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Photochemical Redox Reactivity in Cobalt(II) Complexes

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The photochemical reactivity of the complexes $CoCl_4^{2-}$, $Co(Me_6[14]dieneN_4)^{2+}$ *and* $Co(tet\ a)^{2+}$ *was investigated by continuous and flash photolysis. Intermediates, characterized as* Cl_2^- *and a cobalt(I) complex,* $CoCl_3^{2-}$, *were generated in a photoredox reaction of* $CoCl_4^{2-}$. *The photoinduced solvolysis of the macrocyclic ligand was the only reaction mode observed with* $Co[Me_6[14]dieneN_3]^{2+}$, *while* $Co(tet\ a)^{2+}$ *was photoinert. The possible nature of the reactive charge transfer excited states is discussed.*

Introduction

The photochemical behavior exhibited by cobalt(II) complexes in glassy solutions suggests that some photoredox reactions can be expected in fluid media [1]. Indeed, the stability of the monovalent and tervalent oxidation states in cobalt ions can be used as an indication of the accessability of the charge transfer ligand to metal, CTTM, and metal to ligand, CTTL, excited states in cobalt(II) complexes [2]. The distinctive reactivity of these excited states, CTTL and CTTM, was investigated in $CoCl_4^{2-}$, $Co(Me_6[14]dieneN_4)^{2+}$ and $Co(tet\ a)^{2+}$ by means of continuous and flash photolysis [3].

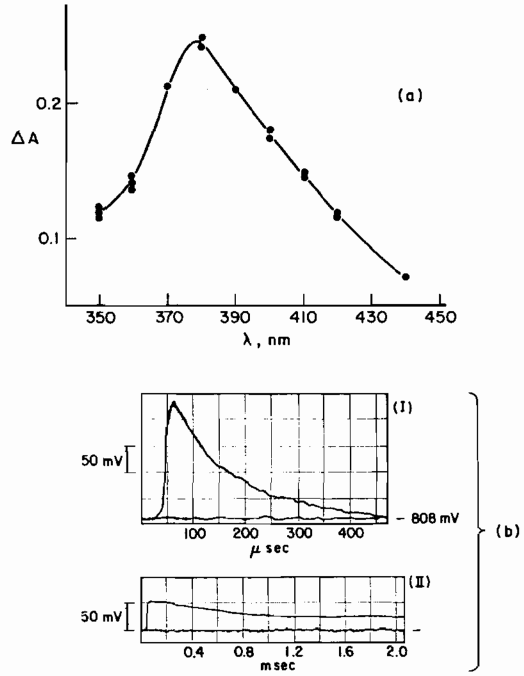

Fig. 1. (a) Absorption spectrum obtained at zero time in flash irradiations of $CoCl_4^{2-}$ in 5 M HCl (see (b) for other conditions). (b) Oscillographic trace produced in flash irradiations of $CoCl_4^{2-}$ in 5 M HCl (I) and in acid (5 M HCl) 1 M CH_3OH (II). Reactions followed at 380 nm. Flash energy: 250 joule/pulse; solutions irradiated at $\lambda \geqslant 240$ nm.

Results and Discussion

The tetrachlorocobaltate(II) complex was flash irradiated ($\lambda_{excit} \geqslant 240$ nm) in deaerated aqueous solutions which were 5–6 M in HCl [4]. These irradiations produce transient absorbances at 400–500 nm, Fig. 1. The disappearance of these absorbances obey a second order rate law with a ratio of the rate constant to the extinction coefficient, $k/\epsilon = 6.5 \times 10^5$ cm × sec^{-1} at 380 nm. In addition, the cobalt(II) complex was flash irradiated in solutions, where methanol (0.1–1.0 M) or 2-propanol (0.05–1.0 M) were used as scavengers of the intermediates. The values of the transient absorbance, measured for $\lambda = 380$ nm and at a zero reaction time, decreased with increasing alcohol concentrations. A limiting value of the transient absorbance was obtained for concentrations of the scavengers equal to or larger than 0.5 M. The decay of the limiting absorbance was observed as a slow process ($\tau_{1/2} \sim 1.6$ msec, Fig. 1b). These results show that two reactive intermediates are generated in photolysis of $CoCl_4^{2-}$. Moreover, these metastable species were assigned as Cl_2^- and a cobalt(I) complex, probably $CoCl_3^{2-}$, by means of their chemical reactivity and optical spectra [5, 6].

