

Photooxidation of Dicyanoaurate(I) Induced by Metal-to-Ligand Charge Transfer Excitation

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The irradiation of $[\text{Au}(\text{CN})_2]^-$ in oxygen-saturated acetonitrile leads to photooxidation of Au(I). In the presence of additional chloride $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ is formed with $\phi = 0.5 \times 10^{-4}$ at $\lambda_{\text{irr}} = 254 \text{ nm}$. It is assumed that $[\text{Au}(\text{CN})_2]^-$ in its metal-to-ligand charge transfer state undergoes an excited state electron transfer to oxygen in the primary photochemical step.

1. Introduction

The light sensitivity of gold complexes has been known since 1737 [1, 2]. Despite this early interest progress in this field has been rather slow. In this context it is quite surprising that numerous reports on the photophysics of Au(I) complexes have appeared during the last decade [3 - 9]. Although the nature of the luminescence is not yet completely understood a variety of different excited states such as metal-centered ds and dp [3, 4a, c, 5a, c-f, 6], ligand-to-metal charge transfer (LMCT) [5g, 7, 8], metal-to-ligand charge transfer (MLCT) [4b] and intraligand (IL) [4f, g] excited states have been suggested to be emissive. All these different excited states may be also reactive. Recently, we have shown that ds [3c, d], LMCT [3b, e, 10] and MMCT [11, 12] excitation indeed induce photoreactions of Au(I) complexes while reactive MLCT states have not yet been identified. We explored this possibility and selected the complex $[\text{Au}(\text{CN})_2]^-$ for the present study. This anion is a suitable candidate because it has a relatively simple electronic structure and is characterized by low-energy MLCT transitions [13]. Moreover, a variety of reducing transition metal cyano complexes undergo a photooxidation following MLCT excitation [14].

2. Results

The electronic spectrum of $[\text{Au}(\text{CN})_2]^-$ in CH_3CN (Fig. 1) shows absorptions at $\lambda_{\text{max}} = 240$ ($\epsilon = 3200 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$), 232 (3800), 214 (sh,

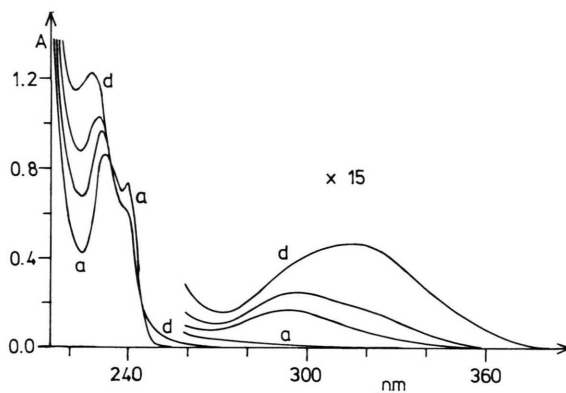


Fig. 1. Spectral changes during the photolysis of $2.34 \times 10^{-4} \text{ M}$ $[\text{NBu}_4]\text{Au}(\text{CN})_2$ in O_2 -saturated CH_3CN in the presence of 10^{-2} M $[\text{NBu}_4]\text{Cl}$ at (a) 0, 2, 4, and (d) 8 h irradiation times, with $\lambda_{\text{irr}} = 254 \text{ nm}$ (Hanovia 977 B-1, 1 kW lamp) and a 1-cm cell.

4900) and 205 (12000) nm in agreement with previous results [13]. In the presence of additional chloride the spectrum (Fig. 1) is unaffected above 220 nm. Deaerated solutions of $[\text{Au}(\text{CN})_2]^-$ in CH_3CN are not light sensitive while oxygen-saturated solutions are photoreactive. In the presence of chloride the photolysis is accompanied by spectral variations which indicate the formation of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ ($\lambda_{\text{max}} = 292 \text{ nm}$, $\epsilon = 1060$ and 220 nm, 21400) [15]. As shown by the isosbestic points at 244 and 235 nm the photoreaction is rather clean during the early stages of irradiation. The formation of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ is monitored by measuring the increase of the optical density at 220 nm. $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ is formed with the quantum yield $\phi = 0.5 \times 10^{-4}$ at $\lambda_{\text{irr}} = 254 \text{ nm}$. At later stages

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of the irradiation the spectral changes are obscured by a secondary photolysis. The primary photoproduct $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ undergoes a photosubstitution. After prolonged irradiation (Fig. 1) the absorption spectrum approaches that of $[\text{AuCl}_4]^-$ ($\lambda_{\text{max}} = 323$ nm, $\epsilon = 5800$; 227 nm, 44800) [15].

3. Discussion

The electronic spectrum of $[\text{Au}(\text{CN})_2]^-$ is characterized by a set of MLCT absorptions [13]. At room temperature solutions of $[\text{Au}(\text{CN})_2]^-$ do not show any emission, and are not photoreactive in the absence of a suitable electron acceptor. However, in the presence of oxygen a photooxidation takes place which in the presence of chloride yields $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ as a well defined product [16]. In analogy to $[\text{AuCl}_2]^-$ and $[\text{AuBr}_2]^-$ [3d] it is suggested that the lowest-energy excited state of $[\text{Au}(\text{CN})_2]^-$ undergoes electron transfer to oxygen in the primary photochemical step. The low quantum yield of photooxidation is certainly related to the small concentration of oxygen in solution. The lowest-energy and reactive excited state of $[\text{AuCl}_2]^-$ and $[\text{AuBr}_2]^-$ is of the metal-centered ds type [3d, 17]. In contrast to these halide complexes the lowest excited state of $[\text{Au}(\text{CN})_2]^-$ is of the MLCT type because by overlap with the gold 6p

the cyanide π^* orbital is pushed below the empty 6s orbital of gold and becomes the LUMO [13] of the complex. Accordingly, MLCT excitation of $[\text{Au}(\text{CN})_2]^-$ induces the photooxidation of Au(I) to Au(III). Although the overall photoreaction is a two-electron oxidation of Au(I) it may initially proceed by a one-electron oxidation generating an Au(II) intermediate which either disproportionates to Au(I) and Au(III) or is oxidized to Au(III) in a second electron transfer step. In this context it is of interest that the existence of Au^{2+} ions in different systems even under ambient conditions has been confirmed quite recently [18, 19].

The photoproduct $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ undergoes a further photolysis. The irradiation leads to a photosubstitution which finally yields $[\text{AuCl}_4]^-$. The nature of the reactive excited state of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ is not clear since low-energy LF as well as LMCT states exist in close proximity [15]. In analogy to other d^8 metals such as Pt(II) [20], LF states are certainly reasonable candidates for inducing substitutions.

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