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Anomalous structure–luminescence relationship in phosphorescent gold(I) isonitrile neutral complexes

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A new compound that exhibits the shortest intermolecular Au···Au distance ever reported for neutral RNCAuX complexes is found to exhibit a counterintuitive higher-energy Au-centered phosphorescence than that in an analogous compound with a much longer Au···Au distance, presumably due to a different extent of excited-state distortion in dimers *vs*. extended chains.

Metal isonitriles have been strongly overshadowed by metal carbonyls despite their greater structural diversity. The electronic structure of RNC is generally similar to that of CO, although RNC is believed to be a somewhat stronger σ donor and weaker π acceptor than CO.[1] Fascinatingly diverse supramolecular structures are exhibited by the RNCAuX class of compounds owing to various intermolecular interactions that have often resulted in liquid crystalline phases.[2] By varying the R group and X, the molecules associate to form dimers, larger linear or cyclic oligomers, one-dimensional (1-D) continuous or pleated extended chains, and two-dimensional (2-D) polymeric sheets.[3–10] The large spin–orbit coupling and the presence of intermolecular Au···Au interactions in members of this class of two-coordinate Au(I) complexes usually lead to Au-centered phosphorescence in the solid state, which is a significant advantage for potential applications in molecular LEDs.[11]

Despite the great attention given to luminescent Au(I) compounds over the past few decades,[12] establishing a clear structure–luminescence relationship remains an elusive goal that continues to frustrate many researchers in this area. What has been clearly established is the need to have intramolecular or intermolecular closed-shell Au···Au interactions (aurophilic bonding)[13] in order to observe Au-centered luminescence in two-coordinate complexes while three-coordinate complexes do not require such interactions.[12] The frustration lies in trying to relate the luminescence energy to the crystallographic Au···Au ground-state distances, as direct,[14] inverse,[15] or no[10] such relationships have been observed.[12] This is in contrast to the situation in luminescent systems of other metals that were studied earlier, such as the tetracyanoplatinates(II) in which a clear correlation has long been established between the luminescence energy and the Pt–Pt distance.[16] In this work, we show that the contrast in the emission energies is based on the association modes instead of the Au···Au distances in RNCAuX compounds such that a linear-chain compound with long but extended Au···Au separations has a lower emission energy than that in a dimeric compound with a short Au···Au distance.

The synthesis, molecular structure, and electronic structure of a new compound, chloro((*p*-tosyl)methylisonitrile)gold(I), **1**, are described in comparison with those for chloro(*tert*-butylisonitrile)gold(I), **2**. Compounds **1** and **2** were synthesized by mixing equimolar amounts of Au(tetrahydrothiophene)Cl and (*p*-tosyl)methylisonitrile (**1**) or *tert*-butylisonitrile (**2**) in CH_2Cl_2.[17] Single crystals used in the X-ray and luminescence studies were grown from CH_2Cl_2–pentane. Fig. 1 shows that the symmetric molecules of **1** associate as crossed dimers with a very short ligand-unassisted intermolecular Au···Au distance of 3.0634(4) Å. This represents the shortest intermolecular Au···Au distance ever observed so far in neutral two-coordinate RNCAuX compounds, to our knowledge. The dihedral angles defined by C(1)–Au(1)–Au(1A)–C(1A) and Cl(1)–Au(1)–Au(1A)–Cl(1A) are 91.16 and 93.73°, respectively. The bond distances and angles within the molecule in **1** (Fig. 1 caption) are normal for RNCAuX complexes.[3–10] The crystal structure of **2** was determined previously[4] and we have confirmed that the sample we synthesized has the same cell constants as those reported. The supramolecular structure of **2** shows molecules packing in infinite polymeric 1-D chains along the *c*-axis with an anti-parrallel arrangement and uniform intermolecular Au···Au distances of 3.695 Å.[4] We have recently reported a series of compounds, CyNCAuX (X = Cl, Br and I) that also exhibit extended 1-D chain structures with long Au···Au distances.[10] Crossed-dimeric complexes like **1** are known to exhibit shorter intermolecular Au···Au distances than those in linear-chain complexes like **2**, according to a database analysis of two-coordinate Au(I) compounds in general.[18] Among 47 RNCAuX structures reported so far according to our survey, only **1** and three other compounds have crossed-dimeric structures. The shortest intermolecular Au···Au distances among all RNCAuX complexes are found in **1** (3.063 Å) and another crossed dimer, $MeOOCCH_2NCAuI$ (3.191 Å).[3a]