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In this regard, the observed photochemistry of the $\mathrm{CoCl_4^{2-}}$ may have its origin in the population of a charge transfer ligand to metal state [7], CTTM, as is indicated for the primary process in eq. 1. The fate of the primary species seems to be well described by eqs. 2 through 9:

$$\mathrm{CoCl_4^{2-}} \overset{+h\nu}{\underset{\leftsquigarrow}{\longrightarrow}} \mathrm{CTTM} \longrightarrow [\mathrm{CoCl_3^-}, \mathrm{Cl}\cdot] \qquad (1)$$

$$[\mathrm{CoCl_3^-}, \mathrm{Cl}\cdot] \longrightarrow \mathrm{CoCl_4^{2-}} \qquad (2)$$

$$[\mathrm{CoCl_3^-}, \mathrm{Cl}\cdot] \longrightarrow \mathrm{CoCl_3^-} + \mathrm{Cl}\cdot \qquad (3)$$

$$\mathrm{Cl}\cdot + \mathrm{Cl^-} \rightarrow \mathrm{Cl_2^-} \qquad (4)$$

$$\mathrm{Cl}\cdot + \mathrm{Cl}\cdot \rightarrow \mathrm{Cl_2} \qquad (5)$$

$$\mathrm{Cl_2^-} + \mathrm{Cl_2^-} \rightarrow \mathrm{Cl_2} + 2\mathrm{Cl^-} \qquad (6)$$

$$\mathrm{Cl_2^-} + \mathrm{CH_3OH} \rightarrow 2\mathrm{Cl^-} + \mathrm{H^+} + \mathrm{\dot{C}H_2OH} \qquad (7)$$

$$\mathrm{\dot{C}H_2OH} + \mathrm{\dot{C}H_2OH} \rightarrow \mathrm{CH_2O} + \mathrm{CH_3OH} \qquad (8)$$

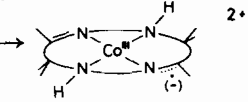
$$\mathrm{CoCl_3^{2-}} + [\mathrm{O}] \xrightarrow{\mathrm{Cl^-}} \mathrm{CoCl_4^{2-}} \qquad (9)$$

$$([\mathrm{O}] = \mathrm{Cl_2}; \mathrm{Cl_2^-}; \mathrm{Cl}\cdot; \mathrm{\dot{C}H_2OH})$$

By contrast with the behavior indicated above for $\mathrm{CoCl_4^{2-}}$, photoredox reactions were not detected with $\mathrm{Co(Me_6[14]dieneN_4)^{2+}}$ (see below) and no photochemistry at all was exhibited by $\mathrm{Co(tet\ a)^{2+}}$ for 254 nm ($I_o = 8.3 \times 10^{-4}$ Einstein/l min) or 225 nm ($I_o = 5.0 \times 10^{-5}$ Einstein/l min) irradiations in acidic aqueous solutions (10^{-1}–10^{-4} *M* $\mathrm{HClO_4}$). Indeed, flash photolysis ($\lambda_{\mathrm{excit}} > 238$ nm) of the $\mathrm{Me_6[14]dieneN_4}$ and tet a complexes in deaerated acidic ($\sim 10^{-3}$ *M* $\mathrm{HClO_4}$) or neutral solutions failed to produce transients with a half life larger than 25 μsec. However, continuous photolyses ($\lambda_{\mathrm{excit}} = 254$ nm) of $\mathrm{Co(Me_6[14]dieneN_4)^{2+}}$ in 10^{-2} *M* $\mathrm{HClO_4}$ produce a gradual decrease of the ultraviolet absorbances. Such a change of the absorption spectrum is expected if the overall photochemical process produces the aperture of the macrocyclic ligand. Indeed, $\mathrm{Co^{2+}(aq)}$ was found to be a product in this reaction. The yield of $\mathrm{Co^{2+}(aq)}$, extrapolated to zero irradiation time, was $\phi = 0.035 \pm 0.007$ for photolyses at 254 nm ($I_o = 8.2 \times 10^{-4}$ Einstein/l min). A value for the quantum yield, $\phi = 0.050 \pm 0.008$, obtained from measurements of the absorbance at 335 nm, was in good agreement with the value of the $\mathrm{Co^{2+}(aq)}$ yield (see above). Also, these results suggest that the only photochemistry exhibited by $\mathrm{Co(Me_6[14]dieneN_4)^{2+}}$ is a photoinduced solvolytic process which bears resemblance with another reported for the related $\mathrm{Cu(Me_6[14]dieneN_4)^{2+}}$ complex [8, 9]. In such a case, reactions 10 through 14 can be a good description of the photochemical transformations of the $\mathrm{Co(Me_6[14]dieneN_4)^{2+}}$.

