

Ligand Field Photoaquation Reactions of Trans-[Co^{III}((DO)(DOH)pn)(amine)(Cl)]PF₆ Complexes

M. Amirnasr* and H. Hadadzadeh¹

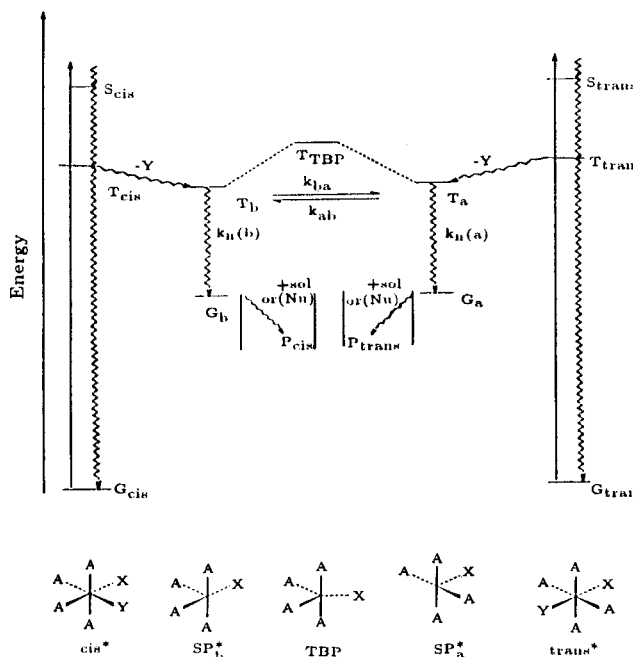
Ligand field excitation of trans-[Co^{III}((DO)(DOH)pn)(amine)(Cl)]⁺ (where (DO)(DOH)pn = N², N^{2'}-propanediylbis (2,3-butanedione-2-imine-3-oxime) and amine = morpholine(mrpln), 1; benzylamine(bzlan), 2; piperidine(pprdn), 3; and pyrrolidine (prldn), 4;), in all cases, lead to preferential amine photolabilization with complete retention of configuration. The overall photoaquation quantum yields are lower (about 1 × 10⁻³ mol/einstein) relative to those for Co^{III}(NH₃)₅Cl²⁺ (5.07 × 10⁻³), trans-[Co^{III}(trien)(H₂O)Cl]²⁺ (< 2.5 × 10⁻³) and trans-[Co^{III}(en)₂Cl₂]⁺ (1.1 × 10⁻³) which, upon irradiation in the ligand field region, undergo some photoisomerization to give a mixture of trans- and cis- photoproducts. These results are discussed in terms of the additive point ligand model (APLM), originally proposed by Vanquickenborne and Ceulemans, and the rigidity of the excited pentacoordinate intermediate, {[Co^{III}((DO)(DOH)pn)Cl]⁺}^{*}.

INTRODUCTION

Ligand field (LF) photochemistry of low spin d⁶ metal complexes has been studied extensively [1,2]. Several related models [3,4] have been proposed to explain the labilization mode and the stereochemical rearrangements often observed during the ligand field photo-substitution reaction of d⁶ transition-metal complexes. The key premise of these models can be briefly outlined as follows:

1. Photosubstitution of [MA₄XY]ⁿ⁺ occurs through selective ligand loss from the complex (dissociative process) in its lowest triplet state resulting in a five-coordinate square-pyramidal fragment which retains its spin-triplet electronic configuration.
2. The rigidity or the flexibility of the pentacoordinate intermediate (SP^{*}_{apical} or SP^{*}_{basal}) [MA₄X]ⁿ⁺ will determine the stereochemistry of the substitution reaction. Thus, specific product geometries are expected and usually observed when rearrangement is faster than triplet → singlet deactivation of the [MA₄X]ⁿ⁺ fragment (Scheme 1).

The extent of stereochemical rearrangement depends on the kinetic barrier for SP^{*}_{apical} → SP^{*}_{basal} (or



Scheme 1. G, ground state; T, triplet; S, singlet; sol, solvent; Nu, nucleophile; P, product; TBP, trigonal bipyramidal.

*. Corresponding author, Department of Chemistry, Isfahan University of Technology, Isfahan, 84154, I.R. Iran.

