Inorg. Chem. **2006**, *45*, 6592–6594

Inorganic Chemistry
Communication

Trinuclear Gold(I) Triazolates: A New Class of Wide-Band Phosphors and Sensors

Chi Yang,[†] Marc Messerschmidt,[‡] Philip Coppens,*,[‡] and Mohammad A. Omary*,[†]

Department of Chemistry, University of North Texas, Denton, Texas 76203, and Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14260-3000

Received May 30, 2006

A new cyclic gold(I) triazolate trimer, $[Au(3,5\text{-}i\text{-}Pr_2Tz)]_3$ (**1**), exhibits fully overlapping aurophilically bonded dimer-of-trimer units that lead to multiple phosphorescence bands in both the solid state and solution. The conformation of the hexanuclear unit exhibits reversible interconversion between C_2 and D_3 effective symmetries, depending on the crystal temperature or solution concentration, the variation of which leads to isoemissive and isosbestic points. Solutions of **1** exhibit remarkable quenching properties that demonstrate molecular recognition with high selectivity and hypersensitivity for some reagents, as influenced by protonation via Brønsted acids, π intercalation, and/or energy transfer. The quenched phosphorescence of **1** by acetic acids can be regenerated by NEt_3.

Recent increasing interest in phosphorescent metal complexes has been driven by their promising photonic applications.[1−4] Particularly attractive are cyclic trinuclear Au^I complexes because they exhibit bright phosphorescence with a short lifetime in the solid state at room temperature, tunable emission colors across the visible region, reasonable charge-transport properties, and sensitivity to multiple stimuli.[4−6] The significance of cyclic trinuclear d^{10} complexes also spans multiple fundamental areas, including ground-state metallophilic bonding, M−M excimeric bonding, supramolecular assemblies, and metalloaromaticity.[4−7]

Structural and photophysical studies for cyclic trinuclear Au^I complexes have thus far involved pyridiniate, imidazolate, pyrazolate, and carbeniate[4−6] but not triazolate bridging ligands.[8a] Compared to imidazole and pyrazole, 1,2,4-triazole is expected to possess a similar coordination affinity to soft metal ions (e.g., Au^I) but with a smaller extent of electron donation because of the inductive effect of the additional nonbridging N atom. Hence, we decided to explore this new class of cyclic trinuclear metallomacrocycles of triazole with d^{10} metal ions, $[MTz]_3$. Derivatives of 1,2,4-triazole show diverse coordination modes and form coordination networks with metal ions.[8] The exo N atoms in $[AuTz]_3$ can serve as sites for H bonding or coordination to metal ions. Thus, $[AuTz]_3$ can be potentially used as building blocks for supramolecular chemistry as well as potential sensors for metal coordination, H bonding, and/or pH detection. Herein, we report the synthesis, structure, and unusual luminescence properties of *cyclo*-tris[$\mu^{N,N}$-3,5-diisopropyl-1,2,4-triazolategold(I)], $[Au(3,5\text{-}i\text{-}Pr_2Tz)]_3$ (**1**).

The synthesis of **1** involves the addition of an excess of freshly distilled anhydrous NEt_3 to a methanol solution of gold(tetrahydrothiophene)chloride and 3,5-diisopropyl-4*H*-1,2,4-triazole. After stirring for 30 min, the product was precipitated as a white solid in ~80% yield.

---

* To whom correspondence should be addressed. E-mail: omary@unt.edu (M.A.O.), coppens@buffalo.edu (P.C.).

[†] University of North Texas.

[‡] University at Buffalo, State University of New York.

(1) (a) Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Nature* **2000**, *403*, 750. (b) You, Y.; Park, S. Y. *J. Am. Chem. Soc.* **2005**, *127*, 12438. (c) Glazer, E. C.; Magde, D.; Tor, Y. *J. Am. Chem. Soc.* **2005**, *127*, 4190 and references cited therein.

(2) (a) Rudzinski, C. M.; Young, A. M.; Nocera, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 1723. (b) Petoud, S.; Cohen, S. M.; Bünzli, J.-C. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2003**, *125*, 13324. (c) Yang, C.; Fu, L.-M.; Wang, Y.; Zhang, J.-P.; Wong, W.-T.; Ai, X.-C.; Qiao, Y.-F.; Zou, B.-S.; Gui, L.-L. *Angew. Chem., Int. Ed.* **2004**, *43*, 5010.

