Temperature-Dependent Solid-state Luminescence and Reversible Phase Transition of $(n\text{-Bu}_4\text{N})[\text{Au}(\text{SC}_6\text{H}_3\text{-3,5-Me}_2)_2]$

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The solid-state luminescence, thermal behavior, and phase transition of the gold(I) complex with 3,5-dimethylbenzenethiolate are discussed. The emission decay process of this complex switches accompanied by the reversible phase transition without destruction of the crystal lattice.

The luminescence is a predominant property of the gold(I) complexes and sensitive to the structural and environmental influence due to solid-state structure and packing arrangement through the non-covalent interactions, such as the gold–gold interaction,[1] hydrogen bonding,[1f] and π–π stacking.[1g] Recently, we reported that the solid-state luminescence of the S–Au–S type of gold(I) benzenethiolate complexes with sterically hindered tetra-*n*-butylammonium counter cations can be an ideal example for understanding the properties of gold(I) thiolate complexes without gold–gold interactions.[2] However, these complexes show structural diversity of the crystal structure based on the rotation of Au–S and S–C bonds owing to conformational flexibility of the linear two coordinate geometry around gold center. The conformational diversity including the polymorphism can be an important factor both in understanding the molecular basis and in material design,[3] however, the crystal structure is generally unpredictable.[4] We describe here the relationship between luminescence properties and the crystal structure of the gold(I) complex coordinated with two 3,5-dimethylbenzenethiolates.

The complex, $(n\text{-Bu}_4\text{N})[\text{Au}(\text{SC}_6\text{H}_3\text{-3,5-Me}_2)_2]$[5] **1** shows temperature-dependent solid-state luminescence as shown in the inset of Figure 1. Emission maximum observed at 516 nm on excitation at 350 nm is tentatively assigned as phosphorescence derived from triplet metal-to-ligand charge-transfer (^{3}MLCT) and/or ligand-centered (^{3}LC) excited state as well as analogous complexes.[2] The emission intensity increased with decrease of temperature from 293 to 173 K without any spectral shift. The emission decay rate can be analyzed by the Arrhenius type equation [$k_{\text{obs}} = k\exp(-E/RT)$] ($k_{\text{obs}}$: the decay rate, k: the pre-exponential factor, E: the activation energy) for an independent deactivation process.[6] The logarithm of inverse of the emission intensity ($\ln 1/I$) also reveals linear relationship toward inverse of the temperature ($1/T$) for the independent deactivation process as well as the logarithm of the decay rate ($ln\ k_{\text{obs}}$).[6] The plot of $\ln 1/I$ vs $1/T$ of the present complex deviates obviously for the linearity as shown in Figure 1. However, these plots were fitted by two independent interpolation lines, and the intersection was observed at 238 K. The activation energies of these two deactivation processes in the low and high temperature regions are 110 and 290 cm^{-1}, respectively. This result can be explained by that two independent deactivation processes are responsible for the luminescence behavior in temperature range of 173–293 K. In practice, differential scanning calorimetry of the complex **1** showed a significant endothermic peak at 238 K (Figure 2) and an enthalpy of this process was 2.1 kJmol^{-1}. It suggests that switching of the emission decay process should be promoted by the thermal behavior of the complex such as the phase transition, cooperating with the alteration of the emission behavior.

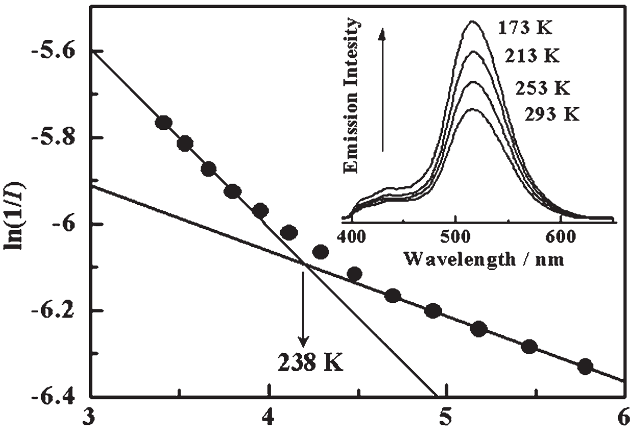


Figure 1. Temperature dependence of the emission intensity (I) of the complex **1**. The inset shows emission spectra in the range of 173–293 K.