1. Department of Chemistry, Isfahan University of Technology, Isfahan, 84154, I.R. Iran.

SP^{*}_{basal} → SP^{*}_{apical}) isomerization. This kinetic barrier is of mainly two origins: (i) Electronic, which is either due to the nature of the central metal ion or the relative

electron donating ability of the ligands in $[MA_4X]^{n+}$ and (ii) Steric, which depends on the structural rigidity or flexibility of the remaining ligands on the metal ion that introduces stereochemical constraints upon isomerization processes. The electronic effects have been treated in detail [3-8], however, there are few reports on the role played by the structure of the remaining ligands [9].

In this paper, the result of the ligand field photolysis of $\text{trans-[Co}^{III}(\text{DO})(\text{DOH})\text{pn}(\text{amine})(\text{Cl})\text{PF}_6$ is reported. These results are interpreted in terms of the APLM and the rigidity of the equatorial ligand $(\text{DO})(\text{DOH})\text{pn}$.

EXPERIMENTAL SECTION

Materials

Reagent grade materials and doubly distilled water were used through out the experiments. The $\text{trans-[Co}(\text{DO})(\text{DOH})\text{pn}(\text{amine})(\text{Cl})\text{PF}_6$ complexes, (1-4), were prepared as described in [10]. The electronic absorption spectral data for all complexes reported are listed in Table 1.

Photolysis Procedures

The photolyses were carried out at 25°C in acidic solutions (pH = 3, HClO_4) with cobalt complexes in the concentration range of $5 \times 10^{-4} - 1.6 \times 10^{-3}\text{M}$ in 1-cm quartz rectangular cells. To dissolve the complexes, and/or to reduce thermal hydrolysis, photolysis solutions were prepared in water-acetone or water-ethanol (3% v/v) mixtures. Three milliliter quantities of test solutions were vigorously stirred and irradiated

during the photolysis with the aid of a 2×6 mm Teflon-coated magnetic stir bar. Light at 436 or 450 nm was selected from a high-pressure mercury lamp (Osram-HBO 200 W) using interference filters. Light intensities were determined by ferrioxalate actinometry and approximated as 10^{-8} einstein s^{-1} . Quantum yields from spectral changes were calculated by plotting incremental quantum yields vs percent reaction and extrapolating to 0% reaction intercept. The initial quantum yields, thus calculated, are independent of perturbations (secondary photoreactions, innerfiltering, etc.) possibly introduced by products.

Instrumentation

All absorption spectra and optical density measurements used to determine quantum yields were recorded on a Shimadzu UV-Vis 240 spectrophotometer. Infrared spectra were obtained as KBr pellets using a Shimadzu 435 IR spectrophotometer. A pH-meter calibrated against commercially available buffer solutions was used to adjust the pH of the photolysis solutions.

RESULTS AND DISCUSSION

LF irradiation of $\text{trans-[Co}^{III}(\text{DO})(\text{DOH})\text{pn}(\text{amine})(\text{Cl})\text{PF}_6$ complexes, 1-4, in an acidic solution (pH = 3.0) leads to the labilization of the amine as the principle reaction pathway. The quantum yields are calculated on the basis of electronic absorption spectral changes and are presented in Table 1. Irradiation wavelengths of 436 and 450 nm correspond to population of the lowest spin allowed ligand field excited state derived from the ${}^1T_{1g} \leftarrow {}^1A_{1g}$ transition in octahedral

Table 1. Spectra and photolysis data for $\text{trans-[Co}^{III}(\text{DO})(\text{DOH})\text{pn}(\text{L})(\text{Cl})^+$ complexes in water-acetone solution (3% v/v)^a.

