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New Insights into the Effects of Self-Association of the Cation $[Au\{C(NHMe)_2\}_2]^+$ on Its Solid State Structure and Luminescence

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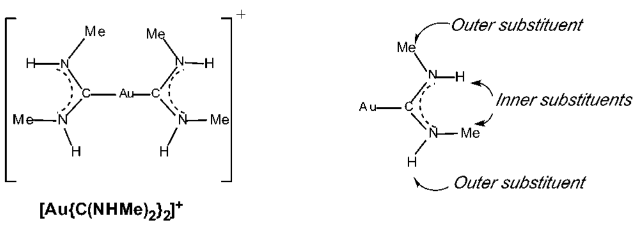
Colorless $[Au\{C(NHMe)_2\}_2]X{\cdot}H_2O$ (X = Cl or Br) crystallize as dimers with Au···Au separations of 3.1231(3) Å (Cl salt) and 3.1297(4) Å (Br salt) between the linear, two-coordinate cations, and there is no direct interaction of Au(I) with the halide ions which are hydrogen bonded to ligand N–H groups and the water molecules. The luminescence of these dimers occurs at higher energy than that observed in extended chains of the same cation in the corresponding $(PF_6)^-$ and $(BF_4)^-$ salts and shows the important effects of aggregation on the observed luminescence.

We recently reported that the colorless complex $[Au\{C(NHMe)_2\}_2][PF_6]{\cdot}0.5$(acetone) displays unique photoluminescence behavior.[1,2] In the solid state at room temperature, crystalline $[Au\{C(NHMe)_2\}_2][PF_6]{\cdot}0.5$(acetone) produces a blue luminescence (λ_{max}, 460 nm) when irradiated with a UV lamp. When dissolved in solvents such as acetone, pyridine, dimethyl sulfoxide, dimethylformamide, and acetonitrile, $[Au\{C(NHMe)_2\}_2][PF_6]{\cdot}0.5$(acetone) produces colorless solutions that are not luminescent at room temperature. Upon freezing in a liquid N_2 bath, these solutions become intensely luminescent. Strikingly, the colors of the emission differ in different solvents (acetone, orange; acetonitrile, green-yellow; dimethyl sulfoxide, blue; pyridine, blue-green; dimethylformamide, no luminescence). The differences in emission have been attributed to varying modes of aggregation of the two-coordinate cation, $[Au\{C(NHMe)_2\}_2]^+$ shown in Scheme 1. Indeed the structures of two solids containing the $[Au\{C(NHMe)_2\}_2]^+$ cation show differences in their luminescence and the mode of aggregation. In crystalline $[Au\{C(NHMe)_2\}_2][PF_6]{\cdot}0.5$(acetone) the cations form extended columns with an Au···Au separation of 3.1882(1) Å. In the related salt $[Au\{C(NHMe)_2\}_2][BF_4]$, the cations are arranged in a slipped, eclipsed fashion into extended stacks with a significantly longer Au···Au distance, 3.4615(2) Å. (Note that Au···Au separations less than 3.6 Å are considered as attractive aurophilic interactions.[3−5]) In both solids there are important hydrogen-bonding interactions between the ligand N−H groups and the anions. In order to understand the differences observed in the emission spectra displayed by $[Au\{C(NHMe)_2\}_2]^+$ under various conditions and to understand factors involved with its aggregation, we have examined the structures and emission spectra of two new salts of this cation.

Scheme 1



Colorless crystals of $[Au\{C(NHMe)_2\}_2]Cl{\cdot}H_2O$ and $[Au\{C(NHMe)_2\}_2]Br{\cdot}H_2O$ were obtained by adding methyl isocyanide and 40% aqueous methylamine successively to aqueous solutions of hydrogen tetrachloroaurate(III) hydrate and hydrogen tetrabromoaurate(III) hydrate, respectively, as described for other salts.[2] After filtration, the solutions were allowed to evaporate for a period of 1 week. The crystals were collected by filtration and washed with water (yield: 77% Cl salt, 45% Br salt).