(3) (a) Wadas, T. J.; Wang, Q.-M.; Kim, Y.-J.; Flaschenreim, C.; Blanton, T. N.; Eisenberg, R. *J. Am. Chem. Soc.* **2004**, *126*, 16841. (b) Grove, L. J.; Rennekamp, J. M.; Jude, H.; Connick, W. B. *J. Am. Chem. Soc.* **2004**, *126*, 1594.

(4) (a) Wong, K. M.-C.; Zhu, X.; Hung, L.-L.; Zhu, N.; Yam, V. W.-W.; Kwok, H.-S. *Chem. Commun*. **2005**, 2906. (b) Wang, Q.-M.; Lee, Y.-A.; Crespo, O.; Deaton, J.; Tang, C.; Gysling, H. J.; Concepcion Gimeno, M.; Larraz, C.; Villacampa, M. D.; Laguna, A.; Eisenberg, R. *J. Am. Chem. Soc.* **2004**, *126*, 9488. (c) Kim, S. J.; Kang, S. K.; Park, K.-M.; Zin, W.-C.; Choi, M.-G.; Kim, K. *Chem. Mater.* **1998**, *10*, 1889.

(5) (a) White-Morris, R. L.; Olmstead, M. M.; Attar, S.; Balch, A. L. *Inorg. Chem.* **2005**, *44*, 5021. (b) Kishimura, A.; Yamashita, T.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 179. (c) Olmstead, M. M.; Attar, S.; Balch, A. L. *Inorg. Chem.* **2005**, *44*, 5021.

(6) (a) Omary, M. A.; Rawashdeh-Omary, M. A.; Gonser, M. W. A.; Elbjeirami, O.; Grimes, T.; Cundari, T. R.; Diyabalanage, H. V. K.; Gamage, C. S. P.; Dias, H. V. R. *Inorg. Chem.* **2005**, *44*, 8200. (b) Yang, G.; Raptis, R. G. *Inorg. Chem.* **2003**, *42*, 261.

(7) (a) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 599. (b) Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412. (c) Tsipis, C. A. *Coord. Chem. Rev.* **2005**, *249*, 2740.

(8) (a) Minghetti, G.; Banditelli, G.; Bonati, F. *Inorg. Chem.* **1979**, *18*, 658. (b) Nomiya, K.; Noguchi, R.; Ohsawa, K.; Tsuda, K. *J. Chem. Soc., Dalton Trans.* **1998**, *24*, 4101. (c) Haasnoot, J. G. *Coord. Chem. Rev.* **2000**, *200−202*, 131 and references cited therein.

10.1021/ic060943i CCC: $33.50

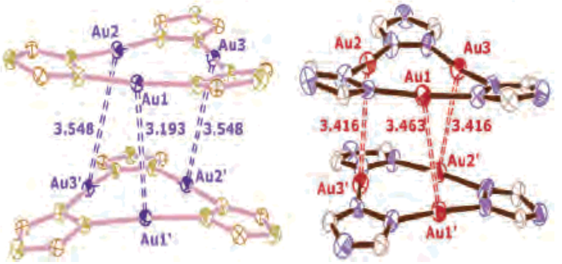


Figure 1. ORTEP plot for the dimer-of-trimer structure of **1** at 95 K (left) and RT (right). For clarity purposes, the *i*-Pr groups are omitted and the thermal ellipsoids are shown at 50% (95 K) and 33% (RT) probability.

