ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2010, Vol. 36, No. 12, pp. 913–917. © Pleiades Publishing, Ltd., 2010.
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Metal Exchange between Cadmium Complexes with Natural Porphyrins and Cobalt Chloride in Ethanol

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Received March 3, 2010

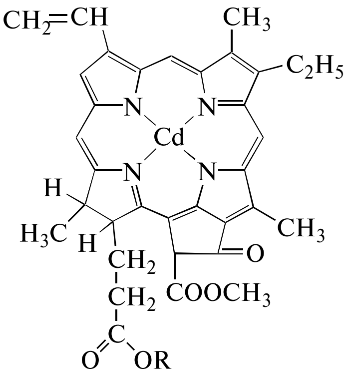
Abstract—Metal exchange reactions between Cd chlorophyll (a) or Cd pheophorbide (a) and cobalt chloride in ethanol were studied by spectrophotometry. The order of the reaction was determined. It was found that the metal exchange follows the stoichiometric mechanism.

DOI: 10.1134/S1070328410120080

All manifestations of life in the Earth are associated with photosynthetic function of plants because of the presence of a porphyrin-based compound. Metal exchange is an essential reaction of porphyrin complexes [1]. Despite much research concerned with transmetalation of metal porphyrins, the kinetics and mechanisms of these reactions and the role of the solvent in them still remain unclear. Accumulation of experimental evidence in this area is of current interest since an exchange of metal ions between complexes is used in isotope exchange [2], in the study of the stability order of complexes with those ligands that cannot be characterized by stability constants [3], in the design of metal clusters [4] and organometallic compounds [5], in the synthesis of coordination compounds [6], and in medicine as antidotes against cyanide derivatives [7]. To determine the distinctive features of metal exchange between cadmium complexes with porphyrins of the chlorophyll group and Co(II) salts in organic solvents and reveal the effects of the solvent and the metal salt on the exchange rate, we studied transmetalation reactions of Cd chlorophyll (a) (CdChl(a)) and Cd pheophorbide (a) (CdPhe(a)) with cobalt chloride in ethanol. The reaction equation has the form

$$\mathrm{CdP} + \mathrm{CoCl_2(Solv)_4} \rightleftarrows \mathrm{CoP} + \mathrm{CdCl_2(Solv)_4}, \quad (1)$$

where CdP is CdChl(a) or CdPhe(a) and Solv is ethanol.



$R = C_{20}H_{39}$ for CdChl(a) and $R = H$ for CdPhe(a)

EXPERIMENTAL

The starting reagents CdChl(a) or CdPhe(a) were prepared and purified as described in [8]. Ethanol was purified as described in [9].

Metal exchange reactions (1) for the porphyrin complexes were studied by spectrophotometry. Kinetic experiments were carried out as follows. A solution of cadmium porphyrinate (CdP) and $CoCl_2$ with a known concentration was placed in a temperature-controlled cell of an SF-26 spectrophotometer at a given temperature. The optical density of the solution at the absorption peak wavelength ($\lambda_{\max}$ = 660.4 nm for CdChl(a) and 655.2 nm for CdPhe(a)) was measured at regular intervals. The temperature range was 298–318 K; the concentration of the salt was $(2.09–3.92) \times 10^{-2}$ and $(1.23–2.3) \times 10^{-3}$ mol/l for CdChl(a) and CdPhe(a), respectively.

Table 1. Rates of the exchange of Cd^{2+} for Co^{2+} in the complex CdPhe(a) in ethanol ($c^{0}_{\mathrm{CdPhe(a)}} = 2.3 \times 10^{-5}$ mol/l)

$c_{\mathrm{CoCl_2}} \times 10^3$, mol/l	T, K	$k_{\mathrm{eff}} \times 10^3$, s^{-1}	k_v, l/(mol s)	E_a, kJ/mol	$\Delta S^{\neq}$, J/(mol K)
2.30	298	1.4 ± 0.09	0.61	91 ± 5	–4 ± 18
	308	4.3 ± 0.22	1.87		
	318	14 ± 0.94	6.09		
1.99	298	1.2 ± 0.04	0.610	91 ± 7	–4 ± 23
	308	3.6 ± 0.28	1.81		
	318	12 ± 0.26	6.03		
1.53	298	0.99 ± 0.61	0.64	89 ± 12	–14 ± 41
	308	2.7 ± 0.10	1.76		
	318	9.4 ± 0.24	6.14		
1.23	298	0.73 ± 0.13	0.59	91 ± 7	–6 ± 25
	308	2.2 ± 0.16	1.79		
	318	7.4 ± 0.19	6.02		

The current concentrations of CdChl(a) and CdPhe(a) were calculated by the equation

$$c = c_0(A_\tau - A_\infty)/(A_0 - A_\infty), \qquad (2)$$

where A_0, A_τ, and A_∞ are the initial optical density of the solution, its density at the instant τ, and the final density, respectively; c_0 and c are the initial and current concentrations of the Cd(II) complexes, respectively.

