J|A|C|S COMMUNICATIONS

Published on Web 08/02/2005

Phosphorescent Excited State of $[Au_2\{(Ph_2Sb)_2O\}_3]^{2+}$: Jahn−Teller Distortion at Only One Gold(I) Center

Vilma R. Bojan,† Eduardo J. Fernández,*,‡ Antonio Laguna,*,§ José M. López-de-Luzuriaga,‡ Miguel Monge,‡ M. Elena Olmos,‡ and Cristian Silvestru†

Facultatea de Chimie si Inginerie Chimica, Universitatea Babes-Bolyai, RO-400028 Cluj-Napoca, Romania, Departamento de Química, Universidad de La Rioja, Grupo de Síntesis Química de La Rioja, UA-CSIC, Complejo Científico-Tecnológico, 26004-Logroño, Spain, and Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009-Zaragoza, Spain

Received May 18, 2005; E-mail: alaguna@unizar.es; eduardo.fernandez@dq.unirioja.es

Among the Au(I) compounds that show photoluminescence are those that exhibit planar three-coordination around the gold atom. In fact, the common two-coordinate AuL_2^+ complexes display gold-based luminescence when *aurophilic* interaction (i.e., gold(I)−gold(I) bonding interaction) with other AuL_2^+ units is present in the molecule, which leads to a decrease in the HOMO−LUMO gap. Moreover, three-coordinate Au(I) complexes in which an additional Au···Au interaction appears are also long-lived emitters. This result is to some extent intriguing since luminescence is usually absent for AuL_4^+ complexes.[1] In this regard, Che and co-workers reported experimental studies for the dinuclear diphosphine complex $[Au_2(dmpm)_3](ClO_4)_2$ (dmpm = bis(dimethylposphine)methane) suggesting that the intrinsic visible emission for this complex derives from monomer-like planar three-coordinate[3] ($(d_{x^2-y^2}, d_{xy}) \rightarrow p_z$) excited state that is only weakly perturbed by the Au−Au interaction.[2] Also, Omary and co-workers showed through DFT calculations that the major excited-state distortion in luminescent mononuclear $[Au(PR_3)_3]^+$ complexes is a Jahn−Teller symmetry change as opposed to a Au−P bond distance shortening.[3]

We wondered whether this Jahn−Teller excited-state distortion would occur in dinuclear three-coordinate Au(I) complexes in both metal centers, or instead, a decrease of the Au−Au distance would be produced as observed in dinuclear two-coordinate complexes of the type $[Au_2(diphosphine)_2]^{2+}$.

The use of bidentate Sb donor ligands represents an interesting challenge since Au−Sb complexes are very scarce (only the cation $[Au(SbPh_3)_4]^+$ with three different counteranions is structurally characterized), and, on the other hand, it has a high coordination number for the Au(I) center, which, in principle, would facilitate the synthesis of three-coordinate complexes.[4] Thus, we have prepared the complex $[Au_2\{(Ph_2Sb)_2O\}_3](ClO_4)_2$ **1** by reaction between the Au(I) precursor $[Au(tht)_2](ClO_4)$ and the ligand $\{(Ph_2Sb)_2O\}$ in a 2:3 molar ratio (see Supporting Information). The crystal structure of **1** was determined by X-ray diffraction studies from single crystals obtained by layering diethyl ether into a solution of complex **1** in THF. The cation (see Figure 1) shows two gold centers in a trigonal-planar environment (ΣSb−Au−Sb = 358.45°) formed by three antimony atoms of three bridging $\{(Ph_2Sb)_2O\}$ ligands.[4] The Au−Sb bond distances, which range from 2.6048(5) to 2.6173(5) Å, are slightly shorter than those found in the tetracoordinate $[Au(SbPh_3)_4]^+A^-$ (A = ClO_4 (2.658−2.657 Å),[4a] $[Au\{C_6H_2(NO_2)_3\}_2]$ (2.647−2.655 Å)[4b]) as expected for a lower coordination number. Nevertheless, in the derivative with $[Au(C_6F_5)_2]^-$ as anion, the range is wider (2.585−2.669 Å).[4c] The Sb−O bonds show typical distances of 1.953(4)−1.969(4) Å.

