Polymorphism and Luminescent Behavior of Linear, Two-Coordinate Gold(I) Complexes

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For those interested in the luminescence of gold(I) complexes, the formation of crystalline polymorphs with different aurophilic interactions between molecules or ions offers a new field where individual crystals of the same substance show differences in their luminescence and in their structures.

While most linear, two-coordinate gold(I) complexes are colorless, many display intense luminescence that is readily detected by the human eye (1, 2). Moreover, the luminescence from these complexes is unusually sensitive to an array of environmental factors. As a consequence, a number of rather remarkable phenomena have been observed in studies of the luminescence from these gold complexes.

For example, the luminescence from the industrially important ion $[Au^I(CN)_2]^-$ can be tuned to occur from 275 to 470 nm depending upon its concentration and solvent employed (3). In related experiments it has been shown that samples of KCl doped with varying amounts of $K[Au^I(CN)_2]$ show multiple emissions whose relative intensities depend upon the doping level, temperature, and excitation wavelength (4). Upon excitation with near UV light, the colorless trimer, $\{Au^I_3(MeN=COMe)_3\}$ displays a yellow emission with an unusually long lifetime (multi-exponential decay with τ = 1.4, 4.4 and 31 seconds) (5, 6). If a solvent (chloroform and dichloromethane work well) is dropped upon a feebly glowing sample of $\{Au^I_3(MeN=COMe)_3\}$, a bright burst of yellow light can be seen. This process has been named "solvoluminescence" and is a property of this unusual solid. In crystals of $\{Au^I_3(MeN=COMe)_3\}$, the trinuclear complexes are stacked into two types of columns, one with a prismatic stacking of the molecules, the other a disordered stack in which neighboring molecules in similar stacks are shifted by 60°. In the solid state, emission from the colorless gold carbene cation $[Au^I\{C(NHMe)_2\}_2]^+$ is effected by the chemical nature of anionic counterions that are present (7, 8). Solutions of this cation become intensely luminescent when they are frozen and that emission can be used to monitor the freezing point of the solution. Colorless crystals of $[(1,3,5$-triaza-7-phospha-adamantane$)_2Au^I]$ $[Au^I(CN)_2]$ are normally non-luminescent, but they become photoluminescent after grinding (9). Similarly, a gold(I) thiouracilate complex also becomes luminescent when subject to mild pressure. This process has been termed "luminescence tribochromism" and in this case results from the pressure-induced loss of acid from the complex and a change in the aurophilic interactions within the solid (10).

In many cases, the observation of luminescence from two-coordinate gold(I) complexes can be associated with the presence of short Au···Au contacts in the solids or within aggregated groups of particular complexes. Attractive aurophilic interactions between closed-shell gold(I) centers are generally considered to be significant whenever the neighboring Au···Au contacts are shorter than 3.6 Å (11, 12). Considerable attention has been paid to the nature of the attraction of gold(I) centers to one another for the synthesis of new molecules (13, 14) and to create a better understanding of the physical forces involved (15). Alternate

theories have suggested that the aurophilic attraction is caused by either electron correlation effects strengthened by relativistic effects (16, 17) or by hybridization of the 6s and 6p orbitals with the 5d orbitals (18, 19). Experimental studies of the barriers to rotation in binuclear Au(I) complexes, where rotation disrupts the Au···Au interaction, have shown that the strength of the attractive aurophilic interaction is comparable to that of hydrogen-bonding: *ca.* 7-11 kcal/mol (20, 21). In cases where multiple Au···Au interactions can occur, aurophilic attractions between molecules can persist in solution even when other conventional donors are present (22, 23).

Since the attraction is a weak force, the nature of aurophilic interactions between molecules and ions can be expected to be highly dependent upon the local environment that surrounds a particular gold(I) complex. In the solid state, crystal packing forces are likely to contribute to the way in which gold(I) complexes interact with each other. Here we describe cases in which linear, two-coordinate gold(I) complexes crystallize as polymorphs. Polymorphic crystals contain the same molecule or ions but differ in the details of molecular or ionic packing (24) Thus, polymorphs of gold(I) complexes may each be expected to show differences in the nature of the aurophilic interactions. However, dissolution of two polymorphs of the same substance should produce solutions with identical properties.

