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Photochemistry of Nitratobis(triphenylphosphine)copper(I)

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Nitrate is an ubiquitous chemical species which also plays an important role in many biological systems. The reduction of nitrate is catalyzed by certain metalloenzymes (nitrate reductases).[1] It seems likely that the reduction occurs in the coordinated state of NO_3^-. Nitrate reduction may occur not only thermally but also as a light-induced reaction. In fact, several observations on the photochemical reduction of NO_3^- have been reported. While in most cases nitrate served simply as an electron acceptor in intermolecular excited-state electron transfer processes,[2] at least one complex, Mn(TPP)(NO_3), with TPP = 5,10,15,20-tetraphenylporphyrinate(2−), was shown to undergo photochemical reduction of coordinated nitrate although with a very low efficiency.[3] However, owing to the complicated electronic structure of this porphyrin complex, the nature of the reactive excited state is not quite clear. Accordingly, it should be of considerable interest to study the electronic spectra and the photochemistry of a simple nitrato complex which contains a redox-active metal. In this context it is quite surprising that very little is known about the participation of the nitrate ligand in electronic transitions of metal complexes.[4,5] Although NO_3^- is an oxidizing species with an empty π^* orbital at relatively low energies,[4,6,7] it has apparently not yet been considered to serve as an electron-accepting ligand for MLCT (metal to ligand charge transfer) transitions. We explored this possibility and selected the complex $Cu(PPh_3)_2NO_3$[8] as a promising candidate for an inner-sphere photoreduction of nitrate. This choice was based on the observation that copper(I) complexes with acceptor ligands such as polypyridyls have available low-energy MLCT states.[9,10] Moreover, $Cu(PPh_3)_2NO_3$ was not expected to display a complicated electronic spectrum owing to the d^{10} configuration of the metal. In addition, the present work should be facilitated by previous studies, particularly those by Kutal and his group, on the spectroscopy and photochemistry of other copper(I) triphenylphosphine complexes.[10] It was observed that such compounds do not undergo efficient intramolecular photodecompositions. A further interesting aspect of our investigation concerns the nature of the products which might be obtained by the photoreduction of nitrate. Nitric oxide, which is one of the possible products, has attracted much recent attention since it is involved in a variety of important biological processes.[11]

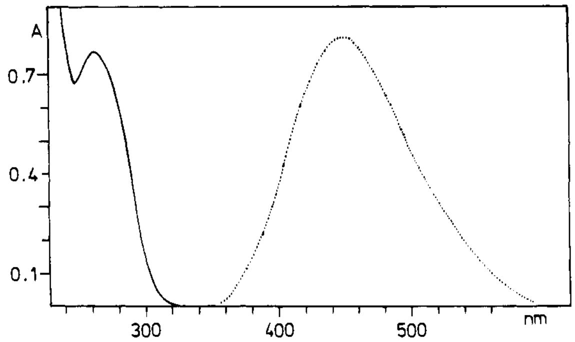

Figure 1. Electronic absorption (—) and emission (···) spectra of $Cu(PPh_3)_2NO_3$. Absorption, 4.06×10^{-5} M in acetonitrile at room temperature under argon, 1-cm cell; emission, in ethanol at room temperature, λ_{exc} = 300 nm, intensity in arbitrary units.

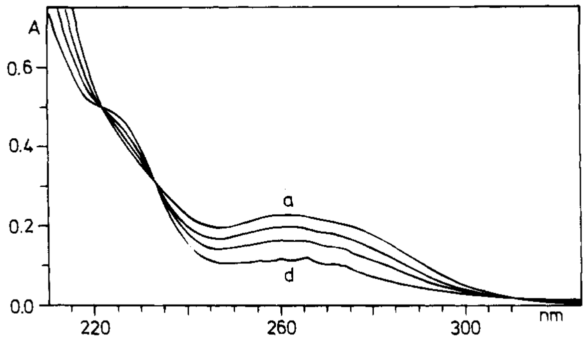

Figure 2. Spectral changes during the photolysis of 1.35×10^{-5} M $Cu(PPh_3)_2NO_3$ in acetonitrile under argon at (a) 0 and (d) 60 s irradiation time with white light (Osram HBO 100 W/2 lamp), 1-cm cell.

