Photooxidation of $AuCl_2^-$ and $AuBr_2^-$ Induced by ds Excitation

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In the presence of electron acceptors such as CH_2Cl_2 or O_2, the irradiation of $AuCl_2^-$ or $AuBr_2^-$ in acetonitrile led to the photooxidation of Au(I) to Au(III). $AuCl_4^-$ and $AuBr_4^-$ were formed as final products when additional halide was present. The reactive excited states were of the metal-centered ds type. The photooxidations were reversed in solutions of ethanol. $AuCl_4^-$ and $AuBr_4^-$ underwent a photoreduction to $AuCl_2^-$ and $AuBr_2^-$, respectively.

Introduction

Metal-centered (MC) excited states play an important role in the photophysics and photochemistry of transition metal complexes.[1] Frequently, MC and dd (or ligand field, LF) states are considered as synonyms since studies of MC states have been indeed largely restricted to dd states. During recent years, the importance of other MC states including those of the ds type was recognized. However, it is quite surprising that mainly polynuclear complexes were investigated while very little is known about the properties of ds excited states of mononuclear complexes.[2] The present study has been undertaken to identify reactive and possibly luminescent ds excited states of simple complexes. In order to avoid complications, the ds states should be the lowest-energy excited states and should be well separated from other excited states. The best candidates are complexes of d^{10} metal ions due to the absence of interfering dd states.[2] Moreover, ds states of d^{10} complexes occur at relatively low energies. However, the choice of suitable complexes depends critically on the metal and ligands. The combination of low-oxidation-state d^{10} metals such as Ni(0), Cu(I), and Au(I) with π-acceptor ligands such as CO, CN^-, and polypyridyls is less suitable since MLCT (metal to ligand charge transfer) states occur at low energies (e.g. $Ni(CO)_4$,[3,4] Cu(*o*-phen)$(PPh_3)_2^+$,[5] and $Au(CN)_2^-$ [6]). If the ligands are strongly reducing, the lowest-energy states can be of the LMCT (ligand to metal charge transfer) type (e.g. $Au(N_3)_2^-$).[7] Taking into account these considerations, copper(I) halide complexes such as CuX_{n+1}^{n-} with X = Cl and Br may be characterized by lowest-energy ds states. However, Stevenson et al., who studied these compounds in aqueous solution, assigned the longest-wavelength bands to CTTS (charge transfer to solvent) transitions.[8] These CTTS states were shown to induce the formation of solvated electrons.[8,9] Alternatively, the lowest excited states of Cu(I) halide anions which are also emissive were assumed to be of ds type.[8f] Interestingly, it has been suggested that CTTS and ds states are quite similar with regard to their photoreactivity since ds transitions terminate at diffuse s orbitals which are exposed to the solvent.[8f,10] For the present study we have chosen $AuCl_2^-$ and $AuBr_2^-$. This choice was based on Mason's work.[11] These complexes, which are stable in solutions of acetonitrile, display longest-wavelength ds absorptions which are well separated from bands of different origin.

Experimental Section

The compounds $[N(C_4H_9)_4][AuCl_2]$, $[N(C_4H_9)_4][AuBr_2]$, $[N(C_4H_9)_4][AuCl_4]$, and $[N(C_4H_9)_4][AuBr_4]$ were prepared according to published procedures.[12] Their electronic absorption spectra agreed well with those reported previously.[11,13] $[N(C_4H_9)_4]Cl$ and $[N(C_4H_9)_4]Br$ were recrystallized from acetonitrile/ether. Acetonitrile and CH_2Cl_2 were spectrograde.

The light sources were an Osram HBO 100 W/2 and a Hanovia Xe/Hg 977 B-1 (1000 W) lamp. Monochromatic light (λ_{irr} = 254 and 280 nm) was obtained by means of a Schoeffel GM 250-1 high-intensity monochromator. The Schott cutoff filters GG 385/1 (λ_{irr} > 350 nm) and WG 295/1 (λ_{irr} > 250 nm) were used to avoid short-wavelength irradiation. The photolyses were carried out at room temperature in 1-cm spectrophotometer cells. 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 light intensities were determined by a Polytec pyroelectric radiometer, which was calibrated and equipped with a RkP-345 detector.

Progress of the photolysis was monitored by UV–visible spectrophotometry, using a 8452A Hewlett Packard diode array spectrophotometer and a Shimadzu UV-2100 spectrometer. Emission spectra of the complexes in the solid state, in butyronitrile or ethanol glasses at 77 K, were obtained on a Hitachi 850 spectrofluorimeter equipped with a Hamamatsu R 928 photomultiplier. The luminescence spectra were corrected for monochromator and photomultiplier efficiency.