Figure 1

A photograph of crystals of $[(C_6H_{11}NC)_2Au^I](PF_6)$ that were obtained by diffusion of diethyl ether into a solution of the complex in dichloromethane. The photograph was taken with the sample illuminated by a hand-held UV lamp and shows the emission from the two crystalline polymorphs that are present. The colorless polymorph produces the bluish colored crystals at the bottom of the photo, while the yellow polymorph produces the greenish-yellow needles that grow toward the top of the photo

Polymorphs of the salt, $[(C_6H_{11}NC)_2Au^I](PF_6)$

Two polymorphs of $[(C_6H_{11}NC)_2Au^I](PF_6)$ have been identified (25). One is colorless but shows a bluish emission, while the other is pale yellow and produces a greenish emission. Figure 1 shows a photograph of the emission coming from a polycrystalline sample of $[(C_6H_{11}NC)_2Au^I](PF_6)$ that contains both polymorphs. Since these have crystallized together from the same solution they are concomitant polymorphs (26). Figure 2 shows the emission and excitation spectra of pure samples of each polymorph.

Both polymorphs have been examined through single crystal X-ray diffraction. Table 1 gives some data regarding the crystallographic parameters for these crystals. Notice that each crystallizes in a different space group and each has different cell dimensions. These differences result in different interactions between the cations in the two polymorphs. Figure 3 shows a portion of the structure of the colorless polymorph. The positions of the anions are not shown. They lie in positions between the chains and buried between the ligands. In the colorless polymorph the gold cations form continuous linear chains with short Au···Au contacts (3.1822(3) Å) that are indicative of strong aurophilic attractions between these cations.
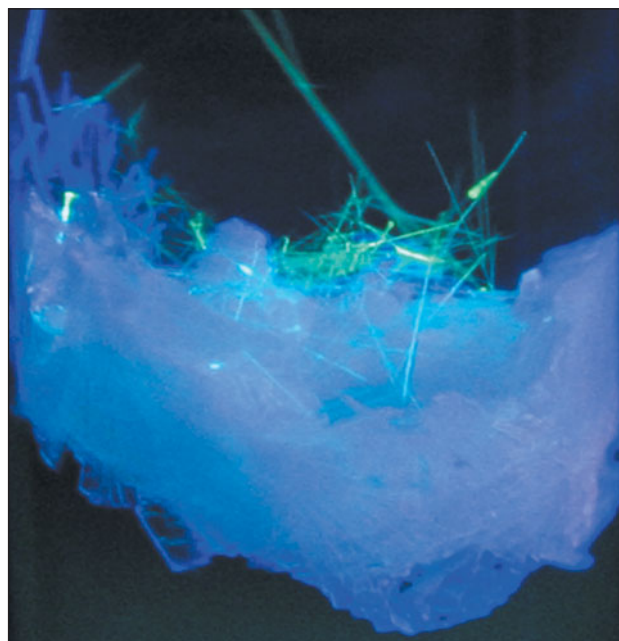
The structure of the yellow polymorph is more complicated as can be seen by turning your attention to Figure 4. Again in this figure the positions of the anions have been removed for the sake of clarity. There are four cations in the asymmetric unit, and these are arranged in a slightly helical chain. The interactions between cations are unusually short with Au···Au contacts of 2.9803(6), 2.9790(6), 2.9651(6), and 2.9643(6) Å. It is particularly significant to note that these short contacts occur between cationic complexes where one might expect coulombic forces to keep the gold centers apart.

The two polymorphs dissolve in a variety of solvents to produce colorless solutions with identical absorption spectra. These solutions are non-luminescent at room temperature. However, freezing solutions of $[(C_6H_{11}NC)_2Au^I](PF_6)$ in liquid nitrogen produces intensely luminescence samples whose luminescence varies depending upon the solvent involved. Each polymorph melts in the 115-120°C range to give a colorless, but luminescent melt. Upon cooling, the melt solidifies to produce the yellow polymorph.

