stantaneous. The activation parameters indicate the addition of water before the loss of Cl^- in the hydrolysis of $ClSO_3^-$.

Above pH 12.5 the reaction between OCl^- and SO_3^{2-} does not have a pH dependence.[4] The indicator method is not suitable at high pH, and the rate of this reaction (followed by the disappearance of OCl^-) is no longer rapid compared to the rate of hydrolysis of $ClSO_3^-$ at lower pH. Although, it is also possible for water to act as a general acid to assist a Cl^+-transfer mechanism, we cannot rule out an oxygen atom transfer path above pH 12.5.

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Registry No. HOCl, 7790-92-3; SO_3^{2-}, 14265-45-3; $ClSO_3^-$, 15181-48-3.

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Synthesis and Characterization of the Luminescent Dithiolate-Bridged Dimer $[n\text{-}Bu_4N]_2[Au(i\text{-}MNT)]_2$ (i-MNT = $S_2C_2(CN)_2^{2-}$) and Its Structurally Characterized, Metal–Metal-Bonded Gold(II) Oxidation Product $[Ph_4As]_2[Au(i\text{-}MNT)Cl]_2$

Sir:

Although Burmeister et al.[1] suggested nearly 10 years ago that Au^I–dichlorocarbamate dimers are oxidized by halogens and pseudohalogens to metal–metal-bonded Au^{II} species, oxidized products could not be characterized structurally due to disproportionation into $[Au^{III}(dtc)_2]Au^IX_2$ (X = halide, pseudohalide).[1] Proton NMR data for the di-n-butyldithiocarbamate derivative $[Au(dtc)(SCN)]_2$, however, was entirely consistent with the metal–metal-bonded formulation. Since this complex appears to be the only metal–metal-bonded Au^{II} dimer not containing Au–C bonds and since the Au^I dimer $[Au^I(dtc)]_2$ has a very short (2.78 Å) Au–Au distance,[2,3] we embarked upon the synthesis and structural characterization of Au^I and Au^{II} dimers with sulfur-bonded ligands.

The Au^I dimer[4] $Au_2(MTP)_2$ (MTP = $CH_2P(S)Ph_2$) has a normal (3.0 Å) $Au^I \cdots Au^I$ separation and is oxidized by halogens to both homovalent Au^{II}–Au^{II} and heterovalent $Au^{III} \cdots Au^I$ species.[5a] The stability of the Au^{II} MTP dimers $[Au(MTP)X]_2$ (X = halides) suggested that by using electron-donating sulfur ligands stronger than dithiocarbamates it might be possible to isolate and characterize Au^{II} dimers with sulfur atom bridging ligands. The i-MNT ligand and other analogues formed from CS_2 proved to be suitable choices. Here we report the first structural characterization of a nonorganometallic Au^{II} metal–metal-bonded dimer containing one of the shortest Au–Au distances known (2.55 Å), the structure of the Au^I precursor, which also has a short (2.79 Å) Au–Au distance, and a preliminary description of the luminescent properties of this Au^I product.

Compound $K_2[Au^I(i\text{-}MNT)]_2$ (**1a**) was obtained quantitatively from the reaction of[6] $[Au(PPh_3)]_2(i\text{-}MNT)$ with 1 molar equiv of $K_2(i\text{-}MNT)$ in CH_2Cl_2 at 22 °C. Addition of $[n\text{-}Bu_4N]Br$ or $[Ph_4As]Cl$ to the CH_2Cl_2 solution of **1a** resulted in the formation of $[n\text{-}Bu_4N]_2[Au(i\text{-}MNT)]_2$ (**1b**) in 80% yield and $[Ph_4As]_2[Au(i\text{-}MNT)]_2$ (**1c**) in 85% yield, respectively. Compound **1b** was characterized by IR spectroscopy and elemental[7] and single-crystal X-ray diffraction analyses.[8]