Crystals of the two salts are isomorphic.[6] Figure 1 shows a drawing of the structure of $[Au\{C(NHMe)_2\}_2]Cl{\cdot}H_2O$, which forms a dimer rather than an extended stack. Selected interatomic distances and angles for each salt are given in

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(6) Crystal data for $[Au\{C(NHMe)_2\}_2]Cl{\cdot}(H_2O)$: $C_6H_{18}AuClN_4O$, M = 394.66, monoclinic, space group $I2/m$, a = 9.2500(4) Å, b = 11.3768(5) Å, c = 11.3137(7) Å, β = 99.228(1)°, V = 1175.19(19) Å^3, μ(Mo Kα) = 12.72 mm^{-1}, Z = 4, T = 90(2) K, 14697 reflections collected, 1923 unique (R_{int} = 0.0353), $R_w(F^2)$ was 0.060 (all data), conventional R1 for 1864 reflections with $I > 2\sigma(I)$ was 0.023. Crystal data for $[Au\{C(NHMe)_2\}_2]Br{\cdot}H_2O$: $C_6H_{18}AuClN_4O$, M = 439.12, monoclinic, space group $I2/m$, a = 9.3997(11) Å, b = 11.4229(14) Å, c = 11.5291(14) Å, β = 101.013(9)°, V = 1215.1(3) Å^3, μ(Mo Kα) = 15.370 mm^{-1}, Z = 4, T = 91(2) K, 7838 reflections collected, 1974 unique, $R_w(F^2)$ was 0.032 (all data), conventional R1 for I > $2\sigma(I)$ was 0.014.

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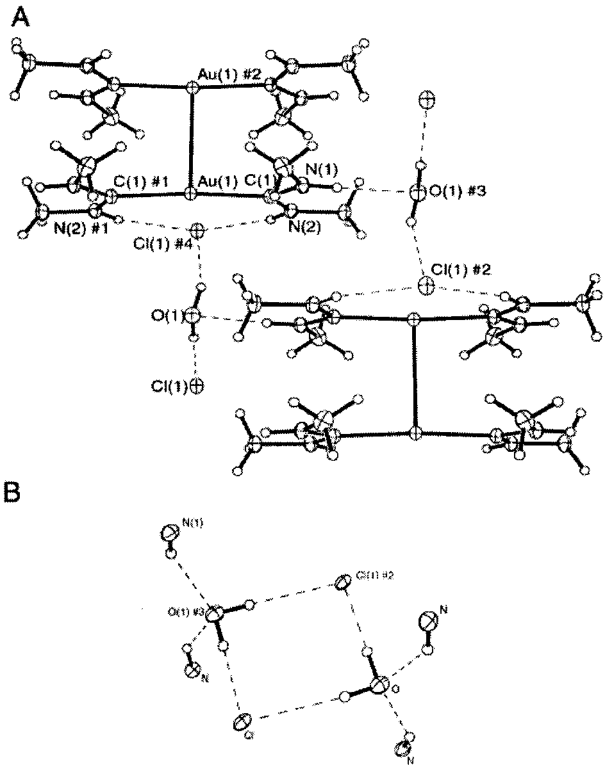

Figure 1. (A) A view of the structure of $[Au\{C(NHMe)_2\}_2]Cl\cdot H_2O$ which shows two dimeric units and part of the hydrogen-bonding scheme. (B) The hydrogen-bonding scheme that connects two chloride ions, two water molecules, and four individual cationic complexes (only the N−H units they contribute are shown).. Selected interatomic distances (Å): Au(1)···Au(1) #2, 3.1231(3); Au(1)−C(1), 2.039(4); C(1)−N(1), 1.326(4); C(1)−N(2), 1.333(4); N(1)···O(1) #3, 2.953(3); N(2)···Cl #4, 3.323(3); O(1)···Cl(1), 3.151(4); O(1)···Cl(1) #4, 3.320(4). Selected interatomic angles (deg): C(1)−Au(1)-C(1) #1, 173.49(17); Au(1)−C(1)-N(1), 125.3(2); Au(1)−C(1)-N(2), 117.1(2); N(1)−C(1)-N(2), 117.62(3), For comparison in $[Au\{C(NHMe)_2\}_2]Br\cdot H_2O$ selected interatomic distances (Å): Au(1)···Au(1) #2, 3.1297(4); Au(1)−C(1), 2.039(2); C(1)−N(1), 1.326(3); C(1)−N(2), 1.333(3); hydrogen bonds, N(1)···O(1) #3, 2.9660(19); N(2)···Br(1) #4, 3.42990(19); O(1)···Br(1), 3.304(2); O(1)···Br(1) #4, 3.438(2). Selected interatomic angles (deg): C(1)−Au(1)-C1(1) #1, 174.17(11); Au(1)−C(1)-N(1), 125.20(15); Au(1)−C(1)-N(2), 117.13(15); N(1)−C(1)-N(2), 117.66(19).

the figure caption. Each individual cation involves nearly linear coordination of the gold by two diaminocarbene ligands with *no coordination by the anion*. Rather the anions are nestled into space between the ligands so that the shortest distance from gold to chloride in $[Au\{C(NHMe)_2\}_2]Cl\cdot H_2O$ is 3.4022(10) Å and the shortest distance from gold to bromide in $[Au\{C(NHMe)_2\}_2]Br\cdot H_2O$ is 3.5357(5) Å.

