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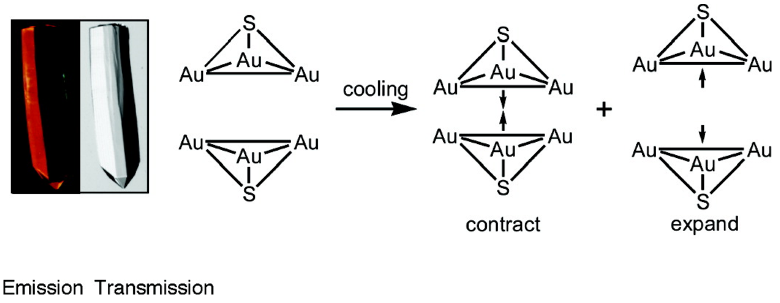

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A Reversible Polymorphic Phase Change Which Affects the Luminescence and Aurophilic Interactions in the Gold(I) Cluster Complex, [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$)

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Attractive interactions between closed-shell (d^{10}) gold(I) ions are a prominent feature that affects both the structure and spectroscopic behavior of linear, two-coordinate gold(I) complexes.[1] As a result of alterations in the aurophilic interactions, gold(I) complexes show a number of unusual and unanticipated luminescence phenomena.[2] Such phenomena include solvoluminescence,[3] emission from previously irradiated samples that is simulated by contact with solvents; luminescence tribochromism,[4] emission that is switched on by grinding; and luminescence that is altered in the presence of volatile organic compounds.[5] The sensitivity of the frequently intense luminescence of such gold(I) complexes to environmental factors suggests that these complexes may find utility in sensing devices. Here, we demonstrate a new level of sensitivity of gold complexes to environmental change and demonstrate that crystals of a gold(I) complex are susceptible to a reversible phase change upon cooling. While most polymorphs of molecular substances involve differences in molecular conformation, molecular orientation, or crystal packing,[6] the phase change reported here alters the nature of the aurophilic interactions and thereby affects the luminescence.

Treatment of an acetone solution of [Au(CNC$_7$H$_{13}$)$_2$](SbF$_6$) or [Au(CNC$_6$H$_{11}$)$_2$](PF$_6$)[7] with a solution of Na$_3$[Au(S$_2$O$_3$)$_2$] in water produces colorless crystals of [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$) (ν(CN) 2233 cm^{-1}) or [μ_3-S(AuCNC$_6$H$_{11}$)$_3$](PF$_6$) (ν(CN) 2235 cm^{-1}), respectively, in ca. 90% yield. The structure of [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$), as determined by X-ray crystallography at 190(2) K, shows two half-cations in the asymmetric unit with the other half of each cation generated by a mirror plane, as shown in Figure 1.[8] The Au$_3$ portion of the cation forms an isosceles triangle with Au⋯Au separations of 3.2472(9) and 3.3502(13) Å that are indicative of aurophilic interactions. The geometry of each individual cation is similar to that of previously reported complexes of the type [μ_3-S(AuPR$_3$)$_3$]$^+$.[9−11] In [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$), these cations undergo self-association to form a pseudo-octahedral array of six gold atoms in which the interionic interactions are longer than the intraionic aurophilic interactions. Although this mode of self-association is unique for cations of the type [μ_3-S(AuL)$_3$]$^+$, a related hexagold cluster with bridging diphosphine ligands has been reported.[12]

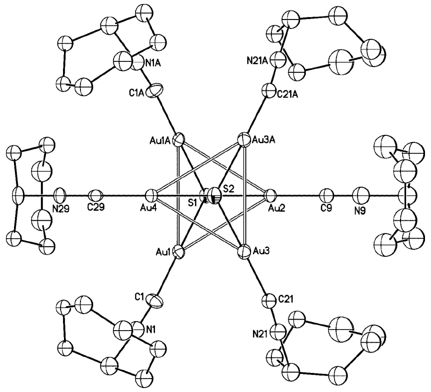

Figure 1. A view of the orientation of a pair of cations in the high-temperature polymorph of [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$) with 10% thermal contours for all non-hydrogen atoms.

The structure of [μ_3-S(AuCNC$_6$H$_{11}$)$_3$](PF$_6$) has also been determined crystallographically and shows a similar arrangement of the two cations to form a pseudo-octahedral array of gold atoms.