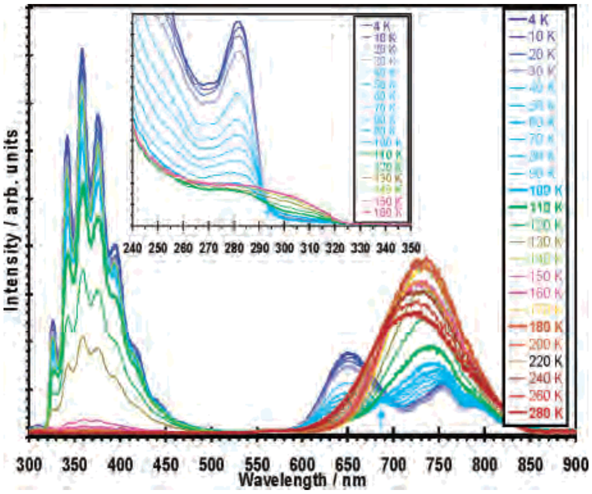


Figure 2. Photoluminescence spectra for crystals of **1** ($\lambda_{ex} = 280$ nm) vs temperature. The inset shows excitation spectra monitoring at $\lambda_{em} = 650$ nm. Sky-blue traces in the emission and excitation illustrate isoemissive and isosbestic points, respectively, as indicated by the arrows.

The structure of **1** has been determined at 95 K and room temperature (RT) (Figure 1). The complex crystallizes in the $C2/c$ space group with the asymmetric unit containing one independent [Au(3,5-*i*-Pr$_2$Tz)]$_3$ trimer molecule, which dimerizes into a fully overlapping dimer-of-trimer prismatic unit via three Au^{I}···Au^{I} aurophilic bonds. The marked thermal contraction of the structure upon cooling of the crystal is evidenced by changes at RT vs 95 K in the crystal density (2.209 vs 2.342 g·cm^{-3}) and the cell volume (6300.15 vs 5943.22 Å^3). Although the crystal packing mode is similar at both RT and 95 K, the conformation of the dimer-of-trimer unit is remarkably different, in which the Au···Au intertrimer distances of 3.19, 3.55, and 3.55 Å at 95 K and 3.46, 3.42, and 3.42 Å at RT suggest C_2 and D_3 effective symmetries, respectively.

Figure 2 shows the photoluminescence spectra for crystals of **1** vs temperature. The emission consists of a higher-energy (HE) band in the UV region and two lower-energy emissions with maxima near 650 nm (LE1) and 750 nm (LE2) at $T < 180$ K, whereas at $T \geq 180$ K, only the LE2 band dominates. Upon heating, the HE band maintains its structured profile but decreases in intensity and ultimately disappears around 160 K, whereas the intensity of the LE1 band decreases concomitantly with an increase in the intensity of the LE2 band.

The HE band for crystals of **1** exhibits a well-resolved vibronic structure with an average spacing of 1350 ± 40 cm^{-1}, which clearly correlates with IR frequencies of **1** and the free ligand (see the Supporting Information). The decay times for this band are 68.5 ± 0.6 μs at 4 K and 28.6 ± 0.1 μs at 77 K. These observations suggest that the HE band is due to a triplet state with a strong ligand character in the lower singly occupied molecular orbital.

The LE1 and LE2 bands exhibit a broad unstructured profile suggestive of excimeric emissions from a dimer-of-trimer unit, in analogy to similar bands exhibited by other coinage-metal cyclic trimers;[6] we have recently verified such an assignment for crystals of [Cu(3,5-(CF$_3$)$_2$Pz)]$_3$ by time-resolved X-ray diffraction.[9] Each of the LE1 and LE2 bands in crystalline **1** decays with an identical single-exponential time constant at the same temperature. Whether λ_{em} is monitored at 650 or 750 nm, the decay times are 62.3 ± 0.5, 27.2 ± 0.3, and 19.1 ± 0.1 μs at 4, 77, and 300 K, respectively. The excitation profiles are very similar for the LE1 and LE2 bands and are different from that for the HE band. These data suggest an assignment to two phosphorescent excimeric states for the LE1 and LE2 bands, which are coupled to one another but are uncoupled from the HE state. The existence of multiple unstructured LE emissions at 95 K or lower temperatures but only one such a band at RT is in agreement with the aforementioned crystal structures showing C_2 and D_3 dimer-of-trimer effective symmetries at 95 K and RT, respectively, because more bands are expected at a lower symmetry. Figure 2 illustrates an isoemissive point[10] at 684 nm (emission spectra) and an isosbestic point at 293 nm (excitation spectra) along with the progressive increase in the LE2/LE1 intensity ratio upon heating of the crystal between 40 and 100 K. This observation, together with the significant change in the luminescence excitation profile (Figure 2, inset), suggests a structural change of the effective chromophore that we interpret as interconversion between C_2 and D_3 effective symmetries for the dimer-of-trimer unit by integrating these spectral observations with the temperature-dependent structural findings above. The gradual red shift in the LE2 emission peak upon cooling (λ_{max} shift ~ 725 → 755 nm) is also consistent with the shorter intertrimer Au···Au distance at 95 K than at RT. We are aware of only one similar precedent, reported recently by the Balch group for [μ_3-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$),[11] in which a reversible temperature-induced structural change resulted in alterations of both aurophilicity and luminescence.