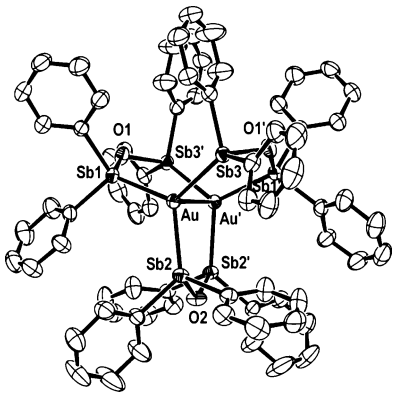

Figure 1. Crystal structure of complex **1**. Selected bond lengths [Å]: Au−Au′ 3.0320(4), Au−Sb(1) 2.6048(5), Au−Sb(2) 2.6137(5), Au−Sb(3) 2.6173(5) Å, Sb(1)−Au−Sb(2) 119.100(16), Sb(1)−Au−Sb(3) 121.294(15), Sb(2)−Au−Sb(3) 118.043(16)°.

Finally, as in other dinuclear gold(I) compounds, complex **1** shows an intramolecular Au···Au contact of 3.0320(4) Å, longer than those observed in the trigonal-planar complex $[Au_2\{(Ph_2P)_2C{=}CH_2\}_2(S_2CNEt_2)]^+$ (2.902 Å)[5] and similar to the intermolecular Au−Au distance found in dinuclear derivatives of the type $[AuX(P{-}P)]_2$ (P−P = diphosphine, X = Cl, I, SCN) (2.951−3.062 Å)[6] that show a square-planar environment for the gold(I) atoms including the Au···Au interaction.

Complex **1** displays very intense luminescence at room temperature in solid state (excitation 369, emission 672 nm) and in degassed acetonitrile (excitation 369, emission 667 nm) and at 77 K in solid state (excitation 370, emission 698 nm). The absorption spectra in 5×10^{-4} M acetonitrile solution shows a shoulder at 360 nm (ϵ = 2570 M^{-1} cm^{-1}), which is assigned to the $^3((d_{x^2-y^2}, d_{xy}) \rightarrow p_z)$ transition.[2] The other dipole-allowed spin−orbit components are probably masked by intense intraligand bands between 250 and 350 nm. Its lifetime in the microsecond range (10 μs) is characteristic of the expected phosphorescent process. Similar assignments have been reported for dinuclear and mononuclear three-coordinate gold(I) complexes.[1,2] The Stokes' shift (around 12 200 cm^{-1}) is larger than typical values of 10 000 cm^{-1} reported by Gray and Fackler[7] for mononuclear derivatives and similar to that reported by Che[2] for the dinuclear three-coordinated gold(I) complex $[Au_2(dmpm)_3](ClO_4)_2$, which suggests a very important distortion of the complex in the excited state.

To rationalize the intrinsic photophysical properties of $[Au_2\{(Ph_2Sb)_2O\}_3]^{2+}$, we carried out correlated MP2 calculations to study the geometries for the ground and first triplet excited states that are expected to be responsible for its luminescence.

First, we fully optimized the model system $[Au(SbH_3)_3]^+$ **A** in the ground (C_{3v} symmetry) and first triplet (no symmetry constrains)

† Universitatea Babes-Bolyai.
‡ Universidad de La Rioja.
§ Universidad de Zaragoza-CSIC.