Spectra		Photochemistry ^a					Stereo- ^f chem	Ref.
Complex (L)	LF ₁ $\lambda_{\text{max}}(\epsilon)^b$	$\lambda_{\text{irr}}(\text{nm})$	$\Phi_L^c \times 10^4$	$\lambda_{\text{ip}}(\text{nm})^d$	P.I. ^e			
1. (mrpln)	495(707)	450	$12.2 \pm 1.5(3)$	470	n.fl.	100% trans	PW	
		436	$3.3 \pm 0.3(3)$	470	n.fl.	100% trans	PW	
2. (bzlan)	489(656)	450	$17.8 \pm 2.1(3)$	450	n.fl.	100% trans	PW	
		436	$9.2 \pm 0.4(3)$	450	n.fl.	100% trans	PW	
3. (pprdn)	481(631)	450	$11.1 \pm 1.3(3)$	445	n.fl.	100% trans	PW	
		436	$7.4 \pm 0.8(3)$	445	n.fl.	100% trans	PW	
4. (prldn)	475(623)	450	$5.1 \pm 0.6(3)$	437	n.fl.	100% trans	PW	
		436	$3.0 \pm 0.5(3)$	437	n.fl.	100% trans	PW	
$\text{CoA}_5\text{Cl}^{2+}$	534	488	$50.7 \pm 1.3(3)$	(NH_3)	fl.		9	
			$17.1 \pm 1.2(3)$	(Cl)	fl.		9	
$\text{trans-[Co}(\text{trien})(\text{H}_2\text{O})\text{Cl}]^{2+}$		488	< 25		fl.		8	
$\text{trans-[Co}(\text{en})_2\text{Cl}_2]^+$	617	488	$10.7 \pm 0.3(3)$	(Cl)	fl.		9	
$\text{trans-[Co}(\text{cyclam})\text{Cl}_2]^+$	637	488	$4.0 \pm 0.1(7)$	(Cl)	n.fl.		9	

^a at 25°C in dilute acid solution, pH \cong 3.0. ^b λ_{max} in nm: ϵ in L/mol cm. ^c Quantum yields in mol/einstein. ^d λ (isosbestic point). ^e P.I. = Pentacoordinate intermediate. fl = fluxional, nfl = non-fluxional. ^f Structure of the photoproducts. PW = Present work.

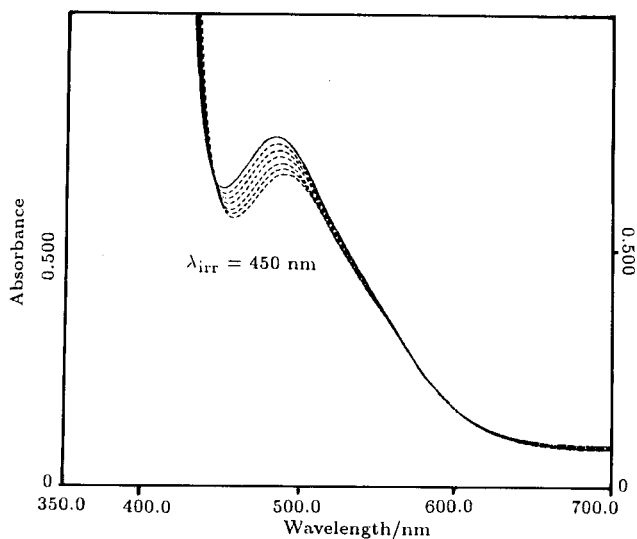


Figure 1. Photolysis of $\text{trans-}[\text{Co}^{\text{III}}((\text{DO})(\text{DOH})(\text{pprdn})(\text{Cl}))]^+$ at 450 nm, 25°C, pH = 3 and $ca\ 1.5 \times 10^{-3}$ M complex, $\Delta t = 30$ minutes.

geometry. Photolyses of the complexes 1-4 led to spectral changes consistent with the replacement of the trans amine ligand by H_2O (Figure 1), to produce $\text{trans-}[\text{Co}^{\text{III}}((\text{DO})(\text{DOH})(\text{pn})(\text{H}_2\text{O})(\text{Cl}))]^+$. Good isosbestic points were maintained for more than 20% of the reactions (Figure 1, Table 1), indicating the absence of spectrally significant secondary photoreactions. (Thermal hydrolysis of the complexes was suppressed under the experimental conditions and showed not to be significant). A lower quantum yield for $\lambda_{\text{irr}} = 436$ nm is probably due to the fact that the LF states immediately above the ${}^3\text{E}({}^3\text{T}_{1g})$ and ${}^1\text{E}({}^1\text{T}_{1g})$ states oppose the labilization and, therefore, the quantum yield is lower for the higher energy irradiations.

