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Mercury(II) Cyanide Coordination Polymer with Dinuclear Gold(I) Amidinate. Structure of the 2-D $[Au_2(2,6\text{-}Me_2\text{-formamidinate})_2]\cdot 2Hg(CN)_2\cdot 2THF$ Complex

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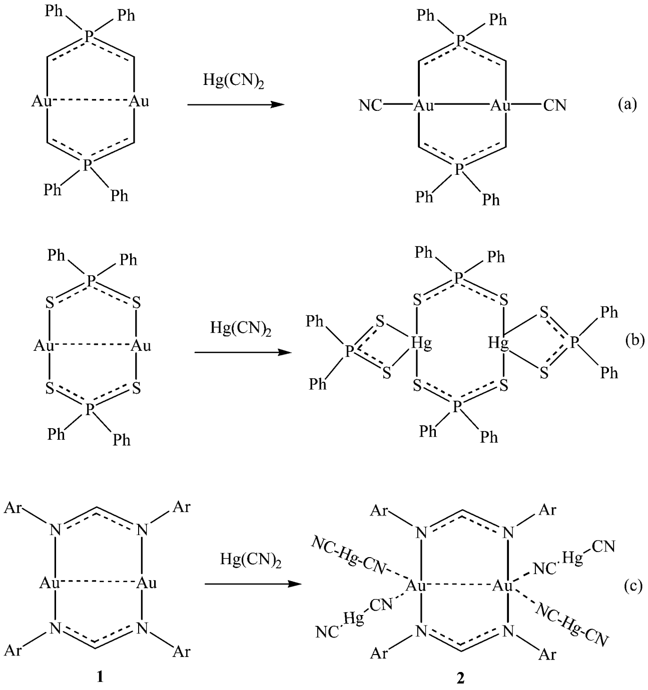
The dinuclear gold(I) amidinate complex $[Au_2(Me_2\text{-form})_2]$, **1**, ($Me_2$-form = 2,6-$Me_2$-formamidinate) reacts with $Hg(CN)_2$ to form a 2D structure, **1**$\cdot 2Hg(CN)_2\cdot 2THF$. Each gold center interacts with two $Hg(CN)_2$ molecules. The Au···Au distance increases from 2.7 Å in the starting dinuclear complex to 2.9 Å in the adduct. The gold centers are connected to four nitrogen atoms with Au–N distances in the range 2.13–2.51 Å. The cyanide stretch is shifted from 2192 cm^{-1} in the $Hg(CN)_2$ to 2147 cm^{-1} in the adduct.

Scheme 1



Mercury(II) cyanide oxidatively adds to d^8 and d^{10} metal complexes. The oxidative addition of $Hg(CN)_2$ to [Ir(β-diketone)(COD)] (COD = 1,5-cyclooctadiene) complexes in acetone produces [Ir(β-diketone)(COD)(CN)(HgCN)] with the CN and HgCN ligands in a cis disposition.[1] The reaction with the dinuclear gold(I) ylide complex, Scheme 1a, adds the cyanide to the gold(I) centers and forms a gold(II) cyanide complex.[2] Recently, there has been interest in the design of multidimensional inorganic coordination polymers.[3–5] The resulting arrangements include chains, planes, and 3D arrays. Mercury(II) cyanide reacts with Lewis bases with nitrogen- and oxygen-donor ligands to give adducts in which the coordination number of mercury is increased. The X-ray crystal structure is reported as a solvated complex rather than a true adduct of $4THF\cdot 5Hg(CN)_2$ due to the long Hg−O distances observed.[6] The addition of mercury(II) cyanide to dinuclear gold(I) thiolates in THF results in ligand exchange, $[Hg_2(S_2PPh_2)_4]$ and AuCN (IR 2236 cm^{-1}) products being formed, Scheme 1b.[7] The mercury thiolate complex $[Hg_2(S_2PPh_2)_4]$ was characterized by X-ray diffraction as triclinic in the space group $P\bar{1}$. The same structure was reported previously, obtained by a protodemetalation reaction of [Hg(PhPy)(OAc)] and $HS(S)PPh_2$ in chloroform. The reaction proceeded via Hg−C cleavage.[8]

Various oxidizing agents such as Cl_2, Br_2, I_2, or CH_3I add to the dinuclear gold(I) amidinate complex $[Au_2(Me_2\text{-form})_2]$, **1**, Au···Au = 2.7 Å, to form oxidative-addition products with Au−Au bonds ~2.5 Å.[9,10] Our attempts to oxidatively

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(7) $[Hg_2(S_2PPh_2)_4]$: Triclinic space group $P\bar{1}$, a = 9.12.7(12) Å, b = 10.5427(18) Å, c = 13.6201(23) Å, α = 92.607(3)°, β = 101.898(3)°, γ = 105.704(3)°, Z = 1.

