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Glowing gold rings: solvoluminescence from planar trigold(I) complexes

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Contents

Abstract

Colorless crystals of the cyclic trigold(I) complex, $Au_3(CH_3OC=NCH_3)_3$, that have previously been irradiated with low energy ultraviolet light, emit bright flashes of yellow light when they make contact with a solvent such as chloroform or acetone. Spectroscopic data as well as information on solvoluminescence for this trinuclear complex are presented herein. The origin of the solvoluminescence is considered in the context of the solid state structure of the complex which shows that these triangular complexes pack to form extended trigonal prismatic columns. © 1998 Elsevier Science S.A.

Keywords: Solvoluminescence; Gold

1. Introduction

An array of triangular trimetallic complexes exist in which linear, two-coordinated metal centers, Au(I), Ag(I) and Hg(II), are connected by simple bridging ligands to form nearly strain-free, nine-membered rings [1–13]. A set of these planar or

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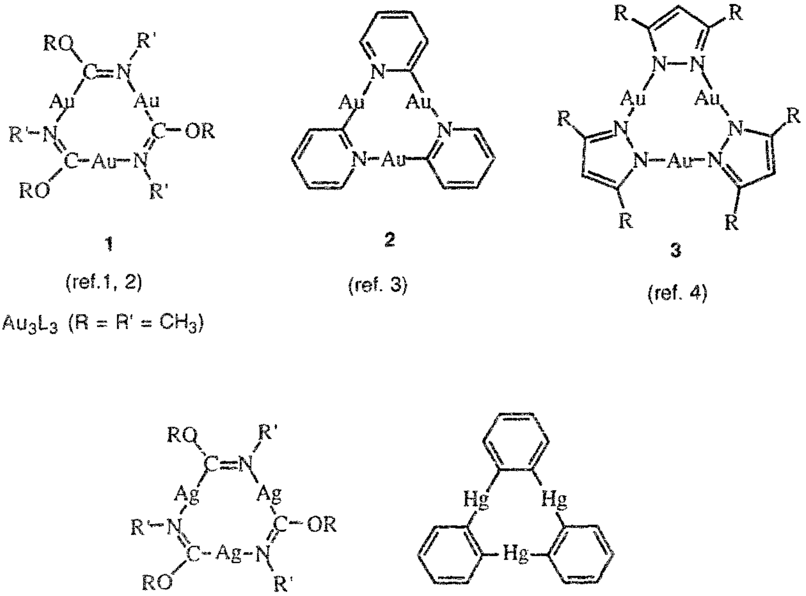


1 (ref. 1, 2) Au_3L_3 (R = R' = CH_3)

2 (ref. 3)

3 (ref. 4)

4 (ref. 5)

5 (ref. 6)

Scheme 1. Triangular metal frameworks

nearly planar complexes is shown in Scheme 1. While molecules of this type have been known for over 20 years, some of their remarkable properties have been recognized only recently. The pyrazolate complexes of type **3** form columnar mesophases at room temperature [14]. The isocyanide-derived complexes of type **1** exhibit a novel class of luminescence behavior, i.e. solvoluminescence, which is the subject of this paper [15].

2. Spectroscopic features of 1, $Au_3(CH_3OC{=}NCH_3)_3$

Colorless crystals of **1** dissolve in chloroform, dichloromethane, dibromomethane, acetone, or toluene to give colorless solutions. The absorption spectrum of a chloroform solution of the complex is shown in trace A of Fig. 1. In solution the complex is weakly emissive. Trace B of Fig. 1 shows the emission spectrum that is recorded from a solution of the compound at room temperature. The excitation profile for this emission parallels the absorption spectrum.

In the solid state at room temperature complex **1** is also emissive. Fig. 2 shows the emission spectrum of the solid that is obtained under continuous irradiation at 380 nm. The excitation profile shows a broad maximum at 380 nm. Comparison of the data in Figs. 1 and 2 suggests that the properties of this complex in the crystalline solid differ significantly from those of its solutions.