Crystallographic examination of [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$) shows that it undergoes a reversible phase change from orthorhombic to monoclinic upon cooling. Remarkably, the phase change lowers the symmetry of the gold cations and results in the creation of two different pairs of cations: one with *expanded* interionic Au⋯Au separations, the other with contracted interionic Au⋯Au separations. The phase change is centered at 150 K and proceeds over a 5° temperature range. The structure of the monoclinic phase has been determined at 90 K, where it was refined as a racemic twin. At this temperature, there are four independent cations in the asymmetric unit with no crystallographically imposed symmetry. These cations form two significantly different pseudo-octahedral arrays of gold atoms. A comparison of the structural parameters within the μ_3-S−Au$_3$ cores of the high- and low-temperature forms of [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$) is presented in Figure 2. At both temperatures, the Au−S distances fall in similar narrow ranges: 2.281(6)−2.305(6) Å at 190 K and 2.283(4)−2.311(4) Å at 90 K. Likewise, the Au−C distances occur in similar ranges: 1.933(18)−1.95(2) Å at 190 K and 1.909(19)−2.043(15) Å at 90 K. However, there are more significant variations in the aurophilic interactions in the clusters. At 90 K, the interionic Au⋯Au separations in one cluster fall in the 3.3214(9)−3.4603(9) Å range and are just slightly longer than the intraionic Au⋯Au separations. In the other cluster, the interionic Au⋯Au separations are much longer: 3.6545(9)−3.7707(10) Å. In contrast, at 190 K, the interionic Au⋯Au separations fall in the range of 3.5421(9)−3.5826(8) Å, which is midway between the range of interionic Au⋯Au distances for the two different clusters seen at 90 K.

Crystals of [μ_3-S(AuCNC$_6$H$_{11}$)$_3$](PF$_6$) do not show any evidence of a phase change over the temperature range from 6 to 298 K.

Crystals of [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$) or [μ_3-S(AuCNC$_6$H$_{11}$)$_3$](PF$_6$) are highly luminescent and produce intense orange−red emission. The emission and excitation spectra for [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$) at 298 K are shown in Figure 3a. There is a single emission at 667 nm with an excitation maximum at 355 nm. The behavior of [μ_3-S(AuCNC$_6$H$_{11}$)$_3$](PF$_6$) is similar: emission max, 678 nm; excitation max, 369 nm at 298 K. On cooling, the emission spectrum of [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$) is significantly altered, as shown in Figure 3b. At 77 K, two emission maxima at 490 and 680 nm are observed. The lifetimes of the two emissions have similar magnitudes: 25 μs for the emission at 680 nm and 10 μs for the emission

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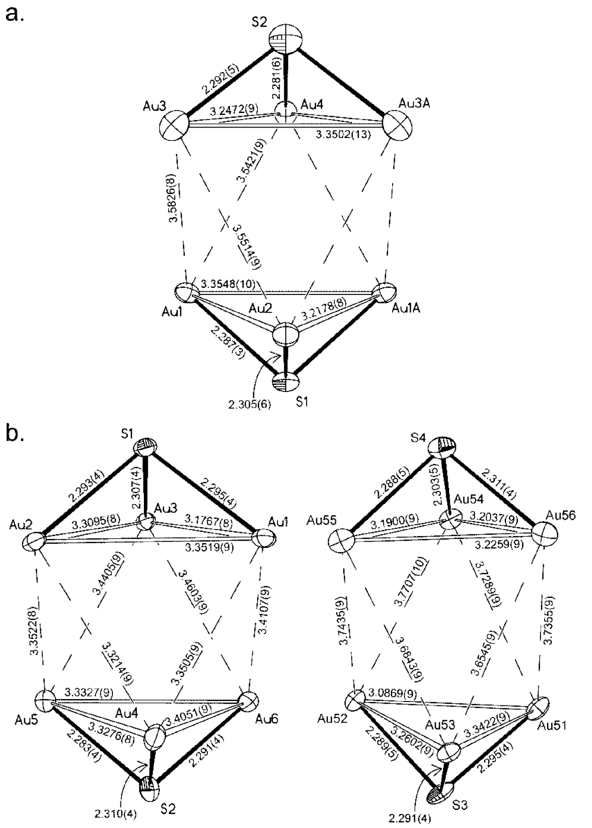

Figure 2. A comparison of the dimensions within the cluster formed by interaction of two cations: (a) the high-temperature, orthorhombic polymorph of [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$); and (b) the low-temperature, monoclinic polymorph of [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$).

