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Contrasting photochemical behavior of $[Au(SH)_2]^-$ and $Au(SMe_2)Cl$

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Abstract

The complexes $[Au(SH)_2]^-$ and $Au(SMe_2)Cl$ display absorption bands in the UV region which are assigned to metal-centered ds and ligand-to-metal charge transfer (LMCT) transitions respectively. In toluene glasses at 77 K, both complexes show an orange–red emission which originates from a ds excited state. At room temperature in solution, the complexes are light sensitive. On LMCT excitation, $Au(SMe_2)Cl$ undergoes photoredox decomposition with the formation of metallic gold, whereas the photolysis of $[Au(SH)_2]^-$ affords Au_2S. The photoreactivity of $[Au(SH)_2]^-$ seems to be a characteristic feature also applicable to other gold(I) thiolate complexes. © 1997 Elsevier Science S.A.

Keywords: Absorption spectra; Gold(I) complexes; Photoluminescence; Sulfur compounds

1. Introduction

Although the photophysics of Au(I) complexes has been studied extensively during the last decade [1–6], few observations have been reported on their photochemistry [7–11]. Au(I) thiolate complexes are of considerable significance because they have found important applications as drugs [12]. Recently, we have shown that some of these drugs, myochrysin and auranofin, are luminescent and photoreactive [13]. However, they have complicated structures and the course of their photoreactions is not clear. In order to gain more insight into the photoactivity of the gold–sulfur bond, we decided to extend our investigation to simpler compounds. We selected the complexes $[Au(SH)_2]^-$ and $Au(SMe_2)Cl$ for the present study. The preparation of $[Au(SH)_2]^-$ has been reported recently [14], while $Au(SMe_2)Cl$ is available commercially.

2. Experimental section

2.1. Materials

The compound $Au(SMe_2)Cl$ was commercially available (Aldrich) and was used as received. The solvents used were of spectrograde quality. $(Bu_4N)[Au(SH)_2]$ was prepared in analogy with $[(Ph_3P)_2N)][Au(SH)_2]$ [14]. The composition of $(Bu_4N)[Au(SH)_2]$ was confirmed by emission spectroscopy and elemental analysis. Analysis: calculated for $C_{16}H_{38}N_2S_2Au$: C, 38.01%; H, 7.57%; N, 2.77%; found: C, 38.05%; H, 7.55%; N, 2.75%.

2.2. Photolyses

The light source was an Osram HBO 100 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light was obtained by means of a Schoeffel GM 250/1 high-intensity monochromator (bandwidth, 23 nm). The photolyses were carried out in solutions of carefully dried CH_2Cl_2, EtOH or CH_3CN in 1 cm spectrophotometric cells at room temperature. All solutions were freshly prepared, saturated with argon and kept in the dark. The progress of photolysis was monitored by UV–visible spectrophotometry. The photoproducts were identified by their absorption spectra. For quantum yield determinations, the complex concentrations were such as to show essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproducts. The absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated by actinometry and equipped with an RkP-345 detector.

2.3. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array or a Shimadzu UV-2100 absorption spec-

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trometer. Emission and excitation spectra were obtained on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations.

3. Results

The cation $(Ph_3P)_2N^+$ was used for the isolation of the complex anion $[Au(SH)_2]^-$ [14]. Since this cation is not transparent in the UV region, it was replaced by Bu_4N^+. The salt $(Bu_4N)[Au(SH)_2]$ is soluble in a variety of organic solvents. In acetonitrile, $[Au(SH)_2]^-$ displays an absorption in the UV region which increases towards shorter wavelengths. Two shoulders can be recognized (Fig. 1) at $\lambda_{max}=250$ nm ($\epsilon=1800$ dm^3 M^{-1} cm^{-1}) and $\lambda_{max}=234$ nm ($\epsilon=2800$ dm^3 M^{-1} cm^{-1}). The complex shows an orange–red emission in toluene glasses ($\lambda_{max}=665$ nm, Fig. 1) or in the solid state ($\lambda_{max}=646$ nm) at 77 K. This luminescence is absent at room temperature. In solvents such as ethanol or acetonitrile, $[Au(SH)_2]^-$ undergoes photodecomposition. The accompanying spectral changes (Fig. 2) show the formation of a colloid which causes an increase in the apparent optical density over the entire absorption spectrum. The brownish colloid was collected by filtration. It consists of Au_2S as indicated by its thermal decomposition which affords metallic gold and sulfur. Owing to the formation of the colloid, it is difficult to determine reliable quantum yields. For a rough estimate, the disappearance of $[Au(SH)_2]^-$ was measured spectrophotometrically after colloidal Au_2S was removed by filtration. At $\lambda_{irr}=254$ nm, the quantum yield is approximately $\phi=0.01$.