Labilization Mode and Stereochemistry

The development of theoretical models to predict the specific labilization site has been stimulated by the empirical rules of Adamson [5], which were later modified by the I^* model [3]. This model applies the angular overlap approximation to calculate orbital populations and to generate a set of parameters, $\text{I}^*(\text{M} - \text{L})$, which are considered to be roughly proportional to metal-ligand bond strengths in the photoactive state. According to this model, the ligand with the lowest value of $\text{I}^*(\text{M} - \text{L})$ will be the one preferentially labilized. In general, $\text{I}^*(\text{M} - \text{L})$ is evaluated as follows:

- (a) The lowest ligand field excited state is determined for the complex. For example, in the present work, assuming an effective D_{4h} holohedron symmetry for the trans-complexes under consideration (with a low spin d^6 configuration and $10 \bar{\text{D}}q_{\text{ax}} < 10 \bar{\text{D}}q_{\text{eq}}$) the photoactive state is ${}^3\text{E}_a$ [11].

- (b) The relevant state functions are written and modified by configuration interaction. The state function for ${}^3\text{E}_a$ after configuration interaction [11] is:

$$\begin{aligned} \Psi[{}^3\text{E}_a({}^3\text{T}_{1g})] &= [1/(1+c^2)^{1/2}] \\ & \{ \{ (3^{1/2} + c)/2 \} \{ (d_{xy})^2 (d_{xz})^2 (d_{yz}) (d_z^2) \} \\ & + \{ (1 - 3^{1/2}c)/2 \} \{ (d_{xy})^2 (d_{xz})^2 (d_{yz}) (d_{x^2-y^2}) \} \}. \end{aligned} \quad (1)$$

The fraction of d_z^2 in ${}^3\text{E}_a$, X , is given [3] by:

$$X = [1/(1+c^2)] [(3^{1/2} + c)/2]^2, \quad (2)$$

where c is defined [11] as:

$${}^3c = (3)^{1/2} (5Dt - 4Ds) / (32B + 10Dt + 8Ds). \quad (3)$$

Substituting for Dt and Ds [12]:

$$Dt = 2/35(3\sigma_{\text{eq}} - 3\sigma_{\text{ax}} - 4\pi_{\text{eq}} + 4\pi_{\text{ax}}),$$

$$Ds = 2/7(\sigma_{\text{eq}} - \sigma_{\text{ax}} + \pi_{\text{eq}} - \pi_{\text{ax}}),$$

the mixing parameter 3c can be expressed in terms of the angular overlap parameters, σ and π ,

$${}^3c = (3)^{1/2} \{ \{ (\bar{\sigma}_{\text{ax}} - \bar{\sigma}_{\text{eq}}) + 8(\bar{\pi}_{\text{ax}} - \bar{\pi}_{\text{eq}}) \} \} / \{ 14 [8B - (\bar{\sigma}_{\text{ax}} - \bar{\sigma}_{\text{eq}})] \}. \quad (4)$$

- (c) The $\text{I}^*(\text{M} - \text{L})$ expressions appropriate for a particular state function (Equation 1 for the present case) are written in terms of the angular overlap parameters, σ and π . $\text{I}^*(\text{M} - \text{L})$ is then calculated for specific ligands using the appropriate values of σ and π parameters.

The $\text{I}^*(\text{M} - \text{L})$ expressions for the present work are determined using the expressions presented in Table I of [3]:

$$\begin{aligned} \text{I}^*(\text{M} - \text{L}_{\text{ax}}) &= X(\sigma_{\text{ax}} + \pi_{\text{ax}}) + (1 - X)(2\sigma_{\text{ax}} + \pi_{\text{ax}}) \\ &= (2 - X)\sigma_{\text{ax}} + \pi_{\text{ax}}, \end{aligned} \quad (5)$$

$$\begin{aligned} \text{I}^*(\text{M} - \text{L}_{\text{eq}}) &= X[(7/4)\sigma_{\text{eq}} + (1/2)\pi_{\text{eq}}] \\ & + (1 - X)[(5/4)\sigma_{\text{eq}} + (1/2)\pi_{\text{eq}}] \\ &= (1/4)(5 + 2X)\sigma_{\text{eq}} + (1/2)\pi_{\text{eq}}. \end{aligned} \quad (6)$$

Using Equations 5 and 6 and the appropriate parameters from Table 2, $\text{I}^*(\text{M} - \text{L}_{\text{ax}})$ and $\text{I}^*(\text{M} - \text{L}_{\text{eq}})$

Table 2. Ligand field and angular overlap parameters (cm^{-1}) for different ligands.