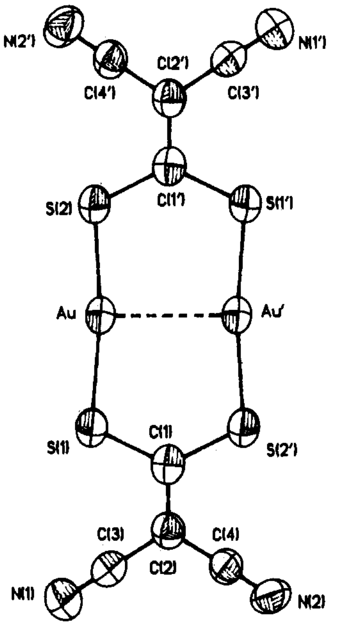

Figure 1. Structure of $[n\text{-}Bu_4N]_2[Au(i\text{-}MNT)]_2$ (**1b**). Bond lengths (Å): Au–Au', 2.796 (1); Au–S(1), 2.283 (2); Au–S(2), 2.280 (2); S(1)–C(1), 1.735 (9); S(2)–C(1); 1.727 (8); C(1)–C(2), 1.37 (1); C(2)–C(3), 1.46 (1); C(2)–C(4), 1.43 (1); C(3)–N(1), 1.13 (1); C(4)–N(2), 1.15 (1). Bond angles (deg): S(1)–Au–S(2), 172.2 (1); S(1)–C(1)–S(2)', 127.5 (4); C(1)–C(2)–C(3), 122.9 (8); C(1)–C(2)–C(4), 123.1 (7); C(2)–C(3)–N(1), 178 (1); C(2)–C(4)–N(2), 177.8 (9); C(3)–C(2)–C(4), 114.1 (7).

The molecular structure and important bond distances and angles of 1b are given in Figure 1. The two gold atoms are bridged by two i-MNT ligands by bonding through the sulfur atoms: Au–S(1) = 2.283 (2) Å; Au–S(2) = 2.280 (2) Å. The coordination of the sulfur atoms to the Au^I center is linear: S(1)–Au–S(2)' = 172.2 (1)°. The anion is nearly planar. The most interesting feature in this molecule is the unusually short Au–Au distance, 2.796 (1) Å, significantly shorter than the distance observed in metallic gold (2.884 Å)[9] and similar to the short Au–Au distances observed in dialkyldithiocarbamate-bridged Au^I dimers (2.76–2.79 Å).[2,3]

The compound $[Au(PPh_3)]_2(i\text{-}MNT)$ displays a strong visible luminescence at 77 K in CH_3CN solution with two emission components at ~525 nm having 33 and 286 μs lifetimes (355-nm

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(7) IR (KBr, Nujol, ν_{CN}): **1b**, 2190 (s), 2200 (sh) cm^{-1}; **2b**, 2200 (s) cm^{-1}. Anal. Calcd for **1b**: C, 41.45; H, 6.22; N, 7.25. Found: C, 41.72; H, 6.03; N, 7.15. Calcd for **2b**: C, 52.71; H, 3.29; N, 4.61. Found: C, 52.52; H, 3.21; N, 4.56.

(8) Crystal data. **1b**: $C_{40}H_{72}Au_2S_4N_6$, M_R = 1157.4, monoclinic, space group, $P2_1/c$, a = 14.228 (3) Å, b = 8.754 (2) Å, c = 20.360 (3) Å, β = 107.49 (1)°, V = 2418.5 (8) $Å^3$, Z = 2, D_{calcd} = 1.59 g cm^{-3}. **2b**: $C_{56}H_{40}Au_2As_2Cl_2N_4S_4$, M_R = 1510.8, triclinic, space group, $P\bar{1}$, a = 11.619 (2) Å, b = 12.404 (5) Å, c = 11.108 (2) Å, α = 98.20 (3)°, β = 105.70 (2)°, γ = 110.54 (2)°, V = 1372.3 (7) $Å^3$, Z = 1, D_{calcd} = 1.80 g cm^{-3}. Data were collected on a Nicolet R3m/E diffractometer. Structure solution and refinements were carried out by using the SHELXTL collection of crystallographic software. The structures of **1b** and **2b** were solved by heavy-atom methods. Convergence to final R values of R = 0.0292 and R_w = 0.0304 for **1b** was obtained by using 2291 reflections $[F^2 \geq 3\sigma(F^2)]$. Convergence to the final R values of R = 0.0272 and R_w = 0.0282 for **2b** was achieved by using 2944 reflections $[F^2 \geq 3\sigma(F^2)]$. Bond distances and angles, final positional and thermal parameters, observed and calculated structure factors, and crystallographic experimental details can be found in the supplementary material.