Although luminescence from solids or rigid glasses of two-coordinate Au^{I} complexes is well-known, it is quite uncommon that fluid solutions of such complexes exhibit Au-centered emissions at RT. This is particularly unusual for emissions arising from *ligand-unassisted* Au^{I}···Au^{I} interactions.[12] Surprisingly, the unstructured LE1 and LE2 bands of **1** are also observed in CH$_2$Cl$_2$ solutions at RT, even at

---

(9) Vorontsov, I. I.; Kovalevsky, A. Yu.; Chen, Y.-S.; Graber, T.; Novozhilova, I. V.; Omary, M. A.; Coppens, P. *Phys. Rev. Lett.* **2005**, *94*, 193003.

(10) For an example illustrating the significance of isoemissive points in photophysics, see: Kowalczyk, A.; Boens, N.; Bergh, V. V. D.; Schryver, C. D. *J. Phys. Chem.* **1994**, *98*, 8585.

(11) Gussenhoven, E. M.; Fettinger, J. C.; Pham, D. M.; Malwitz, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 10838.

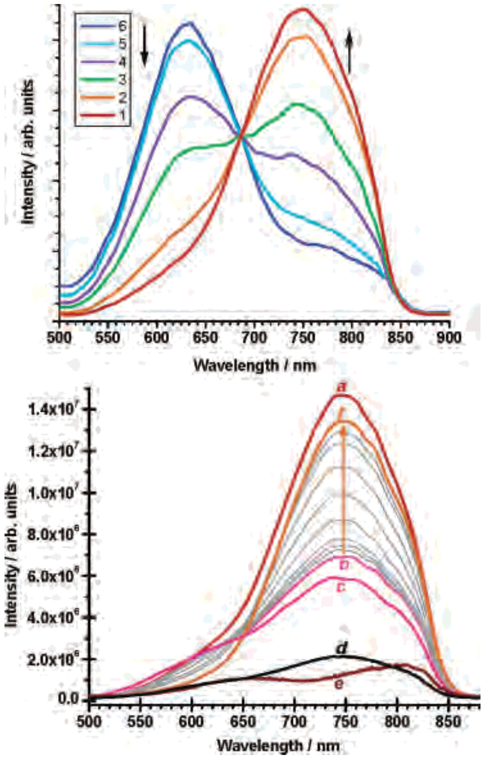
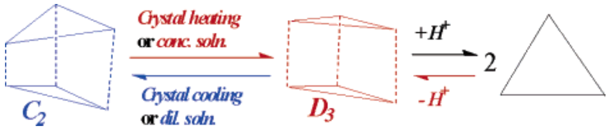


Figure 3. Top: Area-normalized emission spectra of **1** in CH_2Cl_2 at RT. Concentrations ($\times 10^{-4}$ M) are 88, 44, 11, 2.8, 0.68, and 0.16 for traces 1−6, respectively ($\lambda_{ex} = 270$ nm). Bottom: Change in the emission spectrum of a 3.0-mL 5.0×10^{-3} M CH_2Cl_2 solution of **1** (a) upon the addition of 0.20 mL of CH_3COOH (b), 0.23 mL of benzene (c), 0.3 mg of resorcinol (d), or 7.0 μL of CF_3COOH (e). Gray traces show the recovery of the quenched emission in trace b by successive additions of aliquots of NEt_3 to a total of 0.21 mL (f). The added reagents represent 3.5, 2.6, 0.0027, 0.094, and 1.49 mmol for traces b−f, respectively.