Ligand	Dq	σ_L	π_L	Ref.
Cl	1371	6290	1290	10
NH ₃ , en, trien	2155	7183	0	3
mrpln	1919	6395	0	10
bzlan	1988	6627	0	10
pprdn	2039	6797	0	10
prldn	2123	7076	0	10
(DO)(DOH)pn	2780	7933	-1000	PW
TIM	2780	7933	-1000	13

PW = Present work.

can be calculated. As an example, consider $\text{trans}[\text{Co}^{\text{III}}((\text{DO})(\text{DOH})\text{pn})(\text{mrpln})(\text{Cl})]^+$:

$$\begin{aligned}\overline{Dq}_{\text{ax}} &= (1/2)[Dq(\text{mrpln}) + Dq(\text{Cl})] \\ &= (1/2)[1919 + 1371] \\ &= 1645 \text{ cm}^{-1},\end{aligned}$$

$$\begin{aligned}\overline{Dq}_{\text{eq}} &= Dq((\text{DO})(\text{DOH})\text{pn}) \cong Dq(\text{TIM}) \\ &= 2780 \text{ cm}^{-1}.\end{aligned}$$

TIM [13] is a tetradentate macrocyclic amine ligand with a structure close to that of (DO)(DOH)pn. Since $\overline{Dq}_{\text{ax}} < \overline{Dq}_{\text{eq}}$, the photoactive state is considered to be ${}^3E_g({}^3T_{1g})$.

Using the appropriate values for $\overline{\sigma}_{\text{ax}}$, $\overline{\sigma}_{\text{eq}}$, $\overline{\pi}_{\text{ax}}$, and $\overline{\pi}_{\text{eq}}$:

$$\begin{aligned}\overline{\sigma}_{\text{ax}} &= (1/2)(\sigma_{\text{mrpln}} + \sigma_{\text{Cl}}) & \overline{\pi}_{\text{ax}} &= (1/2)(\pi_{\text{mrpln}} + \pi_{\text{Cl}}) \\ &= (1/2)(6395 + 6290) & &= (1/2)(0 + 1290) \\ &= 6343 \text{ cm}^{-1}, & &= 645 \text{ cm}^{-1},\end{aligned}$$

$$\overline{\sigma}_{\text{eq}} \cong \sigma_{\text{TIM}} = 7933 \text{ cm}^{-1}, \quad \overline{\pi}_{\text{eq}} \cong \pi_{\text{TIM}} = -1000 \text{ cm}^{-1},$$

(the values of $\overline{\sigma}_{\text{eq}}$ and $\overline{\pi}_{\text{eq}}$ were approximated using spectral data for $\text{trans}[\text{Co}(\text{TIM})\text{Cl}_2]^+$ and $\text{trans}[\text{Co}(\text{DIM})\text{Cl}_2]^+$ [13]) and letting $B = 700 \text{ cm}^{-1}$ for

Co^{3+} , the fraction of $d_z^2(X)$ and $d_{x^2-y^2}(1-X)$ are calculated to be 0.894 and 0.106, respectively. Using Equations 5 and 6, one obtains:

$$I^*(M - \text{mrpln}) = (2 - 0.894)(6395) = 7073 \text{ cm}^{-1} \quad (7a)$$

$$\begin{aligned}I^*(M - \text{Cl}) &= (2 - 0.894)(6290) + 1290 \\ &= 8248 \text{ cm}^{-1}\end{aligned} \quad (7b)$$

$$\begin{aligned}I^*(M - L_{\text{eq}}) &= (1/4)(5 + 1.788)(7933) - 500 \\ &= 12962 \text{ cm}^{-1}.\end{aligned} \quad (7c)$$