Solutions of $Cu(PPh_3)_2NO_3$[8] in various solvents display an absorption band at λ_{max} = 263 nm (ϵ = 18 900) with a shoulder at 275 nm (ϵ = 16 000) (Figure 1). In low-temperature glasses, $Cu(PPh_3)_2NO_3$ showed a rather intense photoluminescence at λ_{max} = 450 nm. The excitation spectrum matched the absorption spectrum quite well. At room temperature in solution, this emission was largely quenched, but a residual luminescence (ϕ = 3.4×10^{-4} at λ_{exc} = 300 nm) was still detected (Figure 1).

Solutions of $Cu(PPh_3)_2NO_3$ in CH_3CN under argon were stable in the dark but rather sensitive to UV light. The irradiation was accompanied by spectral changes (Figure 2) which clearly indicated the formation of triphenylphosphine oxide. PPh_3O was identified by its characteristic absorption features at 260, 266, 272, and 274 nm. Triphenylphosphine oxide could be also extracted with hexane from the photolyzed solution. Nitric oxide was formed as a further photolysis product. The detection of NO was achieved according to a procedure described by Hoshino and his group.[12] The photolyzed solution was added to a solution of Co(II) tetraphenylporphyrin in toluene under argon. The nitrosyl adduct of this complex, which was formed immediately, showed a typical absorption spectrum with maxima at 439 (Soret band) and 538 nm (Q band).

At later stages of the photolysis, a precipitate separated which contained PPh_3O and Cu(II). The precipitate was treated with 2 M aqueous ammonia. A clear blue solution of $[Cu(NH_3)_4]^{2+}$ (λ_{max} = 616 nm, ϵ = 63) and a solid residue of PPh_3O was

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(1) (a) Delwiche, C. C., Ed. *Dentrification, Nitrification, and Atmospheric Nitrous Oxide*; Wiley: New York, 1981. (b) Payne, W. I. *Denitrification*; Wiley: New York, 1981.

(2) (a) Frank, A. J.; Gratzel, M. *Inorg. Chem.* **1982**, *21*, 3834. (b) Halmann, M.; Tobin, J.; Zuckerman, K. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *209*, 405. (c) Kudo, A.; Domen, K.; Maruya, K.; Onishi, T. *Chem. Lett.* **1987**, 1019. (d) Willner, I.; Lapidot, N.; Riklin, A. *J. Am. Chem. Soc.* **1989**, *111*, 1883. (e) Horvath, A.; Horvath, O.; Stevenson, K. L. *J. Photochem. Photobiol. A: Chem.* **1992**, *68*, 155 and references therein.

(3) Suslick, K. S.; Watson, R. A. *Inorg. Chem.* **1991**, *30*, 912.

(4) (a) Addison, C. C.; Logan, N. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 72. (b) Addison, C. C.; Sutton, D. *Prog. Inorg. Chem.* **1967**, *8*, 195.

(5) Lever. A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984.

(6) Maria, H. J.; McDonald, J. R.; McGlynn, S. P. *J. Am. Chem. Soc.* **1973**, *95*, 1050.

(7) Wagner, I.; Strehlow, H.; Busse, G. *Z. Phys. Chem. (N.F.)* **1980**, *123*, 1 and references therein.

(8) Cotton, F. A.; Goodgame, D. M. L. *J. Chem. Soc.* **1960**, 5267. (b) Reichle, W. T. *Inorg. Chim. Acta* **1971**, *5*, 325. (c) Jardine, F. H.; Vohra, A. G.; Young, F. J. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2941.

(9) Casadonte, D. J.; McMillin, D. R. *J. Am. Chem. Soc.* **1987**, *109*, 331.

(10) Kutal, C. *Coord. Chem. Rev.* **1990**, *99*, 213.