The luminescence observed from $[(C_6H_{11}NC)_2Au^I](PF_6)$ in the solid state, in the melt, or in frozen solutions results from the formation of aggregates of the cations that self-associate through aurophilic attractions. However, when the ions are
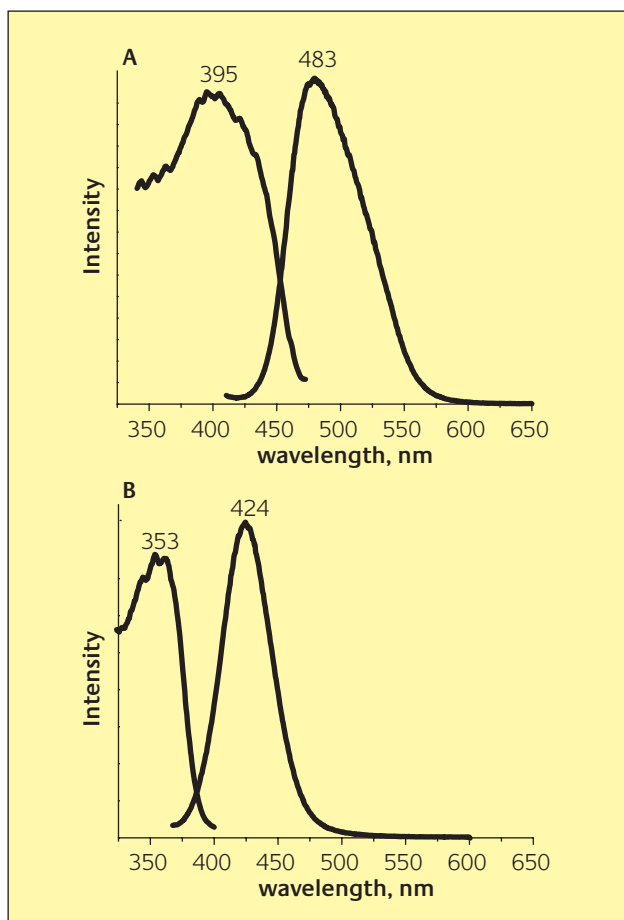
Figure 2
The emission and excitation spectra of crystals of the yellow (A) and colorless (B) polymorphs of $[(C_6H_{11}NC)_2Au^I](PF_6)$

Figure 3
A perspective view of a portion of the chain of cations in the colorless polymorph of $[(C_6H_{11}NC)_2Au^I](PF_6)$ with 50% thermal contours. The Au···Au contact within the chain is 3.1822(3) Å. For clarity, the positions of the anions are not shown

widely dispersed in dilute solution, $[(C_6H_{11}NC)_2Au^I](PF_6)$ is non-luminescent. Additionally, studies of $[(CH_3NC)_2Au^I](PF_6)$, which has no aurophilic interactions in the solid state, show that it is not luminescent in either the solid state or in solution. Within the extended chains of gold atoms in the polymorphs of $[(C_6H_{11}NC)_2Au^I](PF_6)$, overlap of the occupied gold $5d_{z^2}$ orbitals (where z is the axis along the Au···Au···Au chain) produces a filled band of d orbitals, while overlap of the empty gold $6p_z$ orbitals produces a corresponding unoccupied band of p orbitals. Excitation of an electron from the filled $5d_{z^2}$ band to the empty $6p_z$ band strengthens the bonding along these chains by removing what is effectively an anti-bonding electron from the $5d_{z^2}$ band. Emission results from the reverse process, transfer of an electron from the $6p_z$ band back to the $5d_{z^2}$ band.