The approximate values of $I^*(M - L)$ for other complexes are presented in Table 3. In all cases, the axial amine ligand shows the lowest value of $I^*(M - L)$ and, therefore, is predicted to be preferentially labilized. This is in accord with the experimental results obtained in the photolyses of these complexes. The shift to the longer wavelength of the first ligand field band (Figure 1) indicates that the stronger ligand, amine, is replaced by a weaker ligand, H₂O. A comparison between the IR spectra of photoproducts and that of the corresponding $\text{trans}[\text{Co}^{\text{III}}((\text{DO})(\text{DOH})\text{pn})(\text{H}_2\text{O})(\text{Cl})]^+$ complex, prepared by direct synthesis (Figure 2), shows that the amine ligands are released in all cases. The observed mode of labilization is consistent with the nature of the two axial ligands (Cl and amine) and the softer character of the Co(III) ion, being imparted by the electron rich equatorial ligand. The ability to labilize the trans group to halogens in complexes of softer d^6 metal ions such as Rh(III) and Ir(III) has been demonstrated [14,15]. In $\text{trans}[\text{Rh}(\text{en})_2(\text{NH}_3)\text{X}]^{2+}$, for example, the ease of labilization is the largest for the iodo ligand and decreases as $\text{I} > \text{Br} > \text{Cl}$ ($X = \text{I}$ $\Phi(\text{NH}_3) = 0.60$, $X = \text{Br}$ $\Phi(\text{NH}_3) = 0.16$ and $X = \text{Cl}$ $\Phi(\text{NH}_3) = 10^{-3}$ mol/einstein [6]). Therefore, it seems reasonable to assume that the more polarizable triplet excited state of Co(III) (with its new additional soft character imparted by L_{eq}) is more strongly bonded to the Cl ligand than the amine, resulting in photolabilization of the amine ligands.

Table 3. $I^*(M - L)$ and the leaving ligand in $\text{trans}[\text{Co}^{\text{III}}((\text{DO})(\text{DOH})\text{pn})(\text{amine})\text{Cl}]^+$ complexes.

Complex	$I^*(M - L)$ values (in cm^{-1})			X	Leaving L (predicted)	Leaving L (obsd.)	Ref.
	$I^*(M - \text{Cl})$	$I^*(M - N_{\text{ax}})$	$I^*(M - N_{\text{eq}})$				
$\text{Co}(\text{NH}_3)_5\text{Cl}^+$	7265	7973	12175	0.86	Cl	(dominant) Cl, NH ₃	3
$\text{trans}[\text{A}(\text{mrpln})\text{Cl}]^+$	8248	7073	12694	0.894	mrpln	mrpln	PW
$\text{trans}[\text{A}(\text{bzlan})\text{Cl}]^+$	8210	7291	12985	0.900	bzlan	bzlan	PW
$\text{trans}[\text{A}(\text{pprdn})\text{Cl}]^+$	8196	7463	12994	0.902	pprdn	pprdn	PW
$\text{trans}[\text{A}(\text{prldn})\text{Cl}]^+$	8172	7742	13010	0.906	prldn	prldn	PW

PW = Present work. A = $\text{Co}^{\text{III}}(\text{DO})(\text{DOH})\text{pn}$.

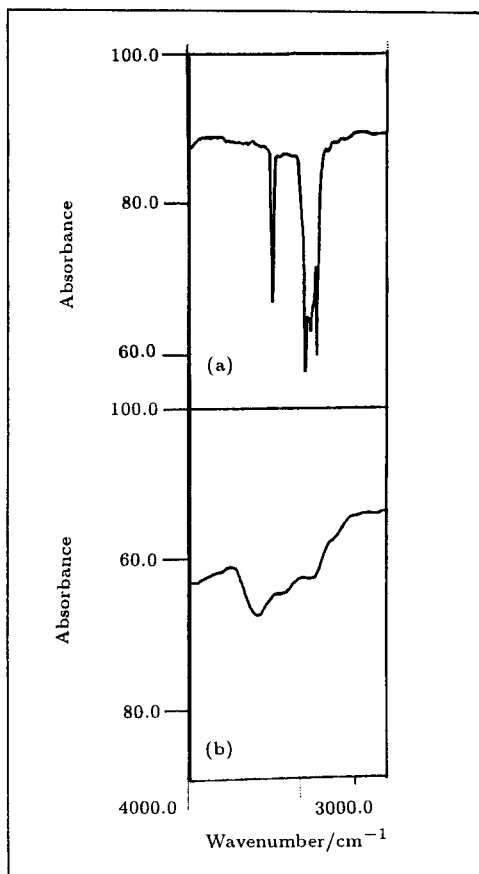
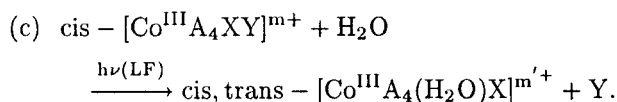
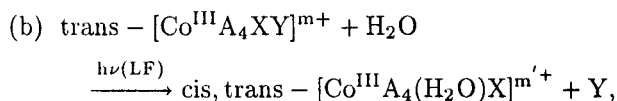
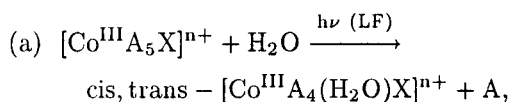