10.1021/ja053237+ CCC: $30.25 © 2005 American Chemical Society

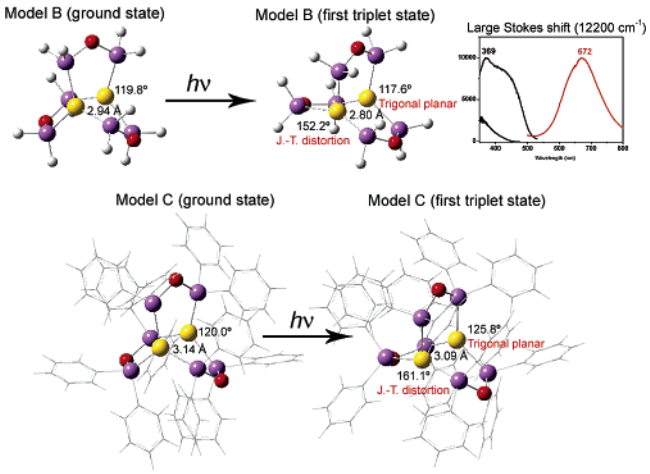

Figure 2. Optimized model systems **B** and **C** for the ground and the phosphorescent (triplet) excited states. Corrected excitation (369 nm) and emission (672 nm) for **1** in solid state at room temperature and absorption spectrum for **1** in 5×10^{-4} M in CH_3CN.

excited state at the MP2 level of theory. In it, the optimized ground state for model **A** displays a trigonal-planar environment for the Au(I) center; full optimization of the first triplet excited state displays a Jahn−Teller distortion that leads to Sb−Au−Sb angles of 148.8° and 105.1° for the phosphorescent excited state but similar Au−Sb distances (2.63 and 2.68 Å) if compared to the ground state (2.64 Å). Therefore, the Jahn−Teller distortion observed for model **A** is similar to the one reported by Omary et al. for trigonal-planar mononuclear $[Au(PR_3)_3]^+$ compounds,[3] for which the degenerate HOMO orbital, which displays a predominant (Au $5d_{xy}$, $5d_{x^2-y^2}$) character in the ground state, suffers a degeneracy rupture in the first triplet excited state as a consequence of the Jahn−Teller distortion.

A further question is if the presence of two trigonal-planar Au(I) units placed at an *aurophilic* interaction distance would give rise to a different distortion for the first triplet excited state for complex **1**, since both a Jahn−Teller distortion and a Au−Au distance shortening could be expected to play a role on this. To account for all the possibilities, we performed full optimization for the ground state and first triplet excited state for model system $[Au_2\{(H_2Sb)_2O\}_3]^{2+}$ **B** (D_3 symmetry) (Figure 2), built up from the X-ray diffraction data and substituting the phenyl rings with H atoms to keep the computational cost feasible. At the MP2 correlated level of theory, we obtain an optimized structure in agreement with the experimental structural parameters (see Supporting Information). Also, as has been previously described, the *aurophilic* interaction observed experimentally can be accounted for theoretically when correlation and relativistic effects are included in the level of calculation. Interestingly, when we carry out the full geometry optimization for the first triplet excited state (no symmetry constrains), we achieve an unexpected result. Instead of reaching a complete Jahn−Teller distortion for both Au(I) centers or, on the other hand, a dramatic Au−Au distance shortening leading to a rupture of the degeneracy, we observe a Jahn−Teller distortion for just one of the Au(I) centers, leaving the second one in an almost perfect trigonal-planar environment, together with a Au−Au distance shortening from 2.943 to 2.797 Å. As a consequence, the Au(I) atoms suffer a slight out-of-plane bending (12° inward). Double Jahn−Teller distortions at both Au(I) centers lead to more unstable triplet excited states, probably due to the ligand architecture (Supporting Information).

To account for the ligand influence on the geometry of both the ground and the first triplet excited states for complex **1**, we carried out the analysis for the model system $[Au_2\{(Ph_2Sb)_2O\}_3]^{2+}$ **C** (Figure 2) that represents exactly the cationic part of complex **1**. Assuming that the optical properties of this complex are intrinsic to the $[Au_2L_3]^{2+}$ unit,[2] we could derive that the results obtained for model **C** would be the closest to the experimental ones. In this case, the hybrid quantum mechanical/molecular mechanical (QM/MM) ONIOM methodology was employed (see Supporting Information for details). The obtained structural parameters for model **C** in the ground state are in agreement with the experimental ones, with the obtained Au···Au distance of 3.14 Å being slightly longer than the experimental one of 3.03 Å, probably due to the inclusion of the Ph rings in the model system. Regarding the fully optimized first triplet excited state for model **C**, we obtained results analogous to those in model **B**. Thus, the structure of the phosphorescent state for model **C** also displays a Jahn−Teller distortion for just one of the gold(I) centers, while the other one remains in a trigonal-planar environment. Moreover, the Au−Au distance shortening for the triplet state is also observed, with that for model **C** being slightly shorter (0.05 Å) than the one observed for model **B** (0.15 Å), but the Jahn−Teller distortion is larger for **C**.