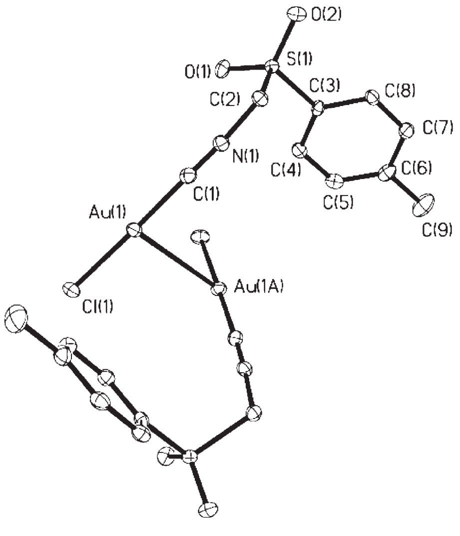

Fig. 1 Molecular structure of **1**;† thermal ellipsoids are at 30%; hydrogen atoms are omitted for clarity. Significant distances (Å) and angles (°): Au(1)–C(1) 1.933(5), Au(1)–Cl(1) 2.2579(11), Au(1)–Au(1A) 3.0634(4), C(1)–N(1) 1.131(6), N(1)–C(2) 1.423(6); C(1)–Au(1)–Cl(1) 178.50(15), C(1)–Au(1)–Au(1A) 90.67(14), Cl(1)–Au(1)–Au(1A) 90.11(3), N(1)–C(1)–Au(1) 178.7(4), C(1)–N(1)–C(2) 174.0(5), N(1)–C(2)–S(1) 109.8(3).

Temperature-dependent luminescence studies were conducted for crystalline samples of **1** and **2**.‡ Neither compound shows bright luminescence at room temperature, but cooling leads to a strong enhancement in the intensity of the blue luminescence of **1** at $T \leq 30$ K and the red luminescence of **2** at

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$T \leq 80$ K. Varying the temperature does not lead to significant changes in the energies or band shapes. Fig. 2 compares the electronic spectra of both compounds. The emission maxima at 4 K occur at 478 and 680 nm for **1** and **2**, respectively. Lifetimes of 76.0 ± 3.0 µs and 663.5 ± 13.5 µs were obtained at the peak maxima of **1** and **2**, respectively, at 4 K. The lifetime of **2** at 77 K decreases to 40.0 ± 1.3 µs, owing to a higher non-radiative decay rate constant, k_{nr}. A similar behavior is observed for **1**, for which temperature-dependent lifetime studies in the very low temperature range (3–15 K) show a linear relationship, giving rise to a radiative decay rate constant, k_r, of 9.1×10^3 s^{-1} at 0 K.

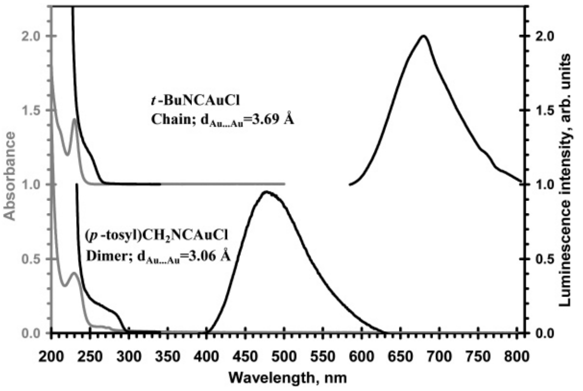

Fig. 2 Photoluminescence corrected excitation (left) and emission (right) spectra of crystalline samples of **1** and **2** at 4 K. Gray lines show the absorption spectra of acetonitrile solutions of **1** and **2** with concentrations of 1.21×10^{-5} and 7.66×10^{-5} M, respectively. The ordinates for the spectra of **2** are offset by one unit for the sake of clarity.

The broad/structureless profiles and the magnitudes of the lifetime values for the emission bands of **1** and **2** are consistent with Au-centered phosphorescent emissions from largely distorted excited states. The corresponding singlet→triplet absorptions are likely the shoulders that appear at ~282 and 252 nm in the corrected luminescence excitation spectra at 4 K for **1** and **2**, respectively. Dilute solutions of **1** and **2** exhibit electronic absorption spectra with a major peak at 230 nm for each ($\varepsilon = 3.3 \times 10^4$ and 8.4×10^4 M^{-1} cm^{-1}, respectively, in acetonitrile), assignable to metal-to-ligand charge transfer (MLCT) in monomeric molecules. It is not surprising that monomers of **1** and **2** absorb similarly, because the chromophore is the NCAuCl unit in both and very slight absorption changes are expected upon varying the substituents on the saturated carbon atom in the methylisonitrile moiety. Weak absorptions in the energy range of the shoulders in the luminescence excitation spectra of the solids appear in solution, especially at high concentration. If the emission peaks and excitation shoulders in the solid-state data in Fig. 2 correspond to the same pair of states,[19] **2** would have a Stokes' shift of ~25000 cm^{-1}! (which would quite possibly be the largest Stokes' shift ever observed for molecular species). On the other hand, the Stokes' shift of **1** would be 15000 cm^{-1}, which is very large but significantly smaller than that of **2**. These luminescence data are consistent with Au–Au bonded excited states. The covalent bonding in this state *vs.* the weak aurophilic bonding in the ground state explains the large excited state distortion. Che and co-workers suggested that excited-state Au–Au bonding alone does not lead to visible emissions in binuclear Au(I) compounds with two bridging phosphine ligands.[20] It was argued that an exciplex with either a solvent molecule or a counter ion must form in order to shift the phosphorescence energy from the UV region to the visible region and the authors suggested that this might be a general phenomenon for Au(I) compounds.[20] The data in this study contradict this conclusion, as visible emissions are seen in *neutral* complexes in the solid state and there are no counter ions or solvent molecules in the samples.