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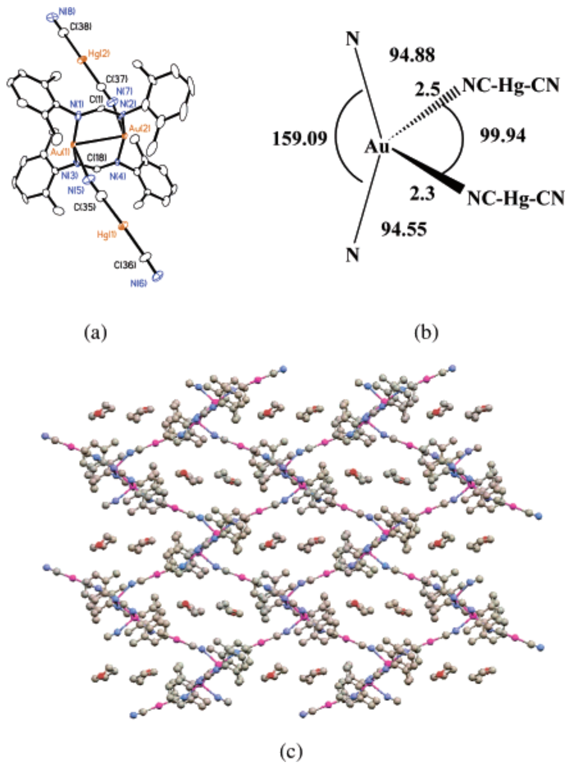

Figure 1. (a) ORTEP (50%) plot of complex **2**. (b) Coordination environment of gold with the four nitrogen atoms. (c) Packing diagram of **2** showing the THF solvent in the voids. Selected bond distances (Å) and angles (deg): Au(1)−N(3) 2.096(16), Au(2)−N(4) 2.11(2), Au(1)−N(5) 2.32(3), Au(2)−N(7) 2.32(3), Au(1)−N(6) 2.51(3), Au(2)−N(8) 2.51(3), Au(1)···Au(2) 2.9047(17), Hg(2)−C(38) 1.95(3); N(3)−Au(1)−N(1) 161.6(8), N(4)−Au(2)−N(2) 160.1(8), N(1)−Au(1)−N(5) 98.9(8), N(3)−Au(1)−N(6) 93.9(7), C(38)−Hg(2)−C(37) 176.5(10), C(36)−Hg(1)−C(35) 178.0(10).

add mercury(II) cyanide to the dinuclear gold(I) amidinate complex resulted in the adduct reported here, not the expected oxidative-addition product. In this reaction, the $Hg(CN)_2$ formed a 2D complex **1**·$2Hg(CN)_2$·2THF, **2**, Scheme 1c.

The reaction of the dinuclear gold amidinate complex, **1**, with $Hg(CN)_2$ (1:2 stoichiometry) in THF forms a white product, **2**, Figure 1.[11] White crystals and a yellow powder are formed while crystals are grown. The white crystals change to yellow powder upon grinding, presumably with loss of THF and possibly some AuCN formation. The product is sparingly soluble in various organic solvents. The infrared spectrum of the adduct shows the cyanide frequency to be shifted from 2192 cm^{-1} in $Hg(CN)_2$ to 2147 cm^{-1} in the adduct. The UV−vis spectrum of **2** in THF, although it is sparingly soluble, shows a red shift from 255 nm in **1** to a broad band centered at 285 nm. The origin of this shift is uncertain but may be related to partial formation of the $Hg(CN)_2$ adduct.

The product **2** forms in THF. An insoluble, noncrystalline product forms in halogenated solvents, acetonitrile, methanol, or 1,4-dioxane.

Thermal gravimetric analysis of **2** shows the release of the THF gradually at >120 °C followed by decomposition at >200 °C. Powder diffraction of the yellow residue after heating above 265 °C shows a diffraction pattern typical of AuCN (IR 2236 cm^{-1}). This result is confirmed by comparison with the powder diffraction pattern of a sample of AuCN obtained from the Aldrich Chemical Co.