(11) (a) Snyder, S. H. *Science* **1992**, *257*, 494. (b) Stamler, J. S.; Singel, D. J.; Loscalzo, J. *Science* **1992**, *258*, 1898. (c) Feldman, P. L.; Griffith, O. W.; Stuehr, D. J. *Chem. Eng. News* **1993**, *71* (Dec 20), 26.

(12) (a) Yamaji, M.; Hama, Y.; Miyazaki, Y.; Hoshino, M. *Inorg. Chem.* **1992**, *31*, 932. (b) Hoshino, M.; Arai, S.; Yamaji, M.; Hama, Y. *J. Phys. Chem.* **1986**, *90*, 2109.

0002-7863/95/1517-0540$09.00/0

obtained. The spectrophotometric analysis yielded a PPh_3O to Cu(II) ratio of 2.03. For a further characterization of this precipitate, it was treated with NBu_4Cl (0.1 M) in acetone. A yellow solution was formed which showed an absorption at λ_{max} = 410 nm. This band is indicative for the compound $Cu^{II}_4OCl_6(PPh_3O)_4$.[13] A large variety of related clusters of the general composition $Cu_4OCl_6L_4$ are formed under comparable conditions.[14]

The efficiency of the photolysis of $Cu(PPh_3)_2NO_3$ in CH_3CN was determined by measuring the decrease of the absorption at 263 nm, taking into account the residual absorption of the photolysis products. The quantum yield for the disappearance of $Cu(PPh_3)_2NO_3$ at room temperature was $\phi = 0.15$ at λ_{irr} = 254 nm.

The following interpretation relies on the assumption that $Cu(PPh_3)_2NO_3$ in CH_3CN remains intact and does not dissociate. In the latter case, the photoreaction could originate from the components such as PPh_3. Several observations show that a dissociation did not occur. The absorption spectrum of $Cu(PPh_3)_2NO_3$ in CH_3CN obeyed the Lambert–Beer law in the concentration range from 10^{-5} to 3×10^{-3} M. The absorption spectrum was almost independent of the solvent, including noncoordinating cyclohexane (λ_{max} = 264 nm, ϵ = 18 600; λ_{sh} = 277 nm, ϵ = 16 700). Moreover, the spectral changes during the photolysis (Figure 2) were also quite similar in CH_3CN and cyclohexane. In addition, free PPh_3 shows a luminescence at λ_{max} = 475 nm, while the emission of $Cu(PPh_3)_2NO_3$ appeared at λ_{max} = 450 nm. Previous observations led also to the conclusion that complexes of the type $Cu(PPh_3)_2X$ (X = bidentate anion) do not lose PPh_3.[8b] In the case of X = BH_4, this was confirmed independently.[15]

The complex $Cu(PPh_3)_2NO_3$ has a pseudotetrahedral structure.[16] Nitrate is coordinated as a bidentate ligand via two oxygen atoms. Which low-energy excited states are available to $Cu(PPh_3)_2NO_3$? Since Cu(I) has a d^{10} electron configuration, LF (ligand field) transitions cannot occur. The nitrate ligand can, in principle, participate in IL (intraligand), LMCT (ligand to metal charge transfer), and MLCT transitions. The lowest energy $n\pi^*$ IL transition of NO_3^- gives rise to an absorption near 300 nm.[4,6,7] Although some absorption bands of nitrate complexes were occasionally believed to be of the LMCT type,[4b,17] such transitions are not expected to occur at reasonably low energies, since NO_3^- is hardly reducing. The oxidation of nitrate to the NO_3 radical requires extremely high potentials (E° = 2.67 V).[18] On the contrary, nitrate is strongly oxidizing ($NO_3^- + 2H^+ \rightleftharpoons NO_2 + H_2O$, E° = 0.78 V)[19] and should thus function as a powerful acceptor ligand for MLCT transitions. However, the one-electron reduction of nitrate is associated with large structural changes since one N–O bond is broken. It follows that even nitrate complexes of reducing metals will not display MLCT absorptions at very long wavelength owing to the large Franck–Condon factor.