Results

Electronic Spectra. The absorption spectra of $AuCl_2^-$ and $AuBr_2^-$ in CH_3CN agreed with those reported by Mason et al.[11] The longest-wavelength band of $AuCl_2^-$ appeared at λ_{max} = 246

(1) (a) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: New York, 1970. (b) *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975. (c) Ferraudi, G. J. *Elements of Inorganic Photochemistry*; Wiley-Interscience: New York, 1988.
(2) Kutal, C. *Coord. Chem. Rev.* **1990**, *99*, 213.
(3) Lever, A. B. P.; Ozin, G. A.; Hanlan, A. J.; Power, W. J.; Gray, H. B. *Inorg. Chem.* **1979**, *18*, 2088.
(4) Kotzian, M.; Rösch, N.; Schröder, H.; Zerner, M. C. *J. Am. Chem. Soc.* **1989**, *111*, 7687.
(5) Casadonte, D. J.; McMillin, D. R. *J. Am. Chem. Soc.* **1987**, *109*, 331.
(6) (a) Mason, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 5182. (b) Chastain, S. K.; Mason, W. R. *Inorg. Chem.* **1982**, *21*, 3717.
(7) Vogler, A.; Quett, C.; Kunkely, H. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 1486.
(8) (a) Stevenson, K. L.; Davis, D. D. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 905. (b) Davis, D. D.; King, G. K.; Stevenson, K. L.; Birnbaum, E. R.; Hageman, J. H. *J. Solid State Chem.* **1977**, *22*, 63. (c) Davis, D. D.; Stevenson, K. L.; Davis, C. R. *J. Am. Chem. Soc.* **1978**, *100*, 5344. (d) Stevenson, K. L.; Kaehr, D. M.; Davis, D. D.; Davis, C. R. *Inorg. Chem.* **1980**, *19*, 781. (e) Kurtz, K. S.; Stevenson, K. L. *Proc. Indiana Acad. Sci.* **1985**, *94*, 187. (f) Stevenson, K. L.; Braun, J. L.; Davis, D. D.; Kurtz, K. S.; Sparks, R. I. *Inorg. Chem.* **1988**, *27*, 3472. (g) Stevenson, K. L.; Grush, M. M.; Kurtz, K. S. *Inorg. Chem.* **1990**, *29*, 3150. (h) Stevenson, K. L.; Berger, R. M.; Grush, M. M.; Stayanoff, J. C.; Horvath, A.; Horvath, O. *J. Photochem. Photobiol., A* **1991**, *60*, 215.
(9) (a) Horvath, O.; Papp, S. *J. Photochem.* **1985**, *30*, 47. (b) Horvath, O.; Papp, S. *J. Photochem.* **1985**, *31*, 211.
(10) The similarity of MLCT and ds transitions of Cu(I) compounds has been recently emphasized: Blasse, G. *Struct. Bonding* **1991**, *76*, 153.
(11) (a) Koutek, M. E.; Mason, W. R. *Inorg. Chem.* **1980**, *19*, 648. (b) Savas, M. M.; Mason, W. R. *Inorg. Chem.* **1987**, *26*, 301.
(12) Braunstein, P.; Clark, R. J. H. *J. Chem. Soc., Dalton Trans.* **1973**, 1845.
(13) Isci, H.; Mason, W. R. *Inorg. Chem.* **1983**, *22*, 2266.

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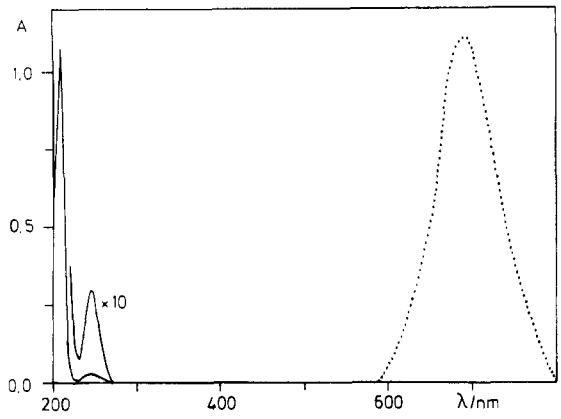

Figure 1. Electronic absorption (—) and emission (···) spectra of $[NBu_4]AuCl_2$. Absorption: 1.64×10^{-4} M in CH_3CN at room temperature, 1-cm cell. Emission: in ethanol at 77 K; $\lambda_{exc} = 250$ nm, intensity in arbitrary units.

