Photochemistry of chlorocarbonyl gold(I) [1]

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Abstract

The complex Au(CO)Cl shows a long wavelength absorption at $\lambda_{max} = 250$ nm which is assigned to a metal-centered ds transition. In the solid state this excited ds state is emissive ($\lambda_{max} = 663$ nm) while in solution it is reactive. It is suggested that CO is released in the primary photochemical step. In CH_2Cl_2 the photolysis of Au(CO)Cl leads finally to a disproportionation with the formation of $AuCl_3$ and metallic gold. © 1997 Elsevier Science S.A.

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1. Introduction

The photophysics and photochemistry of Cu(I), Ag(I), and Au(I) complexes have attracted much attention in recent years (for reviews see Ref. [1]). In contrast to this growing interest, excited state properties of carbonyl complexes of these d^{10} metal ions have not yet been studied in any detail. This lack is quite surprising in view of the general importance of the photochemistry of metal carbonyl complexes [2]. The present investigation was undertaken in order to fill this gap. As a suitable candidate we selected the compound Au(CO)Cl [3,4] which is commercially available and serves as starting material for the preparation of a large variety of other gold(I) complexes [5]. An intriguing aspect of this study is the fact that owing to their closed d shell Au(I) complexes have no available ligand field excited states, which largely determine the photoreactivity of metal carbonyl complexes [2].

2. Experimental section

2.1. Materials

The compound Au(CO)Cl was commercially available (Strem) and used as received. The solvents acetonitrile, dichloromethane and ether were spectrograde.

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 (band width 23 nm). The photolyses were carried out in solutions of carefully dried CH_2Cl_2, ether or CH_3CN in 1 cm spectrophotometer cells at room temperature. All solutions were freshly prepared, saturated with argon, and kept in the dark. Progress of the photolyses 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 have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed

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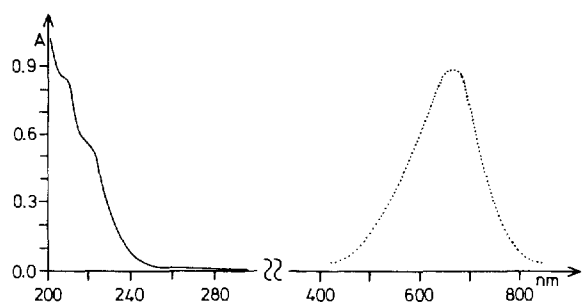[1] Dedicated to Professor Dr. Gottfried Huttner, on the occasion of his 60th birthday.

Fig. 1. Electronic absorption (———————) and emission (· · ·) spectra of Au(CO)Cl at room temperature. Absorption: 1.74×10^{-4} M in dry acetonitrile under argon, 1 cm cell. Emission: in the solid state, $\lambda_{exc} = 280$ nm, intensity in arbitrary units.

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 spectrometer. Emission and excitation spectra were obtained on a Hitachi 850 spectrofluorimeter 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 complex Au(CO)Cl is soluble in a variety of organic solvents such as benzene, CH_2Cl_2 and acetonitrile. The solvents have to be completely dry in order to avoid decomposition [4]. The absorption spectrum of Au(CO)Cl in CH_3CN (Fig. 1) displays bands at $\lambda_{max} = 208$ ($\varepsilon = 4900$ dm^3 M^{-1} cm^{-1}), 220 (3300), and 250 nm
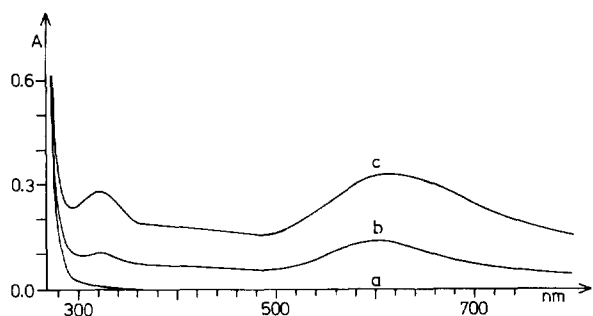

Fig. 2. Spectral changes during the photolysis of 1.08×10^{-3} M Au(CO)Cl in dichloromethane under argon at r.t. after (a) 0, (b) 2 and (c) 5 min irradiation time with $\lambda_{irr} > 280$ nm (HBO 100 W/2, cut-off Schott WG 305), 1 cm cell.