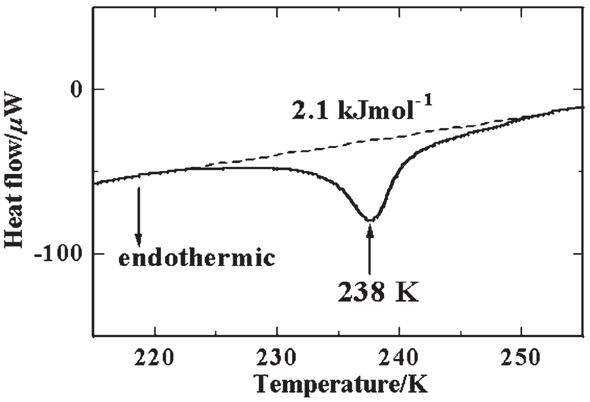


Figure 2. Thermal behavior of the complex **1** in the range of 215–255 K measured by DSC.

This complex displays a reversible single-crystal to single-crystal phase transition characterized by X-ray analyses[7] at 213 and 298 K. Two half complex anions are determined crystallographically independent in low temperature phase (LTP). ORTEP views[8] of two complex anions measured at 213 K are shown

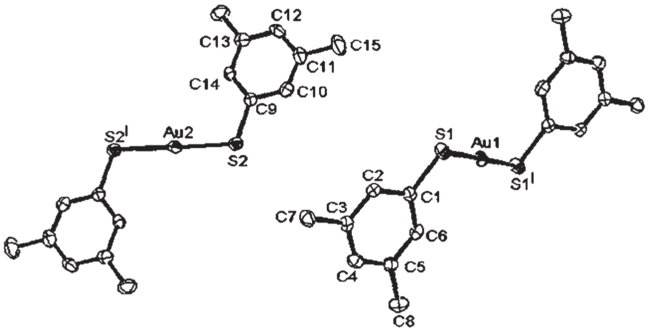
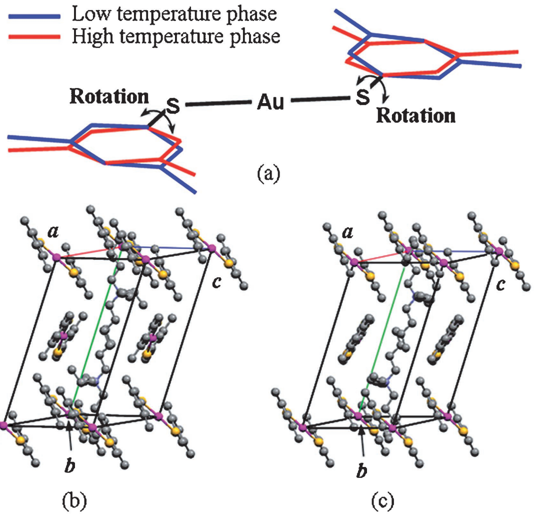


Figure 3. Perspective views of complex anions of **1** in the LTP with the atomic numbering scheme. (Hydrogen atoms are omitted for clarify. Thermal ellipsoids are drawn at the 30% probability level). Selected bond distances (Å) and angles (°): LTP: Au1–S1, 2.289(1); Au2–S2, 2.283(1); S1–C1, 1.767(4); S2–C9, 1.756(4); S1–Au–S1i, 180.0; S2–Au–S2i, 180.0; Au1–S1–C1, 108.6(2); Au2–S2–C9, 108.4(1); HTP: Au1–S1, 2.293(2); Au2–S2, 2.275(3); S1–C1, 1.763(7); S2–C9, 1.755(8); S1–Au–S1i, 180.0; S2–Au–S2i, 180.0; Au1–S1–C1, 108.5(2); Au2–S2–C9, 108.9(3).