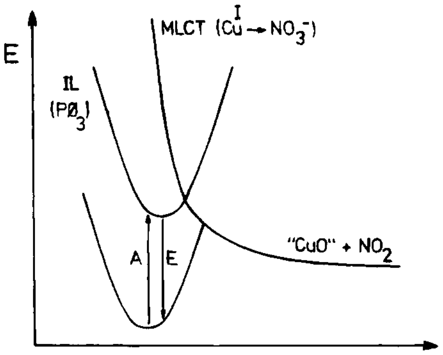

Figure 3. Potential energy surfaces for the ground and lowest energy excited states of $Cu(PPh_3)_2NO_3$.

It can be immediately recognized that the absorption and emission spectra of $Cu(PPh_3)_2NO_3$ (Figure 1) are quite similar to those of other Cu(I) triphenylphosphine complexes.[10,15,20,21] Accordingly, the lowest energy transition of the nitrate complex in absorption and emission is certainly also of the IL (PPh_3) type. However, the efficient luminescence quenching which was observed at room temperature is indicative of a facile radiationless deactivation of this IL state. In agreement with the photochemical results, we suggest that the deactivation is associated with the population of a reactive Cu(I) to NO_3^- MLCT excited state (Figure 3). It is assumed that MLCT population leads to a heterolytic breakage of a NO bond, eq 1:

$$(PPh_3)_2Cu^INO_3 \rightarrow (PPh_3)_2Cu^{II}O + NO_2 \qquad (1)$$

Since NO_2 is a powerful oxygen-transferring agent, it is not surprising that it oxidizes PPh_3 in a subsequent reaction,[22] eq 2:

$$PPh_3 + NO_2 \rightarrow PPh_3O + NO \qquad (2)$$

Finally, the photolysis is accompanied by the formation of a precipitate. Although the nature of this compound is not completely clear, it is assumed to have the composition $Cu(PPh_3O)_2O$. Similar species which tend to polymerize have been described previously.[23] The conversion of this Cu(II) oxide complex to $Cu_4OCl_6(PPh_3O)_4$ in the presence of chloride provides further support for this assumption.

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[13] Bertrand, J. A.; Kelly, J. A. *J. Am. Chem. Soc.* **1966**, *88*, 4746.

[14] (a) Bock, H.; tom Dieck, H.; Pyttlik, H.; Schnöller, M. *Z. Anorg. Allg. Chem.* **1968**, *357*, 54. (b) tom Dieck, H. *Inorg. Chim. Acta* **1973**, *7*, 397.

[15] Segers, D. P.; DeArmond, M. K.; Grutsch, P. A.; Kutal, C. *Inorg. Chem.* **1984**, *23*, 2874.

[16] Messmer, G. G.; Palenik, G. J. *Inorg. Chem.* **1969**, *8*, 2750.

[17] Addison, C. C.; Sutton, D. *J. Chem. Soc. (A)* **1966**, 1524.

[18] Jiang, P.-Y.; Katsumura, Y.; Ishigure, K.; Yoshida, Y. *Inorg. Chem.* **1992**, *31*, 5135.

[19] Milazzo, G.; Caroli, S. *Tables of Standard Electrode Potentials*; Wiley: New York, 1978; p 191.

[20] (a) Grutsch, P. A.; Kutal, C. *J. Am. Chem. Soc.* **1979**, *101*, 4228. (b) Grutsch, P. A.; Kutal, C. *J. Am. Chem. Soc.* **1977**, *99*, 6460.

[21] Fife, D. J.; Morse, K. W. *Inorg. Chem.* **1984**, *23*, 1545.

[22] Addison, C. C. *Chem. Rev.* **1980**, *80*, 21.

[23] (a) Bodek, I.; Davies, G. *Inorg. Chem.* **1978**, *17*, 1814. (b) Davies, G.; El-Sayed, M. A.; Fasano, R. E. *Inorg. Chim. Acta* **1983**, *71*, 95.