The white product crystallizes in the monoclinic space group $P2(1)/c$.[12] Gold centers are coordinated by four nitrogen atoms with Au−N distances in the range 2.09−2.51 Å (Figure). The N−Au−N angles are in the range 95−100° (angles from the cyanide groups). The N−Au−N angles associated with the amidinate ligands decreased from ~170° in **1** to ~161° in **2**, with the N−C−N angles changing from 128° to 124−127°. The 2D lattice contains two THF solvent molecules in the large cavities (~10.2 Å × 13.7 Å), Figure 1c. The bonding to $Hg(CN)_2$ increases the Au···Au distance from 2.7 Å in **1** to 2.9 Å in the adduct, **2**.

The C−Hg−C bond angle in the structure of the unsolvated $Hg(CN)_2$ complex is 175.0(2)°, and the nonbonding Hg−N distance is 2.742(3) Å.[12] In the structure of the solvated complex, $5Hg(CN)_2$·4THF, the C−Hg−C angle is 173−176° compared with 176−178° in **2**. The C−Hg−C angle is close to linear in the adduct, **2**. The Hg−O distance in $5Hg(CN)_2$·4THF is 2.80−2.98 Å, ~4.33 Å in **2**. The reaction of $AgNO_3$ with $Hg(CN)_2$ forms a $Hg(CN)_2$·$AgNO_3$·$2H_2O$ adduct.[14] The structure is infinite chains of silver atoms bridged with $Hg(CN)_2$ molecules. The Hg−O distances range from 2.16 to 3.06 Å, and the C−Hg−C bond angle is 176−177°. In the adduct **2**, the Hg−O interaction is not significant and the C−Hg−C bond angle is close to linear.

The variable behavior of $Hg(CN)_2$ toward dinuclear gold complexes (Scheme1) requires comment. In the case of the mercury(II) cyanide reaction with the dinuclear gold(I) dithiophosphinate, the stability of the gold(I)−carbon bond compared with that of mercury(II)−carbon bond and the strength of the Hg(II)−S bonds compared with the labile Au(I)−S bonds appear to lead to the metathesis products observed. In the case of the ylide, oxidation of the Au(I) to Au(II) results in the formation of a reduced mercury product. With the adduct to the amidinate ligand complex, the cyanide IR stretching frequency shifts to ~2147 cm^{-1}, a value very near to the CN stretching frequency found (2145 cm^{-1}) in the dinuclear Au(II) ylide dicyanide.[2] However, the oxidation of the dinuclear Au(I) amidinate by the $Hg(CN)_2$ is much

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(11) Synthesis of $[Au_2(2,6\text{-}Me_2\text{-}form)_2][Hg(CN)_2]_2$·2THF. The dinuclear gold amidinate complex $[Au_2(2,6\text{-}Me_2\text{-}form)_2]$ (180 mg, 0.2 mmol)[9] was stirred with 100 mg (0.4 mmol) of $Hg(CN)_2$ in THF for 6 h. The volume was decreased under reduced pressure to 5 mL. The crystals for X-ray structure were grown by slow evaporation from THF solution to form white blocks. The white adduct is sparingly soluble in various organic solvents. The product is air stable in the solid state. IR: ν_{CN} 2147 cm^{-1}.

(12) Crystal data for **2**, $C_{46}H_{54}Au_2Hg_2N_8O_2$: M_r =1546.09, monoclinic, space group $P2_1/c$, a = 18.936(4) Å, b = 14.500(3) Å, c = 19.897(4) Å, β = 118.12(3)°, V = 4818.3(17) $Å^3$, Z = 4, R1 = 0.0708, and wR2 = 0.0883. Data were collected using a Siemens (Bruker) SMART CCD (charge coupled device)-based diffractometer equipped with a LT-2 low-temperature apparatus operating at 110 K.

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more difficult than is the oxidation of the dinculear Au(I) ylide. Cyclic voltammetric studies bear this out (vida infra).[15] The differences in the chemistry of these dinuclear gold(I) complexes may be understood by examining their respective HOMOs, which, in the ylide, is a metal−metal σ^* antibonding, while in the dinuclear gold(I) amidinates the HOMO is δ^*.[16] Gold ylides are oxidized in 0.1 M Bu_4NBF_4/THF at low potentials of +0.11 and +0.23 V vs Ag/AgCl (quasi-reversible). The dinuclear amidinate, **1**, oxidizes under the same conditions at +1.22 V vs Ag/AgCl (irreversible). These large differences in chemical character of the dinuclear gold(I) complexes appear to explain the widely diffferent behavior of these compounds toward reaction with mercury cyanide.

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Supporting Information Available: Cif file of complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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