Within the individual cations, the two carbene ligands are planar, and the C1−Au−C1 #1 angle (173.49(17)°) is slightly bent. Figure 1 emphasizes the formation of pairs of cations with Au···Au separations of 3.1231(3) Å (Cl salt) and 3.1297(4) Å (Br salt). These distances are well below the value of 3.6 Å where aurophilic attractions are found. Thus the strength of the aurophilic attraction between these diaminocarbene gold(I) complexes is sufficient to overcome the Coulombic repulsion between these cations. The pairs of cations are arranged so that the two carbene ligands on adjacent cations eclipse one another. However, the ligands bend slightly away from each other so that the nonbonded distance between the carbene carbon atoms (C(1)) of neighboring ligands (3.262(6) Å) is greater than the separation between gold atoms (3.1231(3) Å). The pairs of cations are well-separated from neighboring pairs. The distance from Au(1) to the nearest gold atom in another pair of cations is 6.7246(3) Å. The Au···Au separations in these halide salts are slightly shorter than those in the extended chains in $[Au\{C(NHMe)_2\}_2][PF_6]\cdot 0.5(acetone)$ (Au···Au separation, 3.1882(1) Å) where the cations assume a staggered orientation and considerably shorter than the corresponding Au···Au separations (3.4615(2) Å) in $[Au\{C(NHMe)_2\}_2][BF_4]$, which also has the carbene ligands in an eclipsed arrangement.[1]

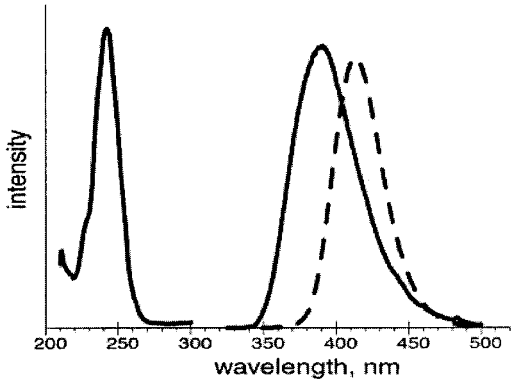

Figure 2. The emission (right) and excitation (left) spectra of crystals of $[Au\{C(NHMe)_2\}_2]Cl\cdot H_2O$ at room temperature. The dashed line shows the emission spectrum from solid $[Au\{C(NHMe)_2\}_2]Br\cdot H_2O$.

An extended network of hydrogen-bonding interactions exists within these solids. The outer N−H groups of the ligands on an individual $[Au\{C(NHMe)_2\}_2]^+$ ion are hydrogen bonded to a chloride or bromide ion as seen in part A of Figure 1. Each chloride or bromide ion is also hydrogen bonded to two water molecules to form a cyclic $[Cl(H_2O)]_2^{2-}$ unit as seen in part B of Figure 1. The water molecules are also hydrogen bonded to two inner N−H groups of neighboring $[Au\{C(NHMe)_2\}_2]^+$ ions in different dimers.

While the $[Au\{C(NHMe)_2\}_2]^+$ ion in solution is nonluminescent,[1] the solids $[Au\{C(NHMe)_2\}_2]Cl\cdot H_2O$ and $[Au\{C(NHMe)_2\}_2]Br\cdot H_2O$ are strongly luminescent. The emission and excitation spectra of $[Au\{C(NHMe)_2\}_2]Cl\cdot H_2O$ along with the emission spectrum of $[Au\{C(NHMe)_2\}_2]Br\cdot H_2O$ are shown in Figure 2. The emission for $[Au\{C(NHMe)_2\}_2]Cl\cdot H_2O$ occurs at 391 nm while that of $[Au\{C(NHMe)_2\}_2]Br\cdot H_2O$ is found at 412 nm. This difference is real and has been reproduced in several individual preparations of these compounds. The difference in emission maxima seen in Figure 2 may result from a larger Stokes shift for the bromide salt where the larger anion allows a greater degree of distortion in the excited state. In these cases where the interaction between cations can be treated as local pairs, the spectroscopic features result from overlap of filled d_{z^2} orbitals and empty p_z orbitals (with the z axis defined by the Au···Au vector) on the gold ions in each dimer much like that seen for other binuclear gold(I) complexes such as $[Au^I_2(Ph_2PCH_2PPh_2)_2]^{2+}$,[7,8] and for d^8 metal complexes:

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$[Rh^{I}(CNR)_4]_n^{n+}$,[9,10] and $[Pt^{II}_2(\mu\text{-}P_2O_5H_2)_4]^{4+}$.[11,12] Thus, the excitation involves a transition from the filled gold $\sigma^*(d_{z^2})$ molecular orbital to the empty $\sigma(p_z)$ molecular orbital, and the emission results from the $^3[d\sigma^*p\sigma]$ state. Since $[Au\{C(NHMe)_2\}_2]Cl\cdot H_2O$ and $[Au\{C(NHMe)_2\}_2]Br\cdot H_2O$ have very limited solubility in solvents other than water, we have not been able to observe the effect of solvents on the luminescent behavior of these salts.

These results are important for several reasons. They extend the range of chemical environments in which the $[Au\{C(NHMe)_2\}_2]^+$ ion exists and show that the counter-anion and hydrogen bonding again play significant roles in determining the solid state structure of these salts. It is significant to note that aggregation of cationic gold(I) complexes is rare. For example, neither the sterically constrained $[Au(PPh_3)_2]^+$ [13] nor the unencumbered $[Au(CNMe)_2]^+$ [14] undergoes self-association in the solid state. The cations in the binuclear complex $\{[(Ph_3P)Au]_2Cl\}X$ self-associate only when the anion, X, is bulky.[15] Moreover, in the two salts reported here, self-association through aurophilic attraction occurs in a situation where coordination of the anion was a distinct possibility. This behavior contrasts with that of another linear, two-coordinate gold(I) complex, $[Au(PPh_3)_2]^+$, which adds chloride ion to form three-coordinate $ClAu(PPh_3)_2$.[16] The steric bulk of the triphenylphosphine ligands inhibits any aurophilic attraction between $[Au(PPh_3)_2]^+$ cations but allows additional coordination by an anion.[13,16] Clearly the linear structure of $[Au\{C(NHMe)_2\}_2]^+$ is not responsible for its inability to coordinate chloride or bromide.

Importantly, the local environment of the $[Au\{C(NHMe)_2\}_2]^+$ ion affects its luminescence behavior. The simple dimers in crystalline $[Au\{C(NHMe)_2\}_2]Cl\cdot H_2O$ and $[Au\{C(NHMe)_2\}_2]Br\cdot H_2O$ emit at higher energy than does $[Au\{C(NHMe)_2\}_2][PF_6]\cdot 0.5(\text{acetone})$ with its extended aggregation of cations into linear stacks despite the fact that Au···Au separations in these halide salts are slightly shorter than those in the extended chains.[1] This shift in emission wavelength can be explained, since extended aggregation produces a band structure with a narrower band gap than the HOMO−LUMO gap in the dimers reported here. However, the structural elements necessary to obtain the low-energy emission seen for the frozen acetone solutions of $[Au\{C(NHMe)_2\}_2][PF_6]\cdot 0.5(\text{acetone})$[1] still remain to be determined.

Although self-association of cationic gold(I) complexes is rare, several anionic gold(I) complexes do form aggregates. In the salt $(C_{12}H_{14}N_2)[AuI_2]_2$, the $[AuI_2]^-$ ions associate into extended chains along a crystallographic 4_2 screw axis with an Au···Au distance of 3.3767(3) Å.[17] The absorption and emission spectra of aqueous and methanolic solutions of $[Au(CN)_2]^-$ indicate that aggregation occurs in concentrated solutions and that a variety of emitting species, oligomers of $[Au(CN)_2]^-$, are formed.[18,19] The variation in the emissive properties of $[Au\{C(NHMe)_2\}_2]^+$ salts, with the dimers and extended oligomers showing significant differences in their emissive properties, is consistent with the suggestions that alterations in the extent of self-association between gold complexes[20,21] rather than the alternative possibility, exciplex formation with anions or solvent molecules,[7] is responsible for the tunable luminescence from $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$.

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Supporting Information Available: An X-ray crystallographic file (CIF) including tables of crystallographic details, atomic coordinates, anisotropic thermal parameters, and interatomic distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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