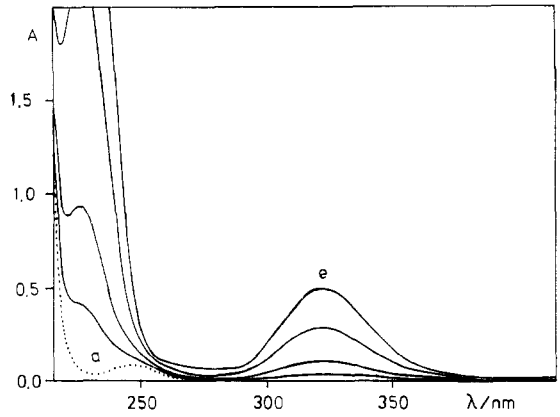

Figure 2. Spectral changes during the photolysis of 4.62×10^{-4} M $[NBu_4]AuCl_2$ in deaerated CH_3CN/CH_2Cl_2, (99:1) at (a (···)) 0-, 5-, 10-, 20-, and (e) 35-min irradiation times with $\lambda_{irr} = 254$ nm and a 1-cm cell.

nm with $\epsilon = 212$ (Figure 1). $AuCl_2^-$ in deaerated CH_3CN was not luminescent at room temperature but emitted strongly at $\lambda_{max} = 687$ nm in low-temperature glasses (77 K) of butyronitrile or ethanol (Figure 1). At $\lambda_{exc} = 250$ nm, the emission quantum yield was estimated to be $\phi = 10^{-1}$. The excitation spectrum matched rather well the absorption spectrum. In the solid state, $[N(C_4H_9)_4][AuCl_2]$ was emissive at 77 K ($\lambda_{max} = 686$ nm) as well as at room temperature ($\lambda_{max} = 642$ nm). The spectral features of $AuBr_2^-$ were quite similar to those of $AuCl_2^-$. The longest-wavelength absorption of $AuBr_2^-$ in CH_3CN occurred at $\lambda_{max} = 256$ nm with $\epsilon = 156$. The emission of $AuBr_2^-$ in butyronitrile or ethanol glasses (77 K) appeared at $\lambda_{max} = 660$ nm. Solid $[N(C_4H_9)_4][AuBr_2]$ emitted at room temperature ($\lambda_{max} = 592$ nm) and also at 77 K ($\lambda_{max} = 660$ nm).

Photochemistry. Solutions of $AuCl_2^-$ and $AuBr_2^-$ in deaerated acetonitrile were not light sensitive. However, in the presence of oxygen or upon addition of CH_2Cl_2, a photolysis took place. Light absorption into the long-wavelength band of $AuCl_2^-$ ($\lambda_{irr} = 254$ nm) in deaerated CH_3CN which contained 0.02 M CH_2Cl_2 led to an efficient photooxidation. The photolysis was accompanied by spectral changes (Figure 2) which clearly indicated the formation of $AuCl_4^-$.[13] At later stages of the photolysis, the spectral variations became more complicated due to a secondary photolysis. At the beginning of the irradiation, the quantum yield of this photooxidation was $\phi = 1.2 \times 10^{-4}$ at $\lambda_{irr} = 254$ nm. At higher concentrations of CH_2Cl_2, the spectral variations during the photolysis were partially obscured by the absorption of CH_2Cl_2. However, it was shown that the photooxidation became more efficient with an increasing concentration of CH_2Cl_2. In neat CH_2Cl_2, the quantum yield was found to be $\phi = 7 \times 10^{-2}$. In this case, about 1% of the light was absorbed by the solvent.

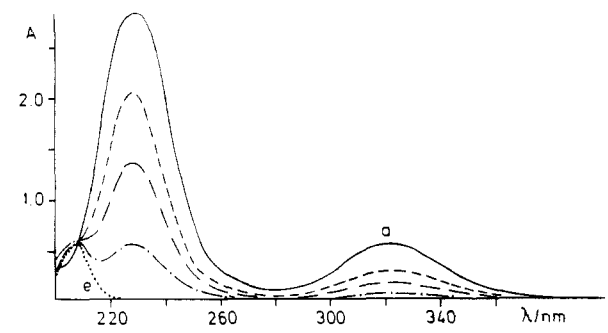

Figure 3. Spectral changes during the photolysis of 6.34×10^{-5} M $[NBu_4]AuCl_4$ in ethanol at (a) 0-, 0.5-, 1-, 2- and (e (···)) 5-min irradiation times, with $\lambda_{irr} > 250$ nm and a 1-cm cell.