$$\mathrm{Co(Me_6[14]dieneN_4)^{2+}} \overset{+h\nu}{\underset{\leftsquigarrow}{\longrightarrow}}$$

CTTL ⟶

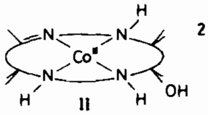


(10)

I

$$(\mathrm{I}) \longrightarrow \mathrm{Co(Me_6[14]dieneN_4)^{2+}} \qquad (11)$$

$(\mathrm{I}) \xrightarrow{\mathrm{H_3O^+}}$



(12)

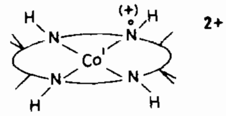
II

$$(\mathrm{II}) \longrightarrow \mathrm{Co(Me_6[14]dieneN_4)^{2+}} \qquad (13)$$

$$(\mathrm{II}) \longrightarrow \mathrm{Co^{2+}(aq)} + \text{hydrolytic products of the ligand} \qquad (14)$$

A comparison of the spectra of the cobalt(II) and copper(II) complexes shows that the energy of the charge transfer metal to ligand transitions is lower for $\mathrm{Co(Me_6[14]dieneN_4)^{2+}}$ (ν: 29.8×10^3 $\mathrm{cm^{-1}}$) [10] than for $\mathrm{Cu(Me_6[14]dieneN_4)^{2+}}$ (ν: 38.2×10^3 $\mathrm{cm^{-1}}$) [8]. Such a difference can be correlated with the tendency toward oxidation that is exhibited by each metal center, cobalt(II) and copper(II), in the field of the macrocyclic ligand [11]. In this regard, it seems likely that the reactive excited state of the cobalt(II) complex is a charge transfer metal to ligand state, CTTL, as in the case of the copper(II) complexes. Therefore, one can expect that the lack of photoreactivity exhibited by $\mathrm{Co(tet\ a)^{2+}}$ can be justified by the absence of accessible CTTL states and, in case of CTTM states, the presence of large energy barriers for redox reactions or a very favorable back electron transfer in a photogenerated Co(I)–ligand radical species, as indicated in eq. 15:

$\mathrm{Co^{II}(tet\ a)^{2+}} \overset{+h\nu}{\rightleftharpoons}$



(15)

Experimental

The complexes $[\mathrm{Co(Me_6[14]dieneN_4)}](\mathrm{ClO_4})_2$ and $[\mathrm{Co(tet\ a)}](\mathrm{ClO_4})_2$ were obtained by reported procedures [11]. The purity of these compounds was investigated by means of the ultraviolet and visible absorptions. Other materials were analytical grade and used without further purifications.

The apparatus used for continuous and flash photolysis have been described elsewhere [8, 9]. Quantum yields were measured with ferrioxalate

[12]. Periodical tests of the intensity were carried out with $Co(NH_3)_5Br^{2+}$ [13].

Cobalt(II) was analyzed with thiocyanate [14].

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3 Ligand abbreviations: $Me_6[14]dieneN_4$: 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. Tet a: 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

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