(140). While solutions of Au(CO)Cl are not photoluminescent, the solid compound shows an orange–red emission (Fig. 1) at $\lambda_{max} = 663$ nm. Solutions of Au(CO)Cl are light sensitive. Upon irradiation of the complex in CH_2Cl_2 a decomposition takes place. The photolysis is accompanied by spectral changes (Fig. 2) which clearly indicate the generation of metallic gold. The colloidal metal gives rise to the characteristic plasmon absorption at $\lambda_{max} = 610$ nm [6]. Simultaneously, a new absorption appears at $\lambda_{max} = 322$ nm. This band is attributed to $AuCl_3$ [7] which is formed with $\phi = 0.02$ at $\lambda_{max} = 280$ nm. When the irradiation of Au(CO)Cl is performed in CH_3CN, metallic gold and $AuCl_3$ are also produced but with a very low efficiency.

4. Discussion

In the free Au^+ ion the lowest energy transition involves the promotion of a 5d electron to the 6s orbital. In linear $Au^I LCl$ complexes (L = π-acceptor ligand) including Au(CO)Cl [8] and Au(PR$_3$)Cl [9] the 6s orbital is destabilized by σ-interaction with the ligands while two degenerate p orbitals of gold are stabilized by π-overlap with π* orbitals of L. Accordingly, it is not quite clear if metal-centered ds or dp transitions occur at lowest energies. The dp transition can also be termed metal-to-ligand charge transfer (MLCT) since the acceptor orbital (3π in $C_{\infty v}$ symmetry) contains a considerable π* contribution of L [9]. In the case of Au(PR$_3$)Cl such an MLCT (or dp) absorption appears near 235 nm ($\varepsilon \sim 2000$) while a ds band which should be much weaker was not detected at longer wavelength [9]. The ds absorption was concluded to appear at shorter wavelength where it is obscured by the stronger MLCT band. In analogy to Au(PR$_3$)Cl we assign the absorption of Au(CO)Cl at $\lambda_{max} = 220$ nm to an MLCT (or dp) transition. However, the carbonyl complex displays an additional weaker band at $\lambda_{max} = 250$ nm which we attribute to a ds transition. The occurence of the ds transition at relatively low energies is certainly related to the small σ-donor strength of the CO ligand which does not destabilize the 6s (σ*) orbital to the same extent as the strong σ-donor PR$_3$. The ds assignment of the longest wavelength absorption of Au(CO)Cl is also supported by other observations.

A variety of Au(I) complexes are known to show photoluminescence [10–15]. Several excited states including those of the MLCT, LMCT and ds type have been assumed to be the emissive states. For Au(CO)Cl we suggest that the luminescence originates from the lowest energy ds excited state. This assumption is in line with the assignment of the longest wavelength absorption band. It is also consistent with the huge

Stokes shift [2] ($\Delta\bar{\nu} = 24917\,cm^{-1}$) which is indicative of large structural changes which are associated with electronic excitation. While the ds transition which leads to the population of the σ^* orbital has certainly a large effect on the bonding and structure of Au(CO)Cl the influence of MLCT excitation which affects only the Au–CO π-bonding would be much smaller. The emission of Au(CO)Cl is observed only in the solid state (the emission may be slightly modified by a weak Au–Au interaction which is present in the solid state [16]) while in solution the complex undergoes a photodissociation which is apparently prevented in the solid compound owing to the rigidity of the medium. This type of rigidity effect has also been observed in other cases [17].

In dichloromethane Au(CO)Cl is quite light sensitive. It is assumed that ds excitation leads to the release of CO in the primary photochemical step. This process is rather similar to ligand field excitation of other metal carbonyl complexes which show the same photoreactivity upon population of σ^* orbitals [2]. The AuCl fragment which is generated photochemically undergoes apparently a disproportionation according to the equation: $3AuCl \rightarrow AuCl_3 + 2Au^0$. This secondary reaction may be facilitated by the thermodynamic instability of AuCl [18]. This disproportionation is less efficient in coordinating solvents such as acetonitrile since AuCl can be stabilized by attaching a solvent molecule as a ligand.

It seems less likely that the photolysis of Au(CO)Cl originates from an MLCT excited state which occurs at higher energy than the ds state. This conclusion is consistent with the general behavior of metal carbonyl complexes which do not release CO ligands upon MLCT excitation [2]. In this context it is quite interesting that the photodissociation of Ni(CO)$_4$ which is also a d^{10} complex was suggested to be induced by ds excitation too [2].

Acknowledgements

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[2] 'Stokes shift' is defined as the energy difference between the absorption and emission maxima of the same electronic transition and multiplicity. However, the emitting excited state often cannot always be identified in absorption, so in the present case we will use the often employed operational definition of the Stokes shift as the energy difference between the absorption and emission maxima.

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