Polymorphs of $(Me_2PhP)Au^ICl$

During the study of the structure and the spectroscopic properties of colorless $(Me_2PhP)Au^ICl$, it became apparent that this complex crystallized in two different forms (23, 27).
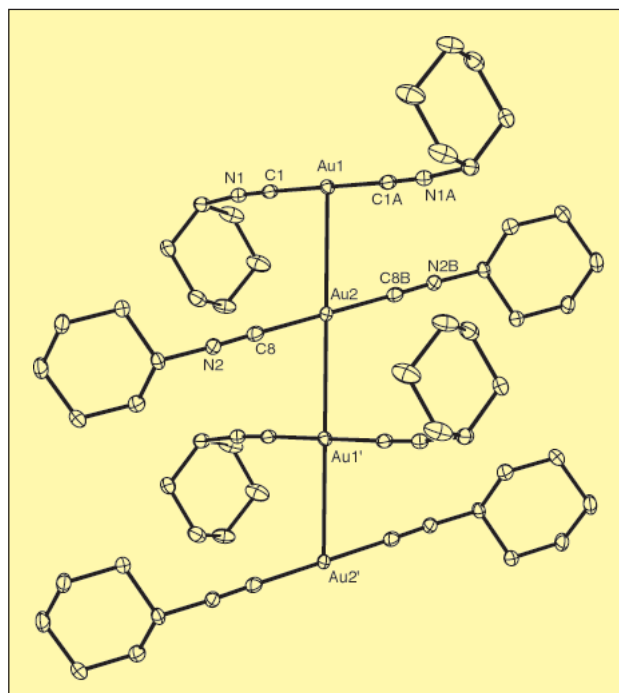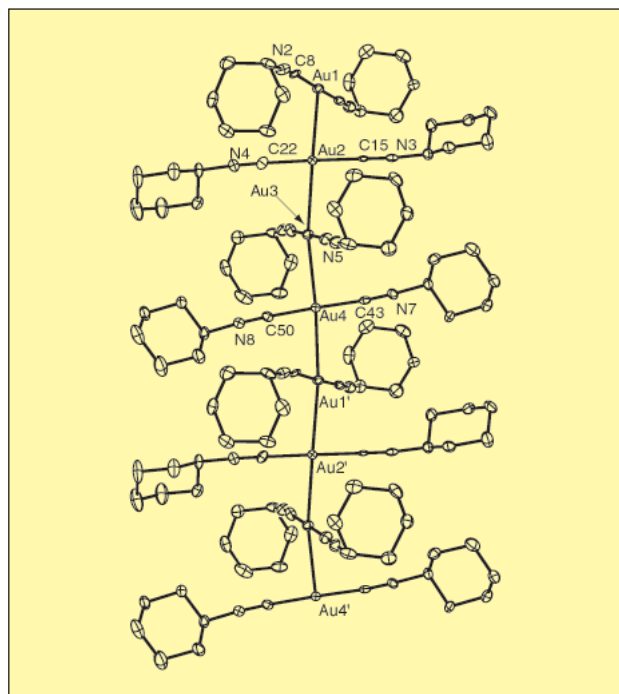

Figure 4
A perspective view of a portion of the kinked chain of cations in the yellow polymorph of $[(C_6H_{11}NC)_2Au^I](PF_6)$ with 50% thermal contours. There are four cations in the asymmetric unit and the Au···Au contacts are 2.9803(6), 2.9790(6), 2.9651(6), and 2.9643(6) Å. Again for clarity, the positions of the anions are not shown

Table 1

Crystallographic Data for Polymorphs

	$[(C_6H_{11}NC)_2Au^I]$ (PF_6)	$[(C_6H_{11}NC)_2Au^I]$ (PF_6)	$\{(Me_2PhP)AuX\}$ dimeric polymorph	$\{(Me_2PhP)AuX\}$ trimeric polymorph
color/ habit formula	colorless needle $C_{14}H_{22}AuF_6N_2P$	yellow plate $C_{14}H_{22}AuF_6N_2P$	colorless blocks $C_8H_{11}AuClP$	colorless hexagonal blocks $C_8H_{11}AuClP$
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a, Å	6.3644(5)	11.5235(7)	9.455(5)	12.141(4)
b, Å	16.9806(15)	24.1416(15)	12.665(5)	8.433(2)
c, Å	16.7224(13)	26.0516(16)	17.059(6)	14.834(3)
α, deg	90	90	90	90
β, deg	92.693(3)	90	90	94.15(2)
γ, deg	90	90	90	90
V, Å^3	1805.2(3)	7247.4(8)	2042.8(15)	1514.8(7)
Z	4	16	8	6
data source	ref. 25	ref. 25	ref. 23	ref. 23

Relevant crystal data in Table 1 show the differences in the types of crystals. Both crystals contain linear, two-coordinate $(Me_2PhP)Au^ICl$ molecules, but the crystals differ in that these molecules dimerize in one polymorph but form trimers in the other. In the initial stages of the investigation, crystals of the trimeric polymorph formed preferentially and were studied spectroscopically. However, anomalies in the spectroscopic features of samples of this complex led to the discovery that a second polymorph was present. After the presence of the dimeric polymorph was established, the amounts of the corresponding trimer polymorph in our preparations diminished to the point where eventually only the dimer polymorph crystallized in this laboratory. The occurrence and disappearance of such "vanishing polymorphs" occurs frequently enough that a review of the topic has been written (28).