The effective rate constants $\boldsymbol{k}_{\mathbf{eff}}$ of reaction (1) were calculated by the equation

$$-\mathrm{d}c_{\mathrm{CdP}}/\mathrm{d}\tau = k_{\mathrm{eff}}c_{\mathrm{CdP}}. \qquad (3)$$

The energy of activation $\boldsymbol{E_a}$ was calculated by the Arrhenius equation:

$$E_a = 19.1\frac{T_1T_2}{T_2 - T_1}\lg\frac{k_2}{k_1}, \qquad (4)$$

where k_1 and k_2 are the true rate constants $k_v = k_{\mathrm{eff}}/c_{\mathrm{salt}}$.

The changes in the entropy of activation $\boldsymbol{\Delta S^{\neq}}$ were calculated by an equation from the absolute reaction rate theory [10]:

$$\Delta S^{\neq} = 8.314\ln k_v^{298} + \frac{E_a}{298} - 253.22. \qquad (5)$$

Experimental data are given in Tables 1 and 2. The metal exchange reaction of CdPhe(a) with cobalt chloride in ethanol (Fig. 1) gave the more stable complex CoPhe(a) (its absorption bands experience hypsochromic shifts). This conclusion follows from the satisfaction of the condition for the spectroscopic criterion of the stability of metal porphyrins [11].

RESULTS AND DISCUSSION

The concepts of chemical bonding in metal porphyrins, phthalocyanines, and chlorophyll [11] and the concepts of the properties of solvate complexes of *d* metals [12], which have been developed in the study of the formation and dissociation of metal porphyrins [8, 11–14], help to explain unsuccessful results in the transmetalation of stable porphyrin complexes. That is why later investigations into cation exchange have been focused on complexes with a considerable ionic character of the M–N bonds [15–18]. Such are

Table 2. Rates of the exchange of Cd^{2+} for Co^{2+} in the complex CdChl(a) in ethanol ($c^0_{CdChl(a)} = 2.3 \times 10^{-5}$ mol/l)

$c_{CoCl_2} \times 10^2$, mol/l	T, K	$k_{eff} \times 10^3$, s^{-1}	k_v, l/(mol s)	E_a, kJ/mol	$\Delta S^{\neq}$, J/(mol K)
3.92	298	3.8 ± 0.19	0.097	18 ± 4	–201 ± 16
	308	5.0 ± 0.63	0.128		
	318	6.6 ± 0.46	0.168		
3.39	298	3.4 ± 0.20	0.100	18 ± 4	–201 ± 14
	308	4.5 ± 0.41	0.133		
	318	5.9 ± 0.17	0.174		
2.61	298	2.6 ± 0.16	0.099	18 ± 4	–201 ± 19
	308	3.4 ± 0.37	0.130		
	318	4.5 ± 0.27	0.172		
2.09	298	2.04 ± 0.12	0.096	18 ± 4	–201 ± 17
	308	2.7 ± 0.22	0.129		
	318	3.5 ± 0.14	0.167		

Mg(II), Cd(II), Hg(II), Pb(II), and Zn(II) complexes.

We found that the rates of the metal exchange reactions of CdPhe(a) and CdChl(a) with $CoCl_2$ in ethanol are described by a first-order equation with respect to the concentration of the complex, which is evident from a linear dependence of $\lg\left(c^0_{CdP}/c_{CdP}\right)$ on the reaction time (Figs. 2, 3).

The order of the reaction with respect to the salt concentration is unity (Figs. 4, 5). The order was determined from the slope of the linear plot of $\lg k_{eff_1}$ vs. $\lg c^0_{CoCl_2}$ (for the reaction of CdPhe(a) with $CoCl_2$ in ethanol) and from the slope of the linear plot of $\lg k_{eff_2}$ vs. $\lg c^0_{CoCl_2}$ (for the reaction of CdChl(a) with $CoCl_2$ in ethanol).