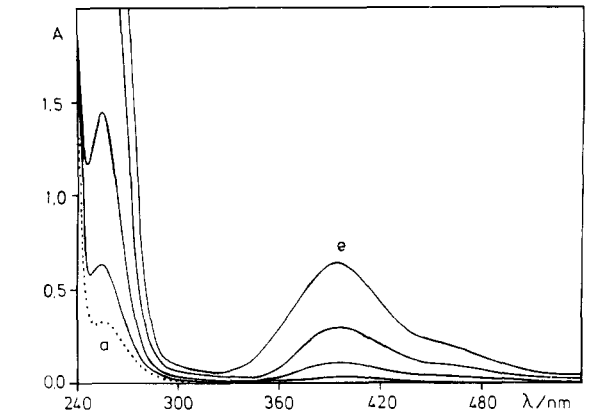

Figure 4. Spectral changes during the photolysis of 2.05×10^{-3} $[NBu_4]AuBr_2$ in CH_3CN in the presence of 10^{-2} M $[NBu_4]Br$ at (a (···)) 0-, 10-, 25-, 60-, and (e) 140-min irradiation times, with $\lambda_{irr} = 280$ nm and a 1-cm cell.

$AuCl_2^-$ was also photooxidized to $AuCl_4^-$ in aerated acetonitrile in the presence of additional chloride. In typical experiments, the concentrations were approximately 10^{-3} M $AuCl_2^-$ and 10^{-2} M Cl^-. The spectral changes were rather similar to those observed during the photolysis of $AuCl_2^-$ in CH_3CN which contained CH_2Cl_2 (Figure 2). However, the quantum yield of the photooxidation in aerated acetonitrile was quite low ($\phi = 3 \times 10^{-5}$ at $\lambda_{irr} = 254$ nm).

The reversal of the photooxidation of $AuCl_2^-$ took place when $AuCl_4^-$ was photolyzed in ethanol. The photoreduction of $AuCl_4^-$ to $AuCl_2^-$ was accompanied by the same spectral variations as those observed during the photooxidation, but in the opposite direction (Figure 3). The photoreduction could be driven to completion since the product $AuCl_2^-$ did not absorb at the irradiating wavelength (>250 nm).

Light absorption into the long-wavelength band ($\lambda_{irr} = 280$ nm) of $AuBr_2^-$ in aerated acetonitrile which contained additional Br^- led also to a photooxidation. The spectral changes (Figure 4) indicated clearly the formation of $AuBr_4^-$.[13] The quantum yield of photooxidation was $\phi = 1.4 \times 10^{-3}$ at $\lambda_{irr} = 280$ nm. Again, the spectral variations which accompanied the photooxidation could be reversed when $AuBr_4^-$ was photolyzed in ethanol (Figure 5). Since light absorption by $AuBr_2^-$ was avoided ($\lambda_{irr} > 350$ nm), a complete photoreduction to $AuBr_2^-$ was achieved.

The photolysis of $AuBr_2^-$ in deaerated acetonitrile which contained 0.02 M CH_2Cl_2 led apparently also to a photooxidation. The spectral features of the photoproduct were similar to those of $AuBr_4^-$ and $AuCl_4^-$. However, the spectral variations during the photolysis of $AuBr_2^-$ in CH_3CN/CH_2Cl_2 did not show a simple pattern, indicating a more complicated course of the photooxidation.

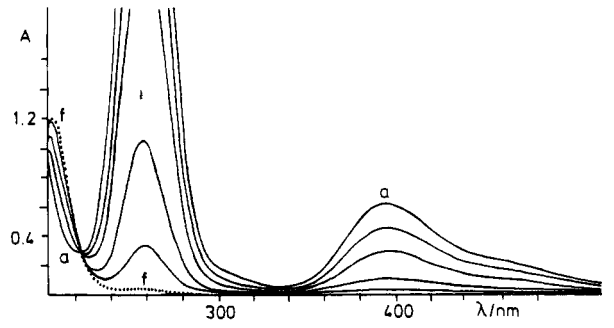

Figure 5. Spectral changes during the photolysis of 1.44×10^{-4} M $[NBu_4]$-$AuBr_4$ in ethanol at (a) 0-, 2-, 10-, 40-, 80-, and (f (···)) 160-min irradiation times, with $\lambda_{irr} = > 350$ nm and a 1-cm cell.

Discussion

Electronic Spectra. Mason et al. assigned the longest-wavelength absorptions of the linear complex anions $AuCl_2^-$ at $\lambda_{max} = 246$ nm and $AuBr_2^-$ at $\lambda_{max} = 256$ nm to the spin-allowed but parity-forbidden ds transitions $2\sigma_g^+ \rightarrow 3\sigma_g^+$.[11] Since the solution and solid-state spectra of both complexes were rather similar, the occurrence of CTTS bands was ruled out. The shorter wavelength absorptions of $AuCl_2^-$ and $AuBr_2^-$ were assigned to dp and LMCT transitions,[11] but they are not relevant to the further discussion.