Fig. 3 illustrates a hypothesis that is consistent with the structural and luminescence data. In **1**, formation of an excimer upon photoexcitation leads to a visible emission in the blue–green region, similar to the situation encountered in organic excimers.[21] In **2**, the molecules pack in extended chains, not as dimers. Hence, the emission will occur from an excited state in which the shortening of Au···Au distances occurs over a longer range than that in dimers. Hence, the excited state distortion is greater and the emission energy is lower. Several observations in the literature of M–M bonded exciplexes are in support of this argument. First, the emission bands in mercury vapor at 335 and 485 nm have been assigned to a $*Hg_2$ excimer and a $*Hg_3$ trimer exciplex, respectively.[22] Second, Patterson and co-workers also suggested that $*[M(CN)_2^-]_n$ (M = Au or Ag) exhibit lower emission energies upon increasing "*n*".[23] Third, Henary and Zink showed that the contrast in the emission energy between two isomers of $Ag_4I_4(PPh_3)_4$ is based on the number of next-neighbor Ag atoms as opposed to the Ag–Ag distance.[24] Finally, heteroatomic Tl–Pt bonded exciplexes also exhibit a similar behavior, as reported by Nagle *et al.*[25] On the other hand, the anomalies reported by Elder *et al.* for $[Au(SCN)_2]^-$ complexes with different counter ions do not seem to point to a specific relationship between the association mode and the emission energy,[15] perhaps because the aforementioned factors discussed by Che *et al.*[20] may be relevant for these ionic species.

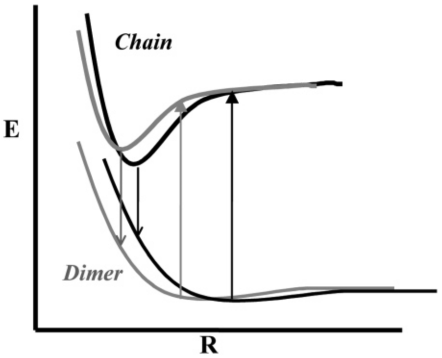

Fig. 3 Proposed model for the ground and emitting excited states of RNCAuX complexes that associate as dimers (gray) *vs.* chains (black).

In summary, the data in this work show an apparent anomaly in which a crossed dimeric Au(I) compound (**1**) exhibits a much higher emission energy despite having a much shorter Au···Au distance compared to extended-chain compounds such as **2** and CyNCAuX.[10] Hence, the emission energies are more sensitive to the association modes than to the ground-state Au···Au distances in RNCAuX complexes. Our efforts are continuing to directly probe the excited-state structure with experimental methods including time-resolved diffraction (photocrystallography), EXAFS and Raman spectroscopy, as well as computational methods that independently optimize the emitting triplet state.

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Notes and references

† *Crystal data*: Data for **1** were collected at 90(2) K with Mo-Kα radiation (λ = 0.71073 Å); $C_9H_9AuClNO_2S$, colorless plate, monoclinic, *C*2/*c*, a = 27.4784(9), b = 5.2120(2), c = 20.9709(7) Å, β = 129.4280(10)° with Z = 8, D_c = 2.449 g cm^{-3}, μ = 13.071 mm^{-1}. Refinement of 2066 reflections and 136 parameters yielded $wR2$ = 0.0542 for all data and a conventional R_1 = 0.0231 based on 1832 reflections with $I > 2\sigma(I)$. CCDC reference number 239752. See http://www.rsc.org/suppdata/dt/b4/b410657a/ for crystallographic data in CIF or other electronic format.

‡ *Spectral data*: Steady-state luminescence spectra were acquired with a PTI QuantaMaster Model QM-4 scanning spectrofluorometer. The

excitation and emission spectra were corrected for the wavelength-dependent lamp output and detector response, respectively. Lifetime data were acquired using fluorescence and phosphorescence subsystem add-ons to the PTI instrument. The pulsed excitation source was generated using the 337.1 nm line of the N_2 laser pumping a freshly-prepared 1×10^{-2} M solution of the continuum laser dye Coumarin-540A in ethanol, the output of which was tuned and frequency doubled to attain the 270 and 265 nm excitations used to generate the time-resolved data for **1** and **2**, respectively. Temperature dependent studies were acquired with an Oxford optical cryostat using liquid helium as coolant. Absorption spectra were acquired with a Perkin-Elmer Lambda 900 double-beam UV/VIS/NIR spectrophotometer for solutions of crystalline samples prepared in HPLC-grade acetonitrile using standard 1-cm quartz cuvets.

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