The metal exchange is a bimolecular reaction and obeys the second-order kinetic equation

$$-dc_{CdP}/d\tau = k_v[CdP][MCl_2]. \quad (6)$$

where k_v is the true constant or the second-order rate constant, CdP is CdPhe(a) and CdChl(a), and MCl_2 is the dominant form of the salt in ethanol.

Our experimental data (Tables 1, 2) suggest that the metal exchange between CdP and $CoCl_2$ in ethanol follows an associative mechanism (Eqs. (7), (8)). In the first, bimolecular step, a binuclear intermediate is produced:

$$\begin{aligned} &CdP + MX_2(Solv)_{n-2} \\ &\rightleftarrows (Solv)_m CdP \cdot MX_2(Solv)_{n-4}. \end{aligned} \quad (7)$$

The formation of this intermediate can immediately result from the mixing of the reagents (in this case, it can easily be detected by spectroscopic methods) or this step can be retarded.

The second, monomolecular step involves slow dissociation of the intermediate:

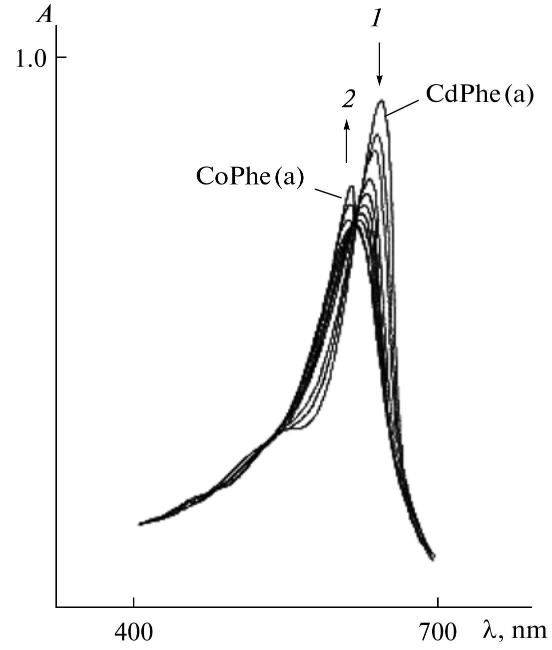


Fig. 1. Electronic absorption spectra of the reaction mixture in the metal exchange reaction of CdPhe(a) with $CoCl_2$ in ethanol ($c^0_{CdPhe(a)}$ = 2.3 × 10^{-5} mol/l, c_{CoCl_2} = 2.3 × 10^{-2} mol/l) for τ = (*1*) 0 and (*2*) 120 min; λ = 655.2 and 644 nm correspond to λ_I CdPhe(a), λ and CoPhe(a), respectively.

$$\begin{gathered}(\mathrm{Solv})_m\mathrm{CdP}\cdot\mathrm{MX}_2(\mathrm{Solv})_{n-4}\\ \rightleftarrows\left[\mathrm{X}_2\mathrm{Cd}^{2+}...\mathrm{P}^{2-}...\mathrm{M}^{2+}(\mathrm{Solv})_m\right]^{\#}\\ \rightarrow\mathrm{CdX}_2(\mathrm{Solv})_m+\mathrm{MP}(\mathrm{Solv})_{n-4}.\end{gathered}\tag{8}$$

This step is characterized by the changing band intensities in the electronic absorption spectra (Fig. 1).

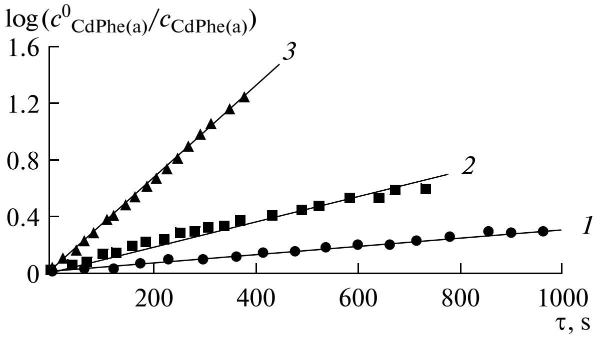


Fig. 2. Plots of $\lg\left(c^0_{CdPhe(a)}/c_{CdPhe(a)}\right)$ vs. the reaction time for the reaction of $CoCl_2$ with CdPhe(a) in ethanol ($c_{CoCl_2} = 2.3\times10^{-2}$ mol/l) at *T* = (*1*) 298, (*2*) 308, and (*3*) 318 K.