$Au(SMe_2)Cl$ is soluble in organic solvents such as ethanol, acetonitrile or methylene chloride. In EtOH, the complex displays two long-wavelength bands (Fig. 3) at $\lambda_{max}=362$ nm ($\epsilon=1200$ dm^3 M^{-1} cm^{-1}) and $\lambda_{max}=312$ nm ($\epsilon=1300$ dm^3 M^{-1} cm^{-1}). In toluene glasses at 77 K, the complex shows an orange–red emission with $\lambda_{max}=660$ nm (Fig. 3). This luminescence also appears in the solid state even at room temperature ($\lambda_{max}=655$ nm). Solutions of $Au(SMe_2)Cl$ are light sensitive. Irradiation leads to decomposition of the complex. The spectral variations (Fig. 4) clearly indicate the formation of colloidal gold which gives rise to the characteristic plasmon absorption [7,9,10] at 598 nm. The colloidal gold can be removed by centrifugation. The disappearance of $Au(SMe_2)Cl$ is then determined by measuring the decrease in the optical density at $\lambda=362$ nm. The quantum yield for the loss of $Au(SMe_2)Cl$ is $\phi=0.03$ at $\lambda_{irr}=366$ nm. In acetonitrile, the photochemical formation of elemental gold is much less efficient. It is assumed that, in coordinating solvents, other processes including ligand substitutions also take place.

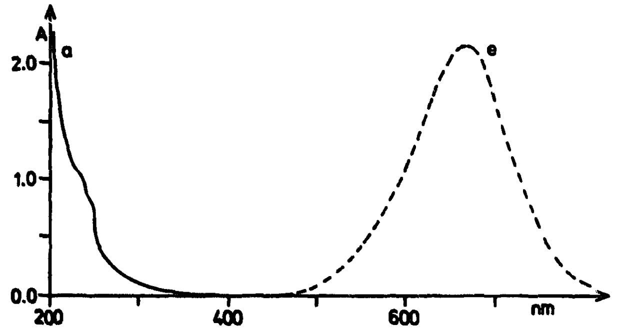

Fig. 1. Electronic absorption (a, ———) and emission (e, · · ·) spectra of $(Bu_4N)[Au(SH)_2]$. Absorption: 3.75×10^{-4} M in dry acetonitrile under argon at room temperature, 1 cm cell. Emission: in toluene at 77 K, $\lambda_{exc}=300$ nm, intensity in arbitrary units.

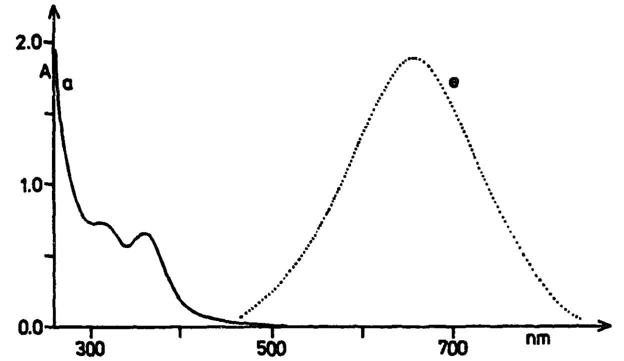

Fig. 3. Electronic absorption (a, ———) and emission (e, · · ·) spectra of $(CH_3)_2SAuCl$ in dry EtOH under argon. Absorption: 5.25×10^{-4} M at room temperature, 1 cm cell. Emission: at 77 K, $\lambda_{exc}=350$ nm, intensity in arbitrary units.

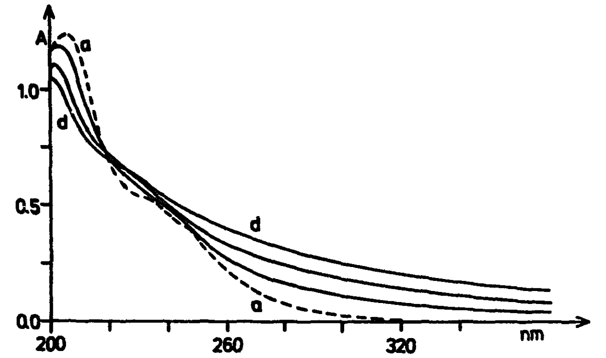

Fig. 2. Spectral changes during the photolysis of 1.91×10^{-4} M $(Bu_4N)[Au(SH)_2]$ in CH_3CN under argon at room temperature after 0 (a, - - -), 2, 5 and 10 (d) min of irradiation time with white light (1 cm cell).