The structure of the self-associated unit found in the dimeric polymorph of $(Me_2PhP)Au^ICl$ is shown in Figure 5 (23). The two adjacent complexes interact through an Au···Au contact of 3.230(2) Å. Notice that although neutral molecules are involved, this Au···Au distance is longer than those observed in the polymorphs of the salt $[(C_6H_{11}NC)_2Au^I](PF_6)$ where cations self-associate.

Figure 6 shows the structure of three $(Me_2PhP)Au^ICl$ molecules that self-associate in the trimeric polymorph (23). The asymmetric unit contains three crystallographically distinct monomers. Thus, within the trimer, there are two somewhat different Au···Au separations of 3.091(2) and 3.120(2) Å.

Crystals of the dimeric and trimeric polymorphs of $(Me_2PhP)Au^ICl$ show emission spectra that are distinct from

one another, but both polymorphs show emissions from two excited states (27). Emission spectra collected at 77 and 1.2 K show that the higher energy emission with an origin at *ca.* 360 nm has the greater relative intensity at low temperatures. This emission has been assigned to intraligand phosphorescence from a phenyl localized $^3\pi\pi^*$ state. The lower energy emission has been assigned to a triplet state arising from a gold-based transition analogous to that seen for $[(C_6H_{11}NC)_2Au^I](PF_6)$. The two polymorphic forms of $(Me_2PhP)Au^ICl$ differ in the intensity of this low-energy emission, which is absent in the 77 K spectrum of the dimeric polymorph, while the emission at 635 nm dominates the emission spectrum of the dimeric polymorph at that temperature.

Polymorphs of $\{(C_6H_{11})_3P\}_2Au^IBr$ and of $\{(C_6H_5)_3As\}Au^ICl$

One rather closely related case of polymorphism in gold(I) complexes deserves mention here. These very interesting studies have shown that $\{(C_6H_{11})_3P\}_2Au^IBr$ crystallizes as three polymorphs that differ in the way the bromide ion approaches the gold center (29). Thus, the structural work shows the conversion of a basically two-coordinate complex into a three-coordinate one as the bromide ion comes closer to the gold center. In none of these polymorphs is there any close contacts between the gold centers themselves. Rather in the α form, the cation is linear and the bromide ion is far from the gold with a Au···Br distance
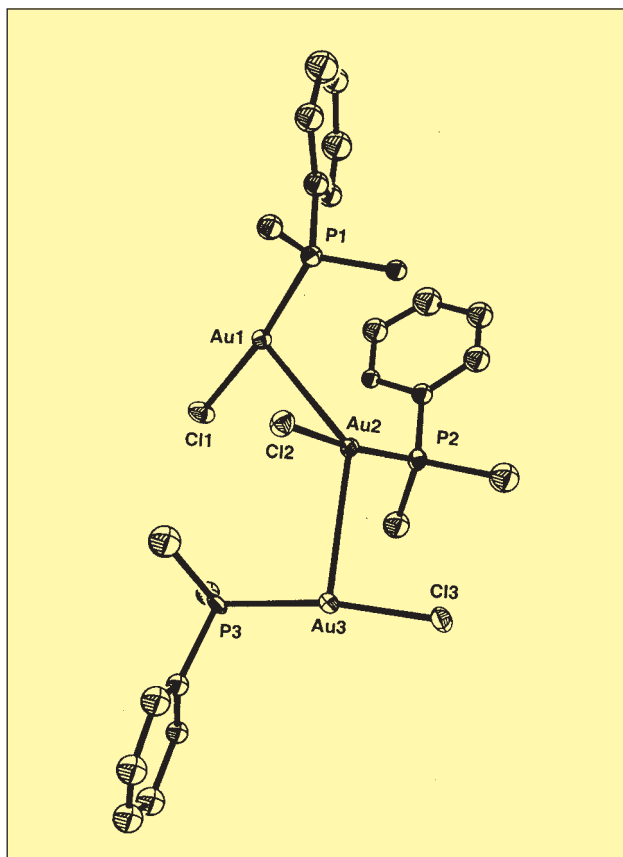
Figure 5
A perspective view of the dimeric unit in the dimer polymorph of (Me₂PhP)AuᴵCl with 50% thermal contours. The Au⋯Au contact is 3.230(2) Å

Figure 6
A perspective view of the trimeric unit in the trimer polymorph of (Me₂PhP)AuᴵCl with 50% thermal contours. The two different Au⋯Au contacts are 3.091(2) and 3.120(2) Å

of 3.764(4) Å. In the β form there are two molecules in the asymmetric unit. One of these has a Au-Br distance of 2.894(1) Å and a slightly bent P-Au-P (162.06(9)°) portion. The other molecule has a shorter Au-Br distance of 2.842(1) Å and a somewhat greater bending (157.71°) of the P-Au-P portion. Finally in the γ polymorph the Au-Br distance is shorter yet (2.777(1) Å) and the P-Au-P portion is bent more sharply (147.5(1)°).

