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The Structural and Functional Equivalence of Aurophilic and Hydrogen Bonding: Evidence for the First Examples of Rotator Phases Induced by Aurophilic Bonding

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There has been considerable interest in the attractive interaction that exists between closed-shell gold(I) centers.[1] This interaction, commonly referred to as “aurophilicity” or “aurophilic bonding”, has been estimated by both experiment[2] and theory[3] to have a strength similar hydrogen bonding (29−46 kJ mol^{-1} vs 10−65 kJ mol^{-1}).[4] Furthermore, Desiraju and co-workers have shown that, like hydrogen bonding, aurophilic bonding is distinctly directional.[5] As might be expected based on this combination of strength and directionality, the use of aurophilic bonds to control the supramolecular structure of gold-containing complexes is becoming increasingly common.[1,6] The striking energetic and structural similarities between aurophilic and hydrogen bonding raises the question: can aurophilic bonding function as a structural and functional equivalent to hydrogen bonding? That is, can aurophilic bonding be used to construct supramolecular architectures that are equivalent to those created by hydrogen bonding, and will the resulting materials exhibit physical properties similar to those seen for their hydrogen bond-based counterparts?

In attempting to answer these questions, we chose to examine the behavior of *n*-alkylisonitrile complexes of gold(I) chloride, RNCAuCl ($R = C_nH_{2n+1}$; $n = 2-12$), because of their geometric similarity to the $(1-n)$-alcohols. In turn, the intermediate strength hydrogen bonds formed by hydroxyl groups offer a good comparison point for aurophilic bonds. At the supramolecular level, the primary alcohols are known to form a well-defined bilayer motif built from chains of molecules held together by hydrogen bonding between the hydroxyl headgroups.[7] Additionally, those alcohols with medium to long alkyl chains display rotator phases.[8]

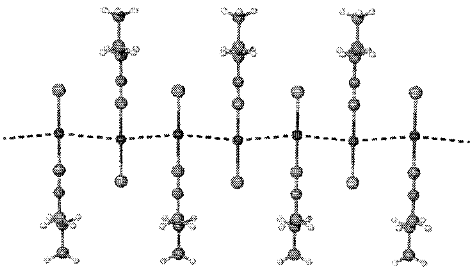

Figure 1. View of the antiparallel chains formed by aurophilic bonding (dashed lines) in $C_3H_7NCAuCl$.

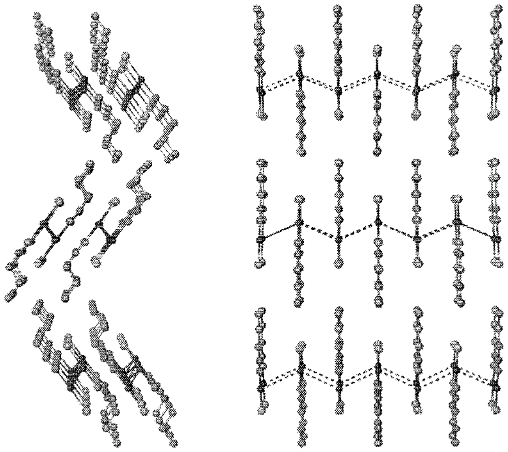

Figure 2. Two views of the packing of $C_3H_7NCAuCl$ perpendicular to the layer stacking direction. Left: View along the *c*-axis. Right: View along the *b*-axis.

In this communication, we present our initial findings on the supramolecular structure and phase behavior of the targeted *n*-alkylisonitrilegold(I) chloride complexes. These simple molecules assemble into structures similar to those seen for the $(1-n)$-alcohols and also show temperature-dependent polymorphism consistent with the formation of rotator phases. To the best of our knowledge, these observations provide the evidence for the induction of rotator phases by aurophilic bonding, or any type of direct metal−metal interaction.

The isonitrile ligands, RNC ($R = C_nH_{2n+1}$; $n = 2-12$), were prepared using a slight modification of the procedure developed by Gokel et al.[9] They were then bound to the gold chloride fragment via displacement of the sulfide ligand from Me_2SAuCl.[6d] This two-step process provided the gold complexes, RNCAuCl, in good yield (55−95%) as white crystalline solids. Crystals of sufficient quality for structural studies were obtained for the two shortest members of the series.

Despite crystallizing in different space groups,[10] the C_1,[6d] C_2, and C_3 complexes display almost identical supramolecular motifs consisting of infinite zigzag chains formed via long (3.637, 3.564, and 3.547 Å, respectively) aurophilic bonds, with adjacent molecules aligned antiparallel (Figure 1). While at the long end of the range typically associated with aurophilic bonding, there is still

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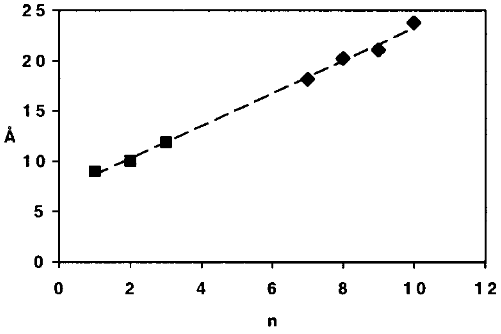

Figure 3. Layer spacing versus alkyl chain length: (◆) determined by XRD, (■) determined by crystallography, and (- - -) linear least-squares fit.

