton of **2**, illustrating the 16-membered gold(I) ring showing a figure-eight conformation [equivalent atoms generated by $i = (-x + 1, y, -z + {}^{3}/_{2})$] with thermal ellipsoids at the 30% probability level. Selected distances (Å) and angles (deg): Au(1)$\cdots$Au(1)$^i$ 2.858(1); Au(1)$-$P(1) 2.326(1); Au(1)$-$P(2) 2.331(1); P(1)$-$Au(1)$-$P(2)$^i$ 160.8(1); P(1)$-$Au(1)-Au(1)$^i$ 102.1(1); P(2)$-$Au(1)$^i-$Au(1) 93.1(1).

To check whether the nine- and 16-membered gold(I) rings retain their structure in solution, wide-angle X-ray scattering and NMR experiments were performed. The solubility of **1** is extremely low in the usual protic and aprotic organic solvents, thus solution X-ray diffraction was not possible. Despite its limited solubility ($<$4 mM), the $^1$H NMR of **1** exhibited sharp resonances in $CD_2Cl_2$ at room temperature. The phosphorus nuclei of **1** at $\delta$ 18.3 ppm are more shielded when compared to the $[(AuCl)_2(\mu\text{-xantphos})]$ complex.[7]

The $^1$H and $^{31}$P NMR spectra for **2** were measured using the same sample (179 mM) prepared for solution wide-angle X-ray diffraction experiments. Noteworthy in the $^1$H and $^{31}$P NMR spectra are the broad resonances found at room temperature (Supporting Information Figures S4 and S5). Temperature-dependent $^{31}$P NMR experiments on **2** were performed, and it was observed that by raising the temperature to +70 °C, the corresponding NMR signals became much sharper, while after recooling (to +25 °C) the complex remained intact. Given that a more dilute (2 mM) solution of **2** behaved similarly, the most plausible explanation for the room-temperature line-broadening is the conformational motion of **2**, rather than self-association or oligomerization processes. This has been further proven by low-temperature $^{31}$P NMR, where a pair of AB phosphorus doublets appeared with a large, two-bond $^{31}$P$-^{31}$P coupling constant ($^2J_{P-P} = 318.3$ Hz, $-30$ °C), indicating that each gold atom is bound to two chemically nonequivalent phosphorus sites. The large $^2J_{P-P}$ scalar coupling mediated by a gold atom fits well within the range of reported values.[13] Coalescence of the $^1$H and $^{31}$P resonances near room temperature is attributed to the interconversion of the mirror image conformers of **2**. The activation enthalpy ($\Delta H^{\ddagger}$) for the process was determined by $^1$H and $^{31}$P temperature-dependent NMR line shape analyses and found to be $\Delta H^{\ddagger}(^1\text{H}) = +48.9$ kJ/mol and $\Delta H^{\ddagger}(^{31}\text{P}) = +48.4$ kJ/mol (Supporting Information Figures S6$-$S9). The good agreement between the $^1$H and $^{31}$P activation parameters suggests that the same exchange phenomenon is followed on both NMR time-scales. Although difficult to separate from steric factors, the experimental $\Delta H^{\ddagger}$ is in agreement with literature data [4,13,14] and is probably only a slight overestimation of the aurophilic interaction energy.

To assess the aurophilicity of **2** after dissolution, the solution X-ray measurement was performed in high-purity nitromethane

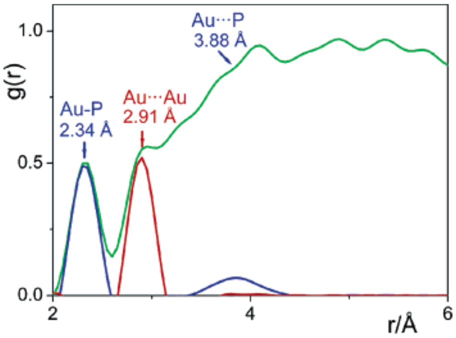

***Figure 4.*** Difference radial distribution function (green line) *g(r)* for solution of 179 mM gold(I) macrocycle **2** in nitromethane; (red line) Au···Au aurophilic interaction; (blue line) Au···P interaction.

solution. The detailed data treatment, the structure, and radial distribution functions obtained are given in the Supporting Information.

The Au−P and Au···Au interactions in **2** arising around 2.3 and 2.9 Å, respectively, are shown in Figure 4. The Au−P distance and root-mean-square deviations were found to be 2.34(1) and 0.10(1) Å, respectively. The diagonal Au···P distances are 3.88(2) Å [$\sigma = 0.30(2)$]. The Au···Au distance resulted in 2.91(1) Å with the root-mean-square deviation $\sigma = 0.17(1)$; thus no significant change in aurophilic distance is observed upon dissolution. The Au···Au, Au−P, and diagonal Au···P distances determined by solution X-ray diffraction agree well with those found in the crystal structure of **2**.

The UV−visible absorption spectrum of **1** closely resembles that of the xantphos ligand, but significantly different spectral characteristics appears for **2**, whose first band with a maximum at 301 nm is red-shifted and more clearly distinguishable (Supporting Information Figure S15a). The energy of the lowest singlet-excited state is quite insensitive to the polarity of the medium because the onsets of the absorption hardly change when ethanol is replaced by dichloromethane. The solutions of both compound **1** and **2** are barely luminescent at room temperature, but intense light emission is observed upon excitation in rigid ethanol glass at 77 K. The spectra obtained with steady-state irradiation correspond to those recorded in the 0.1−30 ms time interval after the excitation with a flash lamp (Supporting Information Figure S15b), thus indicating that the emissions are phosphorescence. The similarity of the spectra of the two gold complexes and xantphos seems to indicate that the emitting states of **1** and **2** have intraligand (IL) type character. The triplet-excited-state lifetimes are 17.4 and 2.8 ms for xantphos and **2**, respectively. The heavy atom effect of gold is probably responsible for the more rapid deactivation of the triplet-excited complex.

In conclusion, we have synthesized and structurally characterized in both solution and solid state two gold(I) rings showing short Au···Au aurophilic interactions. These gold(I) cyclic systems could provide unique materials with new properties for chemical sensing, catalysis, and the manufacturing of nanoscale devices.

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**Supporting Information Available:** Synthetic details, X-ray crystallographic data for of **1** and **2** in CIF format; $^{1}$H and $^{31}$P NMR line shape analysis; experimental and evaluation method for solution X-ray diffraction measurements; absorption and luminescence spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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