Not all polymorphs of gold(I) complexes involve necessarily alterations in the coordination environment of the gold(I) center or in the aurophilic interactions present. For example there are two polymorphs for {(C₆H₅)₃P}AuᴵCl that grow with either needle or prismatic habits (30). Neither of these have close Au⋯Au contacts. The shortest Au⋯Au separations are 5.916(1) Å for the needle form or 6.913(1) Å for the prismatic modification. The polymorphs of {(C₆H₅)₃As}AuᴵCl do differ in the ways the molecules pack together and in some of the torsional angles of the phenyl rings. Both polymorphs are luminescent, but the emission spectra of the two forms show only minor differences. The luminescence is ligand-based and originates in π-π* states, not from transitions involving gold(I) (31).

Conclusions
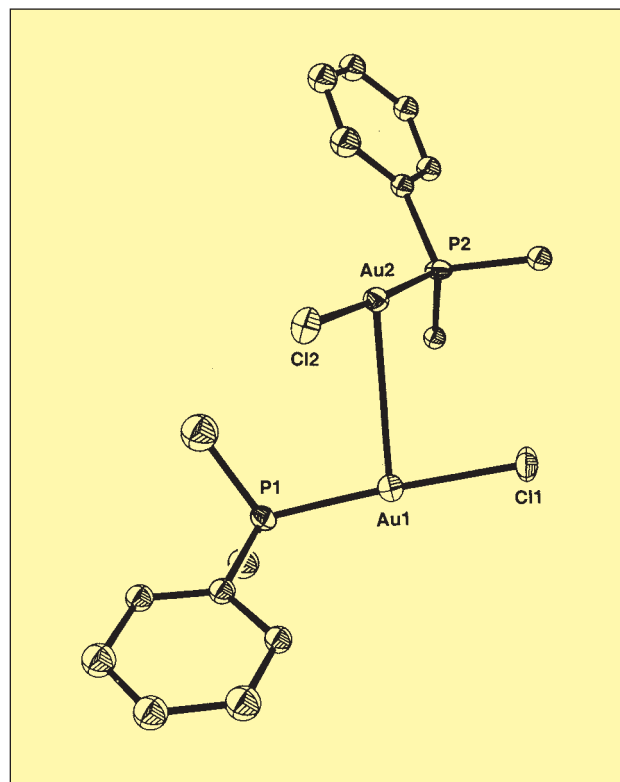
Polymorphs that differ primarily in the nature of the aurophilic attractions between gold complexes are a new feature in the chemistry of two-coordinate gold(I). Although we are unaware of other examples of gold(I) complexes forming polymorphs in which the aurophilic interactions differ, we suspect that other examples will emerge. Indeed we have several unpublished examples that have appeared in our laboratory and are still under investigation. Many questions surrounding these unusual polymorphs remain unanswered. For example, can the crystalline polymorphs be interconverted thermally or chemically? Can crystal growth conditions be manipulated to preferentially favor one polymorph over the other?

Usually the synthetic chemist is happy to get a crystal structure to confirm or establish the structure of the species that she or he has been laboring to prepare. Hence, attempts at crystallization generally stop once a satisfactory crystal has been obtained that allows the molecular structure to be established. However, if one is interested in the nature of intermolecular or inter-ionic interactions, then efforts to obtain additional types of crystals can be rewarding.

The intense luminescence from gold(I) complexes and the sensitivity of that luminescence to environmental factors suggests that the complexes may be developed into sensors and further developments along that line are anticipated.

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About the Author

Alan Balch is Distinguished Professor at the Department of Chemistry, University of California, Davis, California. His research interests include the study of luminescent complexes with weak metal-metal bonds, the chemistry and structures of fullerenes and endohedral fullerenes, and the detection of intermediates during the activation of dioxygen and peroxides by hemes and the role of these in heme degradation.

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