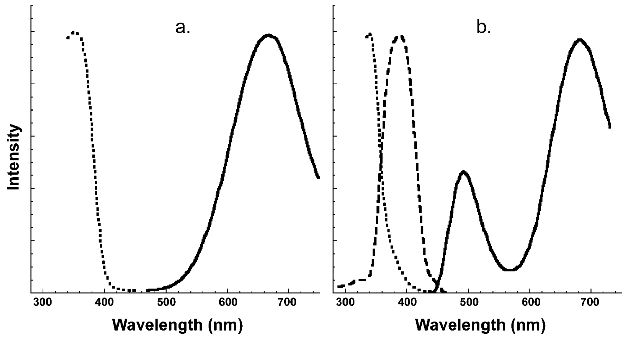

Figure 3. The emission and excitation spectra of a polycrystalline sample of [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$) at 298 K (a) and 77 K (b). At 77 K, the dotted and dashed lines show the excitation spectra for emission at 680 and 490 nm, respectively.

at 490 nm. Thus, these emissions are both likely to result from phosphorescence. The emission at 680 nm has an excitation spectrum with a maximum at 340 nm, while the emission at 490 nm has an excitation maximum at 387 nm. In contrast, the emission spectrum of [μ_3-S(AuCNC$_6$H$_{11}$)$_3$](PF$_6$) does not change upon cooling from 298 to 77 K. The spectral changes seen for cooling crystals of [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$) and [μ_3-S(AuCNC$_6$H$_{11}$)$_3$](PF$_6$) parallel the crystallographic behavior, with the former undergoing a phase change that results in the formation of two different gold clusters, each producing independent emission spectra. For [μ_3-S(AuCNC$_6$H$_{11}$)$_3$](PF$_6$), there is no change in either the emissive behavior or the crystal structure on cooling the crystals.

Previous work has demonstrated that the aurophilic interactions in two-coordinate gold(I) complexes are susceptible to modification when polymorphs form. Thus, [Au(CNC$_6$H$_{11}$)$_2$](PF$_6$) crystallizes as either a colorless (blue luminescent) or a yellow (green luminescent) polymorph.[7] Each polymorph contains chains of cations, but they differ in their Au···Au separations. Colorless Au(PPh$_2$Me)Cl also crystallizes as two polymorphs.[13] One contains a dimer connected through a single Au···Au interaction, while the other contains a trimer with two Au···Au interactions.[13a] Each of these polymorphs has a distinct emission spectrum.[13b] Similarly, Au(P(*p*-tol)$_3$)Cl crystallizes as two polymorphs. One is dimeric with a short Au···Au contact, while the other is monomeric and lacks any close Au···Au interaction.[14] [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$) joins this group in forming polymorphs; however, it is the first of these to show a reversible phase change on cooling. The results presented here demonstrate yet another factor, temperature-dependent, reversible phase changes, that can affect aurophilic interactions and the luminescence of two-coordinate gold(I) complexes. Such phase changes could be responsible for other cases, where crystal luminescence changes markedly upon cooling (e.g., as recently seen for {3,5-(*i*-Pr)$_2$pyrazolate}$_3$Cu$_3$).[15]

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Supporting Information Available: X-ray crystallographic data for [μ_3-S(AuCNC$_6$H$_{11}$)$_3$](PF$_6$), and for the high- and low-temperature polymorphs of [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Crystal data for C$_{24}$H$_{39}$Au$_3$F$_6$N$_3$SSb, colorless block. High-temperature polymorph: orthorhombic, space group *Cmc*2$_1$, $a = 15.1136(8)$ Å, $b = 26.6130(14)$ Å, $c = 15.9880(9)$ Å, $V = 6430.7(6)$ Å^3, $Z = 8$, $D_c = 2.537$ Mg/m^3, $T = 190(2)$ K; $R1 = 0.0675$, $wR2 = 0.1209$ for all data; conventional $R1 = 0.0423$ computed for 7630 observed data ($I > 2\sigma(I)$) with 313 restraints and 241 parameters. Low-temperature polymorph: monoclinic, space group $P2_1$, $a = 14.9353(11)$ Å, $b = 15.7717(12)$ Å, $c = 26.457(2)$ Å, $\beta = 91.1412(14)°$, $V = 6231.0(8)$ Å^3, $Z = 8$, $D_c = 2.619$, $T = 90(2)$ K; $R1 = 0.0665$, $wR2 = 0.1450$ for all data; conventional $R1 = 0.0554$ computed for 34936 observed data ($I > 2\sigma(I)$) with 1 restraint and 1276 parameters.

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