We suggest that the emissions of $AuCl_2^-$ at $\lambda_{max} = 687$ nm and $AuBr_2^-$ at $\lambda_{max} = 660$ nm in butyronitrile or ethanol glasses originate from the lowest-energy ds excited triplet state $^3\Sigma_g^+$ which is not seen in absorption. The population of the antibonding $3\sigma_g^+$ (6s) orbital should weaken the Au–Cl bonds. The concomitant structural changes could explain the very low energy of the emitting state.

At room temperature, the emission spectra of $AuCl_2^-$ and $AuBr_2^-$ in the solid state are different from those in low-temperature glasses. However, in the solid state the emission may be modified by gold–gold interactions which have been shown to be important for salts of $Au(CN)_2^-$.[14]

Photochemistry. The light sensitivity of Au(I) compounds is well-known.[1a] Complexes such as $Au(N_3)_2^-$ are photolyzed to metallic gold.[7] The photoreduction of Au(I) is induced by LMCT excitation. On the contrary, we observed a photooxidation of $AuCl_2^-$ and $AuBr_2^-$. Since the photolysis is achieved by light absorption into the longest-wavelength bands, the reactive excited states are certainly of the ds type. The ds excited complexes are apparently able to transfer electrons to suitable oxidants. Oxygen and chlorinated alkanes such as CH_2Cl_2 have been used successfully as electron acceptors in one-[15,16] and two-electron photooxidations[17-19] of a variety of metal complexes. The reduction of CH_2Cl_2 leads to the release of chloride, which is also needed to complete the coordination of $AuCl_4^-$ as the stable product of the photooxidation of $AuCl_2^-$. When oxygen is used as oxidant, an addition of chloride or bromide is required for the generation of $AuCl_4^-$ or $AuBr_4^-$.

The photooxidation of $AuCl_2^-$ and $AuBr_2^-$ to $AuCl_4^-$ and $AuBr_4^-$ can be completely reversed if $AuCl_4^-$ and $AuBr_4^-$ are photolyzed in ethanol, which serves as reductant. This observation is not surprising since it is well-known that Au(III) can be photoreduced to metallic gold by a variety of reducing species.[20] Gold(I) is certainly an intermediate in these photoreactions.

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Registry No. $AuCl_2^-$, 21534-24-7; $AuBr_2^-$, 23000-74-0; CH_2Cl_2, 75-09-2; O_2, 7782-44-7; $AuCl_4^-$, 14337-12-3; $AuBr_4^-$, 14337-14-5; Cl^-, 16887-00-6; Br^-, 24959-67-9; ethanol, 64-17-5.

(14) (a) Patterson, H. H.; Roper, G.; Biscoe, J.; Ludi, A.; Blom, N. *J. Lumin.* **1984**, *31/32*, 555. (b) Markert, J. T.; Blom, N.; Roper, G.; Perregaux, A. D.; Nagasundaram, N.; Corson, M.; Nagle, J. K.; Patterson, H. H. *Chem. Phys. Lett.* **1985**, *118*, 258. (c) Nagasundaram, N.; Roper, G.; Biscoe, J.; Chai, J. W.; Patterson, H. H.; Blom, N.; Ludi, A. *Inorg. Chem.* **1986**, *25*, 2947. (d) Lacasce, J. H.; Turner, W. A.; Corson, M. R.; Dolan, P. J.; Nagle, J. K. *Chem. Phys.* **1987**, *118*, 289.

(15) Vogler, A.; Kunkely, H. *Inorg. Chem.* **1982**, *21*, 1172 and references cited therein.

(16) Gianotti, C.; Gaspard, S.; Krausz, P. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part D, p 200.

(17) (a) Vogler, A.; Kunkely, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 209. (b) Vogler, A.; Kisslinger, J.; Buchler, J. W. In *Optical Properties and Structure of Tetrapyrroles*; Blauer, G., Sund, H., Eds.; de Gruyter: Berlin, 1985; p 107.

(18) Chassot, L.; von Zelewsky, A.; Sandrini, D.; Maestri, M.; Balzani, V. *J. Am. Chem. Soc.* **1986**, *108*, 6084.

(19) (a) Vogler, A.; Paukner, A. *Inorg. Chim. Acta* **1989**, *163*, 207. (b) Vogler, A.; Nikol, H. *Pure Appl. Chem.*, in press.

(20) Reference 1a, p 273.