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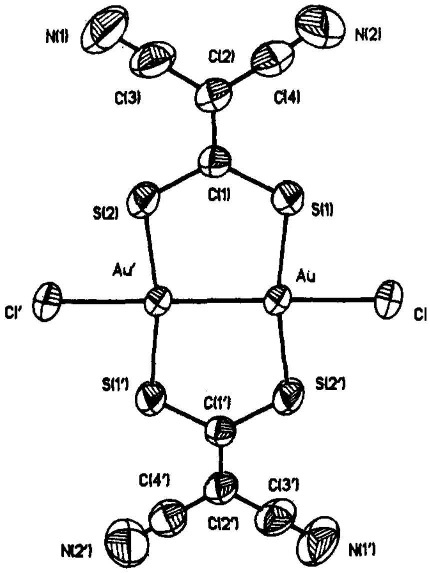

Figure 2. Structure of $[Ph_4As]_2[Au(i\text{-}MNT)Cl]_2$ (**2b**). Bond lengths (Å): Au-Au', 2.550 (1); Au-S(1), 2.286 (2); Au-S(2)', 2.287 (2); Au-Cl, 2.380 (3); S(1)-C(1), 1.716 (8); S(2)-C(1), 1.699 (7); C(1)-C(2), 1.38 (1); C(2)-C(3), 1.43 (1); C(2)-C(4), 1.41 (1); C(3)-N(1), 1.14 (1); C(4)-N(2), 1.15 (1). Bond angles (deg): S(1)-Au-S(2)', 168.3 (1); Au'-Au-Cl, 178.7 (1); S(1)-Au-Cl, 84.3 (1); S(1)-C(1)-S(2), 124.0 (4); C(1)-C(2)-C(3), 121.2 (7); C(1)-C(2)-C(4), 121.5 (8); C(3)-C(2)-C(4), 117.3 (7); C(2)-C(3)-N1), 178 (1); C(2)-C(4)-N(2), 177 (1).

excitation). Compound **1b** gives a broad emission at 510 nm with 1.9- and 40-μs lifetimes under the same conditions. As a solid, the emission of **1b** at 77 K shows two components with 0.74- and 5.0-μs lifetimes. Compound **1c** displays a similar behavior with somewhat shorter lifetimes, particularly in frozen solution. Unlike other dinuclear gold(I) compounds under study by us, these sulfur-containing complexes show no luminescence in solution at room temperature.

Compounds **1b** and **1c** react readily with Cl_2, Br_2, and I_2 at −78 °C in CH_2Cl_2 or THF to yield the corresponding halogen adducts. The purple compound $[Ph_4As]_2[Au^{II}(i\text{-}MNT)Cl]_2$ (**2b**) was obtained in crystalline form in 70% yield from ether/CH_2Cl_2 or ether/THF solution at −20 °C, and was characterized by IR spectroscopy and elemental[7] and X-ray diffraction[8] analyses. The green compound $[n\text{-}Bu_4N]_2[Au^{II}(i\text{-}MNT)Br]_2$ also has been structured, but details will be reported elsewhere. The anions of both Au^{II} species are very much alike.

The structure of the anion $[Au(i\text{-}MNT)Cl]_2^{2-}$ in **2b** and important bond lengths and angles are shown in Figure 2. The two *i*-MNT ligands bridge the two gold atoms as found in **1b**: Au-S(1) = 2.286 (2) Å; Au-S(2) = 2.287 (2) Å. The S(1)-Au-S(2)' angle of 168.3 (1)° in **2b** is considerably smaller than that in **1b** (172.2 (1)°). This is due to the strong Au-Au bond formed upon oxidation. The Au-Au distance of 2.550 (1) Å is one of the shortest known Au-Au bonds. The Au-Cl distance is normal, 2.380 (3) Å, while the 3.0 Å separation between S(1) and S(2)' atoms indicates the presence of significant nonbonding interactions between the two sulfur atoms. The anion is on a center of symmetry and is planar (maximum deviation 0.06 Å).

It is well known that 1,1-dithiolate ligands such as *i*-MNT and dithiocarbamates can stabilize unusual oxidation states of metal ions.[10] The *i*-MNT ligands, by virtue of their strong σ donation (dianionic) to the metal centers, appear to stabilize the Au^{II} dimers more effectively than do dithiocarbamate ligands. The complexes are structurally similar to the gold(II) ylide dimers.[5b] However, these complexes display an interesting low-energy electronic transition not found in the ylide complexes. These bands with peak maxima for Cl, Br, and I at 550, 586, and 640 nm, respectively, with $\epsilon = 3000\ M^{-1}\ cm^{-1}$, appear to have considerable $\sigma \rightarrow \sigma^*$ character and are currently under investigation in our laboratory. These compounds decompose to mononuclear complexes in solution at 22 °C. The products and the decomposition process are under study.

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Supplementary Material Available: Details of the X-ray diffraction analysis and listings of atomic coordinates, crystallographic data, thermal parameters, bond lengths, and bond angles (13 pages); tables of calculated and observed structure factors (55 pages). Ordering information is given on any current masthead page.

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