The theoretical emission maximum as the difference between the excited- and ground-state energies, calculated at the excited-state equilibrium geometry, is 752 nm (experimental at 672 nm), displaying a good agreement. Moreover, the Jahn−Teller distortion is slightly influenced by the medium and temperature, as observed for the experimental emission energies.

In summary, these results illustrate that the main distortion for the phosphorescent excited state of complex **1** arises from a surprising Jahn−Teller distortion for only one of the gold(I) centers together with a moderate Au−Au distance shortening going further than the previously reported results. Therefore, our study proposes the mechanism of distortion for the phosphorescent excited state for complex **1**, which could be extrapolated to other dinuclear trigonal-planar d^{10} metal complexes.[8] Studies on ligand variations are now in progress.

Acknowledgment. The D.G.I.(MEC)/FEDER (CTQ2004-05495) project is acknowledged. M.M. thanks the MEC-UR for his contract "Ramón y Cajal". EC through the Socrates/Erasmus program (V.B.) and a NATO research fellowship (C.S.) is also acknowledged.

Supporting Information Available: X-ray crystallographic data in CIF format for **1**; experimental and theoretical details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Forward, J. M.; Fackler, J. P., Jr.; Assefa, Z. In *Optoelectronic Properties of Inorganic Compounds*; Roundhill, D. M., Fackler, J. P. Jr., Eds.; Plenum: New York, 1999; pp 195−226.
(2) Leung, K. H.; Phillips, D. L.; Mao, Z.; Che, C.-M.; Miskowski, V. M.; Chan, C.-K. *Inorg. Chem.* **2002**, *41*, 2054.
(3) Barakat, K. A.; Cundari, T. R.; Omary, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 14228.
(4) (a) Jones, P. G. *Acta Crystallogr., Sect. C* **1992**, *48*, 1487. (b) Vicente, J.; Arcas, A.; Jones, P. G.; Lautner, J. *J. Chem. Soc., Dalton Trans.* **1990**, 451. (c) Jones, P. G. *Z. Naturforsch, B: Chem. Sci.* **1982**, *37*, 937.
(5) Fernández, E. J.; Lopez-de-Luzuriaga, J. M.; Monge, M.; Olmos, E.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Inorg. Chem.* **1998**, *37*, 5532.
(6) (a) Fu, W.-F.; Chan, K.-C.; Cheung, K.-K.; Che, C.-M. *Chem.−Eur. J.* **2001**, *7*, 4656. (b) Fu, W.-F.; Chan, K.-C.; Miskowski, V. M.; Che, C.-M. *Angew. Chem., Int. Ed.* **1999**, *38*, 2783. (c) Schmidbaur, H.; Pollok, T.; Reber, G.; Muller, G. *Chem. Ber.* **1988**, *121*, 1345. (d) Bardají, M.; Jones, P. G.; Laguna, A.; Villacampa, M. D.; Villaverde, N. *J. Chem. Soc., Dalton Trans.* **2003**, 4529.
(7) (a) McCleskey, T. M.; Gray, H. B. *Inorg. Chem.* **1992**, *31*, 1733. (b) King, C.; Khan, M. N. I.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **1992**, *31*, 3236. (c) Forward, J. M.; Assefa, Z.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1995**, *117*, 9103. (d) Assefa, Z.; Forward, J. M.; Grant, T. A.; Staples, R. J.; Hanson, B. E.; Mohamed, A. A.; Fackler, J. P., Jr. *Inorg. Chim. Acta* **2003**, *352*, 31.
(8) Barakat, K.; Cundari, T. R. *Chem. Phys.* **2005**, *311*, 3.

JA053237+