in Figure 3. Two gold centers of each anion have completely linear geometry, where the S–Au–S angle is 180°, since gold atoms are situated on a crystallographic center of symmetry. The Au–S–C, the Au–S and the S–C bond distances are in the normal range of reported complexes, (*n*-Bu$_4$N)[Au(SC$_6$H$_4$-R)$_2$] (R = *o*-Me, *o*-Cl, *m*-Cl) [Au–S–C; 108.8(8)–111.8(8)°, Au–S; 2.256(8)–2.292(9) Å, S–C; 1.71(2)–1.85(2)].[2] The C–S–(Au)–S–C torsion angles of 180° show flatter conformation similar to the reported *m*-Cl derivative.[2] The structural difference between two independent anions is found in the averaged Au–S–C–C torsion angles, which are 21.3° for Au1 component and 10.9° for Au2, respectively, giving a twist conformation. There is no significant intermolecular gold–gold interaction because of the steric hindrance of bulky tetra-*n*-butylammonium counter cation.[2] In the high temperature phase (HTP), two half complex anions are also determined independently. The gold centers are still situated on the crystallographic centre of symmetry and have completely linear geometry. All bond distances and angles of the complex anion are in the normal range in each conformation, but the averaged Au–S–C–C torsion angles show different values, which are 20.0° for Au1 component and 1.5° for Au2, respectively. The phenyl rings of the Au2 component with the twist form in the LTP rotate ca. 10° around the S–C bonds in the crystalline solid associate with the phase transition, giving the flat conformation in the HTP (Figure 4a). In addition, the terminal carbon atom of the cation also changes its conformation showing unusual bond distances of the C31–C32 and the C27–C28 in the HTP caused by the thermal disorder. The packing diagrams of these two phases are depicted in Figures 4b and 4c. It is clearly shown that the complex anions with the twist form in LTP transform to the flat form in HTP, and the cations also changed their conformation of the terminal C32–C31 bond. It seems that the terminal carbon atoms of the cation has slightly large degree of freedom and might be disordered cooperatively with the complex anion. The lattice parameters of the complex are slightly expanded during the phase transition to the HTP. In particular, the *a* axis of the unit cell is lengthened about 2.4%, and the volume of the unit cell is expanded about 3.5% in comparison with the LTP. Because of such relatively small structural transformations, the phase transition has been observed reversibly without destruction of the crystal lattice.



(b) (c)

Figure 4. (a) Structural transformation by rotational motion of the phenyl rings in the phase transition. Packing diagrams of the complex **1** in (b) the LTP and (c) the HTP.

In conclusion, the gold(I) complex with two 3,5-dimethylbenzenethiolates shows two independent emission decay processes switched by the conformational transformation due to the reversible phase transition at 238 K. Sensibility of the luminescence behavior to the relative small structural change such as the rotation of the phenyl ring of the ligand moieties suggests that the metal-perturbed ^{3}LC [S(n) $\leftarrow \pi^*$] excited state is significantly responsible for the emission origin of the present complex.

References and Notes

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5 Synthesis of the complex **1** is according to the literature method.[2] The yellow crystal was obtained by recrystallization from methanol (isolated yield 77%). Anal. Calcd for C$_{32}$H$_{54}$NS$_2$Au: C, 53.84; H, 7.62; N, 1.96%. Found: C, 53.49; H, 7.73; N, 1.99%.

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7 Crystal data for the low temperature phase (213 K): C$_{32}$H$_{54}$NAuS$_2$, M = 713.87, triclinic, space group $P\bar{1}$, $a = 12.402(1)$, $b = 16.802(1)$, $c = 8.7365(9)$ Å, $\alpha = 104.783(4)°$, $\beta = 106.768(2)°$, $\gamma = 72.711(1)°$, $V = 1635.5(3)$ Å^3, $\lambda = 0.71069$ Å, $Z = 2$, $D_c = 1.449$ g cm^{-3}, $T = 213$ K, μ(Mo Kα) = 46.61 cm^{-1}, The structure was solved by the direct methods (SIR92). 5249 reflections ($I > 3.0\sigma(I)$, $2\theta_{\max} = 55.0°$) converged at $R_1 = 0.027$ ($R = 0.038$ and $R_w = 0.082$). Crystal data for the high temperature phase (298 K): C$_{32}$H$_{54}$NAuS$_2$, M = 713.87, triclinic, space group $P\bar{1}$, $a = 12.694(2)$, $b = 16.874(4)$, $c = 8.7945(7)$ Å, $\alpha = 105.529(2)°$, $\beta = 105.469(4)°$, $\gamma = 72.1449(3)°$, $V = 1692.2(4)$ Å^3, $\lambda = 0.71069$ Å, $Z = 2$, $D_c = 1.401$ g cm^{-3}, $T = 298$ K, μ(Mo Kα) = 45.05 cm^{-1}, The structure was solved by the direct methods (SIR92). 4050 reflections ($I > 3.0\sigma(I)$, $2\theta_{\max} = 55.0°$) converged at $R_1 = 0.039$ ($R = 0.045$ and $R_w = 0.097$). All H atoms were placed in calculated positions (C–H = 0.95 Å) but were not refined.

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