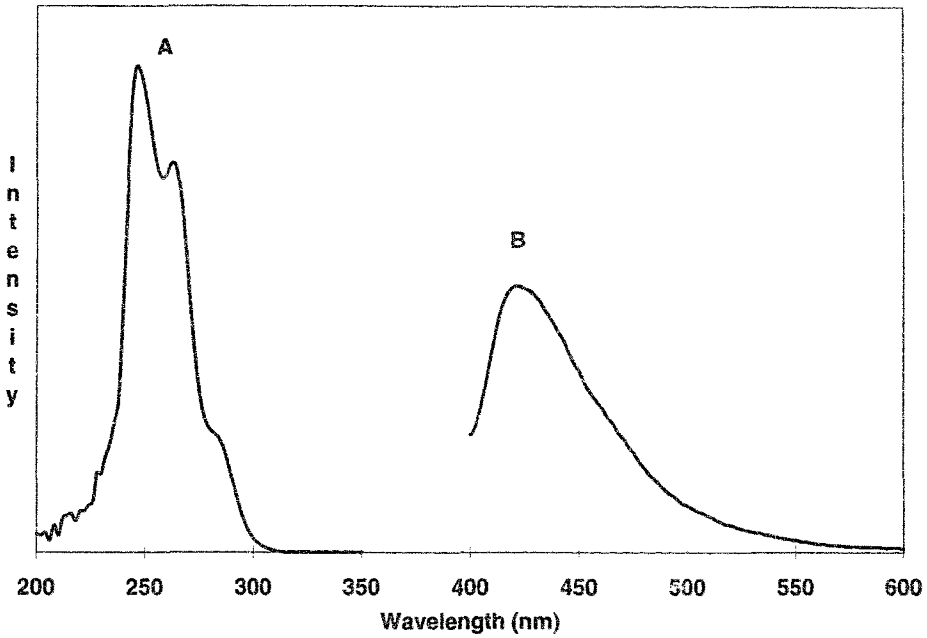


Fig. 1. The absorption (A) and emission (B) spectra of a chloroform solution of $Au_3(CH_3OC{=}NCH_3)_3$ at 25 C. At 290 nm the extinction coefficient (ϵ) is 2040 l mol^{-1} cm^{-1}. The excitation wavelength for the emission spectrum is 250 nm.

3. Solvoluminescence of 1, $Au_3(CH_3OC{=}NCH_3)_3$

Crystals of **1** that have been previously photo-irradiated display a new luminescence phenomenon, solvoluminescence [15]. The process involves light emission that is triggered by contact of the solid with a liquid. The emission is intense and readily detected by the human eye even under normal laboratory lighting conditions. Fig. 3 shows the spectrum of the light emitted from a sample of the crystalline solid that was initially irradiated with a small hand-held UV lamp and then exposed to a drop of acetone after the lamp was switched off. Similar yellow emission can be visually observed with a number of other liquids: chloroform, dichloromethane, toluene, methanol, hexane, and water. Qualitatively, there appears to be a correlation between the intensity of the luminescence and the solubility of the complex: hence the name, solvoluminescence. The emission phenomenon occurs in air, as well as under an atmosphere of either nitrogen or argon.

No chemical transformation appears to be involved in the emission process. If the solid sample is not entirely dissolved during one cycle of irradiation and liquid contact, it will produce the same emission after a second or third cycle of irradiation and liquid contact. Additionally, sequential addition of several drops of solvent to one batch of previously photo-irradiated crystals of **1** can produce several bursts of light. This phenomenon is documented in Fig. 4, which shows the bursts of light emission from one sample of **1** that result from the successive additions of six drops