Figure 2. IR spectra of $\text{trans-}[\text{Co}^{\text{III}}((\text{DO})(\text{DOH})(\text{pprdn})(\text{Cl}))^{\text{+}}]$ in the amine region. (a) before and (b) after prolonged photolysis.

From a stereochemical point of view, the photoactivity of low spin $[\text{Co}^{\text{III}}\text{A}_5\text{X}]^{\text{n}+}$ and $[\text{Co}^{\text{III}}\text{A}_4\text{XY}]^{\text{m}+}$ can be presented by the following reactions [7]:



X and Y are acido ligands and $\text{A}_4 = (\text{NH}_3)_4$ or $(\text{en})_2$. When $\text{X} = \text{Y} = \text{Cl}$ and $\text{A}_4 = (\text{en})_2$, the same product mixture of 70% trans and 30% cis is obtained for reactions (b) and (c). The product stereochemistries are principally interpreted in terms of the comparative energies of the resulting five-coordinate square-pyramidal fragments, $[\text{Co}^{\text{III}}\text{A}_4\text{X}]^{\text{n}+}$, in which X appears apical for trans starting materials (SP_a^*) and basal for cis starting materials (SP_b^*) (Scheme 1). The energy barrier between (SP_a^*) and (SP_b^*)

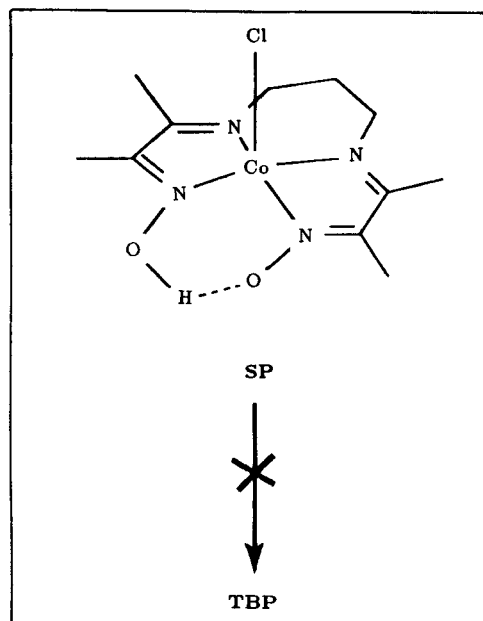


Figure 3. The non-fluxional pentacoordinate intermediate.

is low enough that rearrangement ($\text{SP}_a^* \leftrightarrow \text{SP}_b^*$, with a thermodynamic preference for SP_a^*) occurs faster than intersystem crossing (triplet \rightarrow singlet). This observation would be consistent with the SP^* species being sufficiently long lived to reach equilibrium; i.e. $k_{ba}, k_{ab} \gg k_n(a), k_n(b)$. For the systems described in this work the rigid $[\text{Co}^{\text{III}}\text{L}_{\text{eq}}\text{Cl}]^{\text{+}}$ five-coordinate fragment, with Cl in the apical position (Figure 3), is not capable of apical \rightarrow basal rearrangement; i.e., k_{ab} should be smaller while nonradiative deactivation, $k_n(a)$, should be larger. This rigidity, which is imparted by the structure of $\text{L}_{\text{eq}} = (\text{DO})(\text{DOH})\text{pn}$, leads to the stereoretentive aquation of amine ligands to give $\text{trans-}[\text{Co}^{\text{III}}((\text{DO})(\text{DOH})\text{pn})(\text{H}_2\text{O})\text{Cl}]^{\text{+}}$ with lower quantum yields relative to $[\text{CoA}_4\text{XY}]^{\text{m}+}$ complexes having stereomobile intermediates (Table 1).