Scheme 1



low concentrations (Figure 3). The lifetime for a 1.0×10^{-3} M solution is 2.06 ± 0.02 μs. These spectral observations suggest that the aurophilically bonded dimer-of-trimer unit is preserved in a CH_2Cl_2 solution. Though persistence of unassisted $d^{10}\cdots d^{10}$ interactions in solution has been encountered earlier,[6,12] the unusual behavior herein is the *observation of* Au^I−Au^I *bonded excimer phosphorescence in dilute solutions at RT* for **1** in CH_2Cl_2. The LE1/LE2 intensity ratio is concentration-dependent. As shown in Figure 3 (top), progressive dilution of a 8.8×10^{-3} M solution results in a gradual decrease of the LE2 band intensity accompanying the increasing dominance of the LE1 band. More importantly, the area-normalized spectra shown in Figure 3 (top) display an apparent isoemissive point at 686 nm, reminiscent of the crystal emission behavior upon cooling. Both situations are, therefore, attributed to a conformation change between C_2 and D_3 effective symmetries in the Au_6 unit.

The concentration-dependent solution emission of **1** encouraged us to explore its potential sensor action. As demonstrated in Figure 3 (bottom), the emission of **1** in CH_2Cl_2 can be quenched by the addition of CH_3COOH or benzene and, more efficiently, by CF_3COOH or resorcinol. No quenching is observed upon the addition of $CHCl_3$, methanol, diethyl ether, or *n*-hexane. Most importantly, the quenched emission of **1** by CH_3COOH or CF_3COOH can be recovered by the addition of NEt_3, whereas the quenching by benzene and resorcinol cannot be reversed using NEt_3. Because the solution emission of **1** is due to intertrimer interactions in dimer-of-trimer units, the quenching will be caused either by loss of the excitation energy or by dissociation to two monomer-of-trimer units in solution. For the latter case, dissociation can be induced by guest intercalation between the two planar trimers in the dimer-of-trimer unit or by protonation or H bonding of the exo N atoms of the triazole ring. The quenching of the emission of **1** by CH_3COOH or CF_3COOH and its reversible restoration by NEt_3 suggest that protonation likely induces repulsion between the two bound trimers, leading to dissociation to two separate monomer-of-trimer units.[13] In the case of benzene, π intercalation is possible between the two planar trimers in the dimer-of-trimer unit. However, the hypersensitive quenching of the emission of **1** by resorcinol (a weak Brønsted acid) suggests that resorcinol also serves as an energy trap, which is facilitated by H bonding and/or π interactions in the cooperative quenching mechanism. Further work to quantify the quenching processes and delineate their multiple mechanisms will follow.

In conclusion, **1** represents a new class of phosphorescent complexes with a remarkable photophysical behavior, several aspects of which are summarized in Scheme 1. Work is underway to further characterize **1** and other coinage-metal cyclic trinuclear triazolates and assess their potential in photonic and sensor applications.

Acknowledgment. This work is supported by the National Science Foundation (CAREER Award, Grant CHE-0349313, to M.A.O.), the Robert A. Welch Foundation (Grant B-1542 to M.A.O.), and the U.S. Department of Energy (Grant DE-FG02-02ER15372 to P.C.).

Supporting Information Available: Crystallographic data (CIF) and further experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC060943I

---

(12) (a) Rawashdeh-Omary, M. A.; Omary, M. A.; Patterson, H. H.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 11237. (b) Tang, S. S.; Chang, C. P.; Lin, I. J. B.; Liou, L. S.; Wang, J. C. *Inorg. Chem.* **1997**, *36*, 2294. (c) Ma, B.; Li, J.; Djurovich, P. I.; Yousufuddin, M.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2005**, *127*, 28. (d) Crowley, J. D.; Steele, J. M.; Bosnich, B. *Inorg. Chem.* **2005**, *44*, 2989.

(13) Note that emission quenching of **1** in CH_2Cl_2 by CF_3COOH also changes the spectral profile: trace e in the bottom of Figure 3 is similar to the emission profile of **1** in its C_2 conformation, which exists in dilute CH_2Cl_2 solutions (see Figure 3, top). The detailed mechanism will be addressed in the full paper.