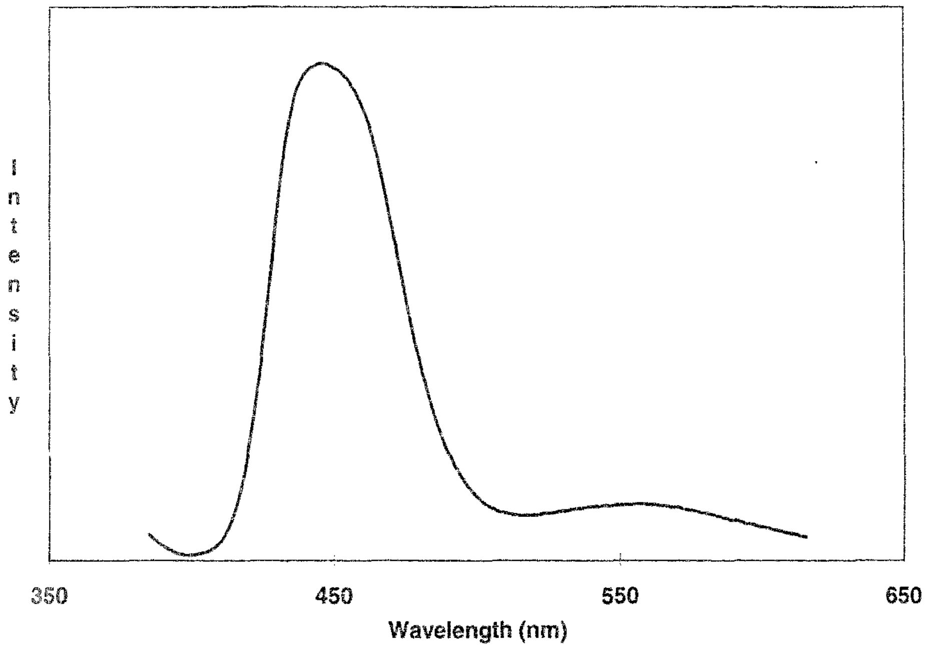


Fig. 2. The photoemission spectrum of crystalline $Au_3(CH_3OC=NCH_3)_3$, taken under conditions of continuous irradiation at 380 nm.

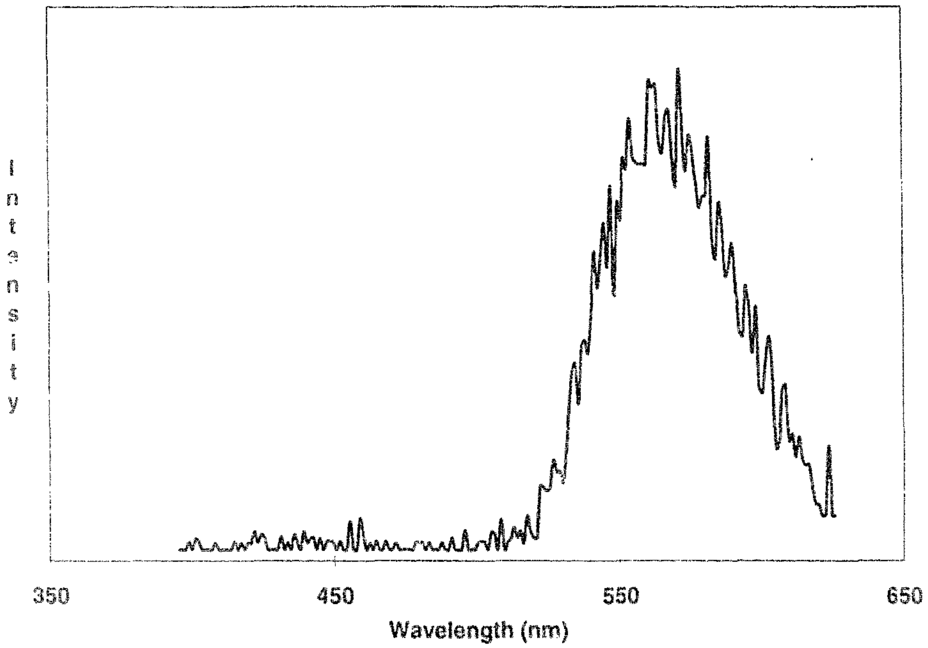


Fig. 3. Solvoluminescence: spectrum of the light emitted from a previously photo-irradiated sample of crystalline $Au_3(CH_3OC=NCH_3)_3$ upon contact with acetone.

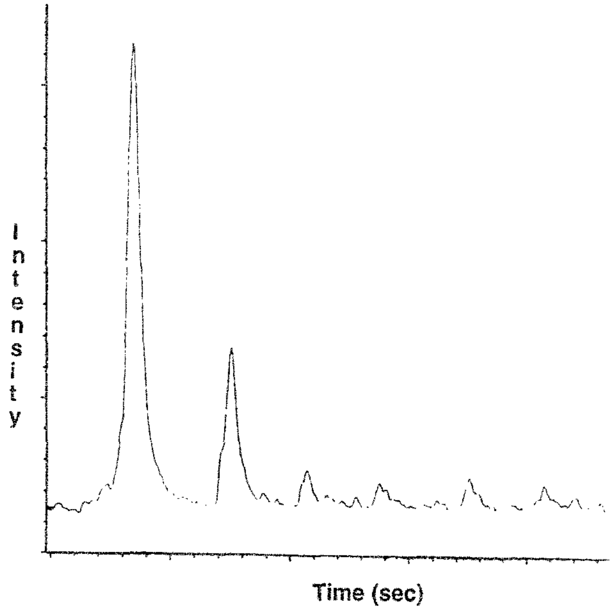


Fig. 4. Solvoluminescence: effect of the addition of multiple, sequential drops of chloroform on the emission spectrum of a previously photo-irradiated solid sample of $Au_3(CH_3OC=NCH_3)_3$.

of chloroform to the solid. The liquid that has been used to trigger the luminescence may be removed from undissolved solid, collected, and subsequently evaporated to recover colorless crystals of **1**; the recovered solid displays the same solvoluminescence.