Table 1. Transition Temperatures (°C, Heating/Cooling) and Enthalpies (kJ/mol) for RNCAuCl as Measured by DSC[a]

chain length	K → R	R → I
C_7	44.5/41.8 (3.58)	54.5/51.8 (8.54)
C_8	48.2/46.0 (4.17)	53.7/51.4 (9.92)
C_9	49.7/47.0[b]	51.0/49.6
C_{10}	52.2/49.0 (5.22)[c]	54.3/51.3 (11.60)
C_{11}	49.9 (7.78)[d]	58.7/55.4 (25.29)

[a] The enthalpies are the average of the heating and cooling cycle values. [b] Peak overlap prevented calculation of $\Delta H_{\text{trans.}}$ [c] An additional transition is observed in this material at 46.8/44.0 (9.58). [d] No transition to the solid is observed during the experiment. ΔH_{trans} is based on the heating transition only.

a significant attractive interaction between gold atoms.[3] The 1-D chains stack together to create a bilayer structure with the molecules tilted approximately 40° with respect to the basal plane (Figure 2). There are no additional aurophilic bonds between the chains. In the C_1 and C_2 cases[6d,10] the tilt direction is the same for all layers, while the C_3 complex forms a herringbone stacking pattern. Within each layer, the molecules are arranged into a primitive rectangular lattice with dimensions of 4.64 × 6.26 Å. The methyl groups of adjacent layers are centered over the midpoint of this rectangle to create an ABAB-type stacking. Significantly, the dimensions of this lattice preclude the possibility of significant interdigitation of the alkyl chains.

The structures of the C_7-C_{10} derivatives were probed by powder X-ray diffraction (XRD). The XRD patterns are dominated by a series of strong low-angle peaks that we assign to "$0k0$" ($k = 1, 2, 3$, etc.), providing a direct measure of the layer spacing. For the C_7, C_8, and C_{10} complexes, we were also able to index the XRD patterns to monoclinic cells as follows: $a = 4.5$ Å, $b = L$, $c = 6.2$ Å, $\beta \approx 94°$, where L is the layer spacing. Assuming an anti orientation of the alkyl chains, the spacing values correspond to a tilt angle of ≈40°, consistent with the angle observed for the C_1-C_3 derivatives. Given the monotonic behavior (Figure 3) of the layer spacing and the similarity of the other two lattice dimensions, it is likely that the supramolecular structure is the same in all cases. Overall, the supramolecular structure of RNCAuCl can be described as a tilted bilayer composed of two alternating interfaces: interdigitated headgroups engaged in aurophilic bonding and methyl surfaces of the hydrocarbon tails. This motif is *strictly analogous* to that of the $(1 - n)$-alcohols, with aurophilic bonding replacing hydrogen bonding.[8]

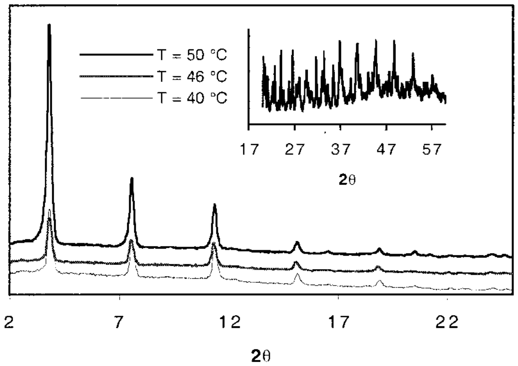

Figure 4. Variable-temperature XRD data for $C_{10}H_{21}NCAuCl$. Main figure: Low-angle data for all three phases with data taken on the cooling cycle. Inset: High-angle region at room temperature.

DSC reveals the presence of additional phases between the solid and isotropic phases for C_7 to C_{11} (Table 1). Polarized microscopy indicates that while these intermediate phases are crystalline, they are mechanically soft and may be deformed by gentle pressure. These physical traits, along with the cylindrical shape of the molecule, suggest that these phases are best described as rotator phases. This assignment is also consistent with the cross-sectional area of the alkyl chains (21.5 Å^2), which is typical for rotator phases.[11] As with the supramolecular structure, the phase behavior is analogous to that observed for the $(1 - n)$-alcohols.

Variable-temperature XRD studies performed on the C_8 and C_{10} derivatives indicate that layer spacing is maintained in the rotator phases (Figure 4). Unfortunately, we have been unable to obtain detailed information about the supramolecular structure within the layers. Given the constancy of the layer spacing and the rectangular packing of the crystalline phase, we favor assignment of these materials to a tilted rectangular (R_V) phase; however, the tilted hexagonal phases (R_{III} or R_{IV}) cannot be definitively excluded.

These studies demonstrate that the aurophilic bond is capable of playing a role structurally and functionally equivalent to the hydrogen bond. We have also provided the first evidence that aurophilic bonding can be used to induce the formation of mesomorphic phases *in the absence* of traditional mesogenic units such as aromatic rings. We are currently working to answer several of the outstanding questions arising from this study, including the details of the intralayer packing pattern in the rotator phases.

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Supporting Information Available: Tables of crystal and refinement data, atomic coordinates, bond lengths and angles, and anisotropic parameters for C_2 and C_3 and least-squares unit cell refinements for C_7, C_8, and C_{10} based on PXRD data (PDF); an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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