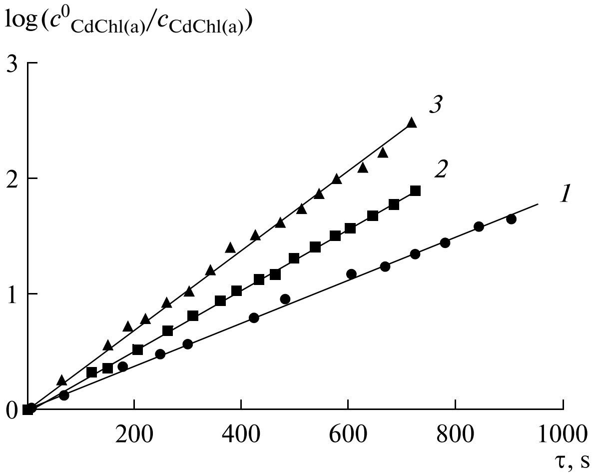


Fig. 3. Plots of $\lg\left(c^0_{CdChl(a)}/c_{CdChl(a)}\right)$ vs. the reaction time for the reaction of $CoCl_2$ with CdChl(a) in ethanol ($c_{CoCl_2} = 3.92\times10^{-2}$ mol/l) at *T* = (*1*) 298, (*2*) 308, and (*3*) 318 K.

When the strong coordinating dipolar aprotic solvent (DMSO) is replaced by protic ethanol, the rates of the metal exchange reactions of CdPhe(a) and CdChl(a) with $CoCl_2$ increase sharply. We found that CdPhe(a) and CdChl(a) are virtually inert to metal exchange with $ZnCl_2$ in ethanol. Comparison of the transmetalation rates for the reactions of CdPhe(a) and CdChl(a) with $CoCl_2$ in ethanol showed that the former is more reactive under these conditions. This is due to the effect of the substituent in position 4 of the macrocyclic molecule: the OH group in H_2Phe(a) is the stronger donor of σ-electrons than the group $OC_{20}H_{39}$ in H_2Chl(a), which makes the complex

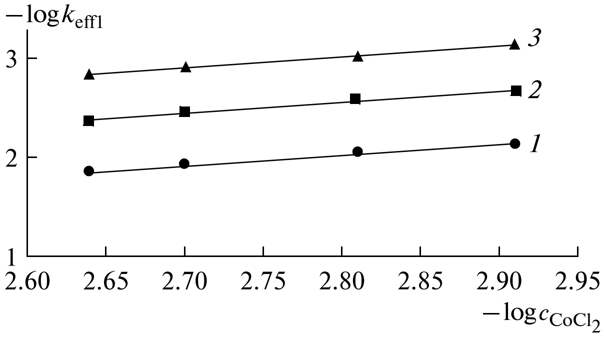


Fig. 4. Plots of $\lg k_{эфф_1}$ vs. $\lg c^0_{CoCl_2}$ in the metal exchange reaction of CdPhe(a) with $CoCl_2$ in ethanol at *T* = (*1*) 298, (*2*) 308, and (*3*) 318 K.

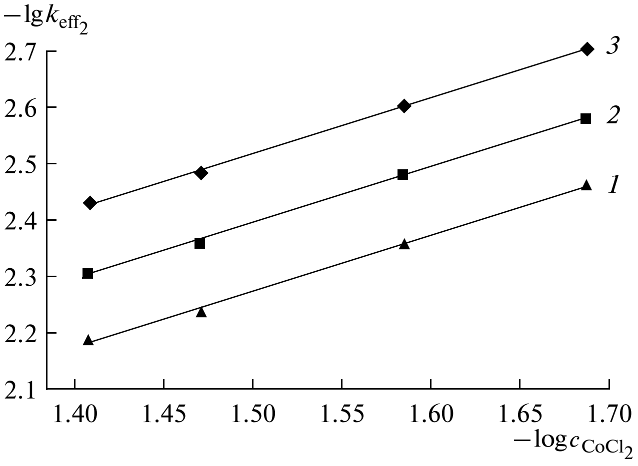


Fig. 5. Plots of $\lg k_{\text{эфф}_2}$ vs. $\lg c^0_{\mathrm{CoCl}_2}$ in the metal exchange reaction of CdChl(a) with $CoCl_2$ in ethanol at T = (*1*) 298, (*2*) 308, and (*3*) 318 K.

CdPhe(a) less stable than CdChl(a) and thus more tending toward metal exchange with $CoCl_2$ in ethanol.

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