The solvoluminescence phenomenon is distinct from a number of other unusual phenomena. Crystalline **1** is not triboluminescent [16]. Triboluminescent materials emit light under mechanical stress. However, the mechanical manipulation of either dark-adapted crystals of **1** or those of previously photo-irradiated sample of **1** does not trigger any detectable luminescence. We have not detected light emission during the crystallization of **1**, and hence this material does not display crystalloluminescence [17]. The phenomenon described here is also distinct from solvatochromism. Solvatochromic compounds show color changes upon exposure to the vapors of organic solvents but no light emission [18]. Solvatochromism appears to involve uptake of solvent into the crystalline lattice of certain materials. However, compound **1** crystallizes as a solvate-free material. In addition, we have not observed any color changes in the crystals in the presence of various solvents, or any changes in the solvoluminescence emission wavelength that depends on the nature of the solvent. The phenomenon of solvoluminescence is related to lyoluminescence, a phenomenon in which light is emitted upon dissolution of solids that were previously irradiated with ionizing radiation [19]. Note, however, that the irradiation energy utilized in the solvoluminescence behavior of **1** is much lower. Lyoluminescence has been attributed to the formation of color centers in alkali–metal halides and organic radicals. When these previously-irradiated materials are dissolved, generally in water, radical recombinations and solvated electrons are believed to be involved in the emission process.

4. Molecular and crystal structure of 1, $Au_3(CH_3OC{=}NCH_3)_3$

$Au_3(CH_3OC{=}NCH_3)_3$, **1**, crystallizes in the hexagonal space group *P6/m* [15]. Fig. 5 shows the structure of an individual molecule, which has crystallographically imposed $\bar{6}$ symmetry. The intramolecular $Au^I \cdots Au^I$ separation, 3.308(2) Å, is shorter than 3.6 Å, and so some bonding between gold centers may be present [20–26]. Nevertheless, the C–Au–N angles are all 180°, and there is no evidence that the interactions distort the molecular structure. The other distances and angles within the molecule follow normal expectations. Individual molecules of Au_3L_3 aggregate in the solid state along the *c* axis to form columnar stacks. Fig. 6 shows a portion of one such column, which has an intermolecular $Au^I \cdots Au^I$ distance of 3.346(1) Å. In addition to these ordered stacks, there are other parallel stacks in which there are two sets of positions for the gold triangles. There are two ordered stacks for every disordered stack. For more details on the disorder in the solid state, see ref. [15].

The stacking of molecules of **1** is apparently not a common feature of molecules of the types shown in Scheme 1. The analog with R = benzyl for example crystallizes as simple molecular units with no Au...Au contact shorter than 3.8 Å. This compound also does not show any sign of solvoluminescence. The analog with R = ethoxy and R′ = *p*-tolyl crystallizes as a dimer with only a pair of close Au···Au contacts [27]. The Au···Au contacts seen in the columnar structure of **1** do not appear to be found in the columnar meso phases exhibited by the liquid crystalline pyrazolate complexes, **3** [14]. For these, the estimated interplanar spacing of 4.7 Å is well in excess of the distances wherein Au···Au contacts are significant. However, the columnar structure observed in **1** is related to the prismatic stacks of $[Pt_3(\mu\text{-}CO)_3(CO)_3]_n^{2-}$, $n = 2$–5 [28,29]. These anions form a set of finite, prismatic columns with Pt–Pt bonds connecting the triangular units. These Pt–Pt bonds are shorter than the Au···Au contacts seen in **1**.

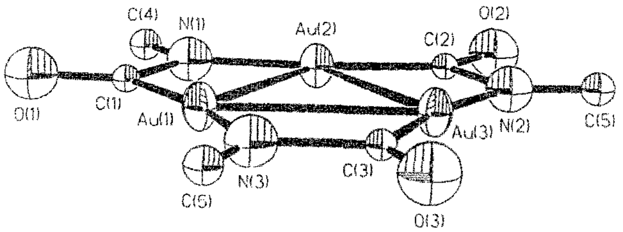


Fig. 5. The structure of an individual molecule of $Au_3(CH_3OC{=}NCH_3)_3$ (adapted from data in ref. [15]).