CONCLUSIONS

Theoretical predictions based on the evaluation of $I^*(M-L)$ are in agreement with the observed mode of labilization. In the presence of strongly sterically constraining ligands such as cyclam [9] or $(\text{DO})(\text{DOH})\text{pn}$, the pentacoordinate triplet species, (SP_a^*), will not isomerize but deactivate to give the spin-paired (ground state) intermediates (SP_a), which are then trapped immediately by water molecules and yield trans-products.

REFERENCES

- Zinato, E., *Concepts of Inorganic Photochemistry*, Adamson, A.W. and Fleischauer, P.D., Eds., Wiley Interscience, N.Y., USA, Chapter 4 (1975).

- Ford, P.C., Hintze, R.E. and Petersen, J.D., *Concepts of Inorganic Photochemistry*, Adamson, A.W. and Fleischauer, P.D., Eds., Wiley Interscience, N.Y., USA, Chapter 5 (1975).
- Vanquickenborne, L.G., and Ceulemans, A. "On the photochemical substitution reactions of hexacoordinated transition metal complexes", *J. Am. Chem. Soc.*, **99**, pp 2208-2214 (1977).
- Strauss, D. and Ford, P.C. "Concomitant photoaquation-photoisomerization of cis-dichlorotetraamminerhodium(III), cis-[Rh(NH₃)₄Cl₂]⁺", *J. Chem. Soc. Chem. Commun.*, pp 194-195 (1977).
- Adamson, A.W. "Whither inorganic photochemistry? A parochial view", *Pure. Appl. Chem.*, **51**, pp 313-329 (1979).
- Clark, S.F. and Petersen, J.D. "Stereochemistry and quantum yield for the ligand field photolysis of rhodium(III) complexes. 3. cis- and trans-Rh(en)₂XIⁿ⁺", *Inorg. Chem.*, **19**, pp 2917-2921 (1980).
- Vanquickenborne, L.G. and Ceuleman, A., "Photo-stereochemistry and electronic selection rules in strong-field d⁶ transition-metal complexes", *Inorg. Chem.*, **17**, pp 2730-2736 (1978).
- Sheridan, P.S. and Adamson, A.W. "Photochemistry of coordination compounds. XIV. Triethylenetetramine and β, β', β'', triaminotriethylamine complexes of cobalt (III)", *Inorg. Chem.*, **13**, pp 2482-2489 (1974).
- Pribush, R., Poon, C.K., Bruce, C.M. and Adamson, A.W. "Photochemistry of complex ions. XII. Photochemistry of cobalt(III) acidoammines", *J. Am. Chem. Soc.*, **96**, pp 3027-3032 (1974).
- Amirnasr, M. and Hadadzadeh, H. "Synthesis and characterization of amine (chloro)cobaloxime derivatives. Approximate values of the angular overlap parameter, σ, for the coordinated amines", *J. Sci. I.R. Iran*, **7**, pp 164-168 (1996).
- Incorvia, M.J. and Zink, J.I. "A ligand field interpretation of quantum yields of photosolvation of d⁶ complexes", *Inorg. Chem.*, **13**, pp 2489-2494 (1974).
- Lever, A.B.P., *Inorganic Electronic Spectroscopy*, 2nd Ed., Elsevier, Amsterdam, p 70 (1984).
- Jackels, S.C., Farmery, K., Barefield, E.K., Rose, N.J., and Busch, D.H. "Some tetragonal cobalt(III) complexes containing tetradentate macrocyclic amine ligands with different degrees of unsaturation", *Inorg. Chem.*, **11**, pp 2893-2901 (1972).
- Balzani, V. and Carassiti, V., *Photochemistry of Coordination Compounds*, Academic Press, N.Y. (1970).
- Kelly, T.L. and Endicott, J.F. "Photochemistry of iodoammine complexes of rhodium(III). A case for inefficient internal conversion between charge-transfer and d-d excited states.", *J. Am. Chem. Soc.*, **94**, pp 1797-1804 (1972).