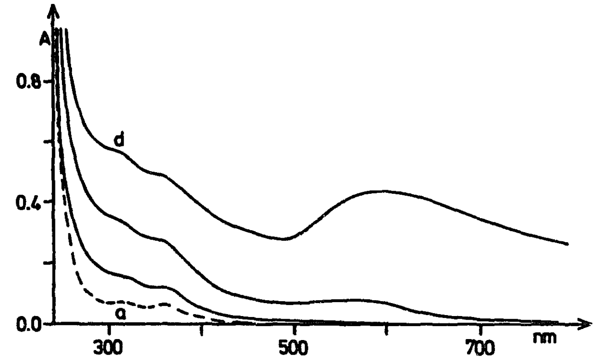

Fig. 4. Spectral changes during the photolysis of 5.3×10^{-5} M $(CH_3)_2SAuCl$ in EtOH under argon at room temperature after 0 (a, - - -), 5, 10 and 20 (d) min of irradiation time with white light (1 cm cell).

4. Discussion

Au(I) with its d^{10} electron configuration forms a variety of linear complexes. In the absence of π-acceptor ligands, the electronic spectra of Au(I) complexes are characterized by absorptions which are assigned to metal-centered 5d → 6s and ligand-to-metal charge transfer (LMCT) transitions [15,16]. If the ligands, such as thiolates, are quite reducing, LMCT transitions occur at rather low energies and can mix with ds transitions [13]. According to these considerations, the absorption bands of $[Au(SH)_2]^-$ and $Au(SMe_2)Cl$ are assigned to LMCT and ds transitions which may partially be mixed. The orange–red emission of both complexes should originate from the lowest ds/LMCT state. The large Stokes shifts ($\Delta\bar{\nu} > 12\,350\ cm^{-1}$) are an indication of a considerable excited state distortion, which is probably caused by the population of the σ^* (Au 6s) orbital. In solution at room temperature this emission is quenched and the complexes undergo a photoreaction which is induced by LMCT excitation. It has been suggested that the reactive LMCT state can be populated thermally from the emissive ds/LMCT state [13].

While the photolyses of $[Au(SH)_2]^-$ and $Au(SMe_2)Cl$ are initiated by LMCT excitation, the photoreactions of the two complexes take a different course. In analogy with various other Au(I) complexes, LMCT excitation of $Au(SMe_2)Cl$ leads to the reduction of Au(I) to metallic gold which appears as a red–violet colloid [7,9,10]. In contrast with this normal behavior of $Au(SMe_2)Cl$, the irradiation of $[Au(SH)_2]^-$ leads to rather unexpected results. The photolysis can be described by the equation

$$2[Au(SH)_2]^- \xrightarrow{h\nu/\mathrm{LMCT}} Au_2S + H_2S + 2HS^-$$

This type of reaction is apparently not unique, but also applies to other Au(I) thiolate complexes. For example, the photolyses of myochrysin and auranofin do not yield metallic gold [13]. In the case of myochrysin, the formation of colloidal Au_2S has been observed. We suggest that the course of this reaction is determined by two effects. The formation of Au_2S may be facilitated by the preference of Au(I) to bind to sulfide. This tendency is illustrated by the existence of a series of polynuclear complexes with the general formula $[S(AuPR_3)_n]^{(n-2)+}$ with $n = 2$–6 [17–21]. Moreover, alkyl sulfur compounds undergo dealkylation reactions catalyzed by metal complexes [22]. Usually, suitable nucleophiles are required to accept the alkyl cations. If thiolates themselves act as nucleophiles, a dismutation may take place ($2SR^- \rightarrow S^{2-} + SR_2$). Gold(I) should favor this reaction by the formation of Au_2S or other complexes with sulfide as ligand. As shown by the present work, the photolysis of $[Au(SH)_2]^-$ with R = H proceeds apparently according to this mechanism. In this context, it is quite interesting that alkyl thiols which are self-assembled on the surface of solid gold also undergo C–S bond scission on exposure to UV light [23].

In the case of $Au(SMe_2)Cl$, the photolysis does not yield Au_2S. However, a simple demethylation of dimethylsulfide would only generate SMe^- but not S^{2-}. Moreover, in the absence of a strong nucleophile, the transfer of CH_3^+ may not take place. Accordingly, $Au(SMe_2)Cl$ prefers to undergo a photoredox reaction on LMCT excitation.

Acknowledgements

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