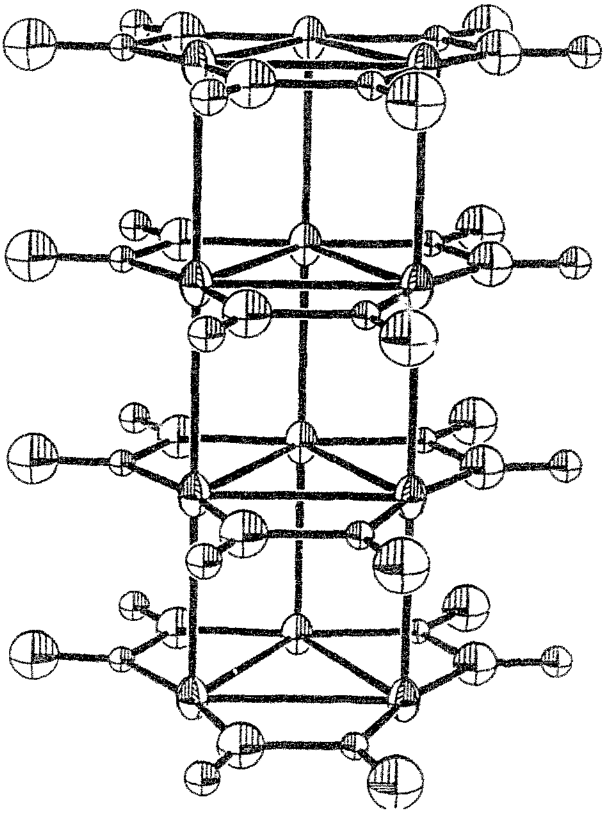
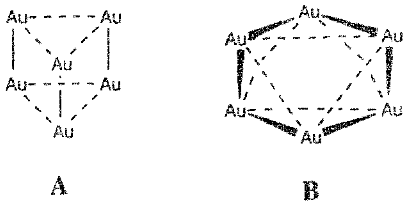


Fig. 6. A view that shows how molecules of $Au_3(CH_3OC{=}NCH_3)_3$ form a columnar structure in the solid state. The intermolecular Au...Au separations are 3.346(1) Å, while the intramolecular Au...Au separations are 3.308 Å (adapted from data in ref. [15]).

5. Discussion

Many gold(I) complexes are luminescent. A concise review of recent developments in gold(I) photochemistry is available [30]. The solvoluminescence exhibited by $Au_3(CH_3OC{=}NCH_3)_3$ is a remarkable new phenomenon that clearly warrants further examination. Applications of this emission to developing sensors of fluids seem feasible.

Several models for the origin of the solvoluminescence present themselves. Two questions may be asked. How is the energy stored? How does solvent release that energy? In the initial model for energy release that we considered, we imagined that dissolution of the photo-irradiated solid resulted in the release of molecules in an excited state into solution with the subsequent emission of light. However, comparison of the data in Figs. 1 and 3 indicates that such a model is not tenable. The solvoluminescence from the solid sample of **1** occurs at much lower energy (λ_{max}, 552 nm) than the observed emission (λ_{max}, 422 nm) from the molecules of **1** in solution. Comparison of the data in Figs. 2 and 3 indicates that the solvolumines-



Scheme 2. Local sites within a disordered stack

cence corresponds to the low energy emission seen for the solid. This emission feature is long-lived with tri-exponential decay where $\tau = 1.4$, 4.4 and 31 s, whereas the higher energy emission is much shorter lived ($\tau =$ ca. 1 ms) [15]. As a result of this low energy emission, previously photo-irradiated samples of $Au_3(CH_3OC{=}NCH_3)_3$ can be seen to glow faintly in a dark room for a minute or two after photo-irradiation. During that period, contact with solvent brings about the more intense solvoluminescence.

At this time, we believe that energy storage involves charge separation within the solid, and that this charge separation is facilitated by conduction of electrons along the columnar structures shown in Fig. 6. The presence of a considerable degree of disorder within the solid may be responsible for creating sites where electrons and holes can be trapped. For example, if just a pair of trimeric molecules in the disordered stacks are considered, there are two local environments for the pair as shown in Scheme 2. At site **A**, the pair has a prismatic structure, whereas at site **B** the pair has an octahedral geometry. Different local sites such as these, which may also involve larger number of molecules, may act as donor and acceptor sites within the solid to trap the separated charges. Consequently, the redox behavior of these triangular complexes is under investigation. Preliminary studies show that $Au_3(CH_3OC{=}NCH_3)_3$ undergoes electrocrystallization to form long, fine needles upon oxidation. Further studies of both oxidation and reduction of these triangular complexes are in progress. Release of energy by the solvent contact may come about by facilitating alteration of those unique sites in the solid where the electrons and holes are trapped.

Acknowledgements

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