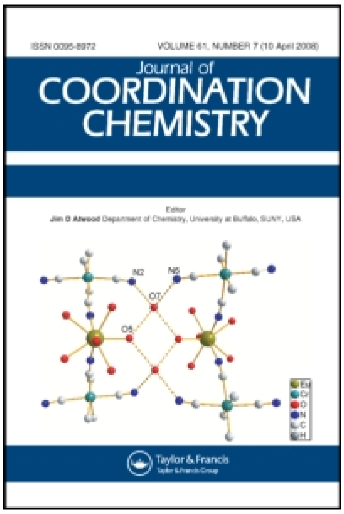

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INTERACTION OF MULTIDENTATE COBALT(II)-CHELATE COMPLEXES WITH FERRICYANIDE ION. III. Co^{II}PDTA (1,2 PROPYLENEDIAMINETETRAACETIC ACID)

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The intereaction of Co^{II}PDTA (PDTA = 1,2-propylenediaminetetraacetic acid) and $Fe(CN)_6^{3-}$ is reported in accordance with the reaction scheme

$$Co^{II}PDTA^{2-} + Fe(CN)_6^{3-} \overset{K_1(k_1)}{\rightleftharpoons} [PDTA\text{–}Co^{III}\text{–}NC\text{–}Fe^{II}(CN)_5]^{5-}\ (I_1)$$
$$I_1 \xrightarrow{k_3} Co^{III}PDTA^{-} + Fe(CN)_6^{4-}$$

The values of K_1, k_1 and k_3 at 25°C, *p*H 5.00 and $I = 0.66$ M(associated thermodynamic parameters follow in parentheses) are 637 M^{-1} ($\Delta H_1{}^0 = -17.6$ kcal/mole), 8×10^4 M^{-1} sec^{-1} and 3.17×10^{-3} sec^{-1} ($\Delta H_3{}^* = 26.5$ kcal/mole and $\Delta S^* = 14.5$ cal/deg.–mole.) The binuclear cyanide bridged intermediate, I_1, forms by displacement of an in-plane acetate group by $Fe(CN)_6^{3-}$. In the PDTA complex the reaction is believed to occur via the acetate group which is "remote" from the methyl group in the ethylenediamine ring. Rate and equilibria data are discussed in terms of the effects of this methyl group on the acetate group.

INTRODUCTION

Recent reports[1,2] on the interaction of ethylenediaminetetra acetatocobaltate(II) and related complexes with ferricyanide ion have supported the mechanisms proposed[3,4] for the electron transfer process between these species. These mechanisms involve an inner-sphere electron transfer reaction to form a cyano bridged Co^{III}—Fe^{II} intermediate which subsequently dissociates to the observed products, viz.,

$$Co^{II}Y^{n-} + Fe(CN)_6^{3-} \rightleftharpoons [YCo^{III}\text{—}NC\text{—}Fe^{II}(CN)_5]^{(3+n)-} \quad k_1,\ k_{-1},\ k_1$$
$$[YCo^{III}\text{—}NC\text{—}Fe^{II}(CN)_5]^{(3+n)-} \rightarrow Co^{III}Y^{(n-1)-} + Fe(CN)_6^{4-} \quad k_3$$

(Y = multidentate chelating agent)

Changes in the nature or structure of the chelate group Y are expected, and have been shown, to cause changes in the reaction parameters k_1, K_1 and k_3. These changes can be rationalized on the basis of steric hindrance of a displaced acetate group[1] or charge effects.[2,5] This paper reports some initial results of our efforts to determine the factors important to these effects. The ligand 1,2-propylenediaminetetraacetic acid (PDTA) was chosen because of its close structural similarity to EDTA and CyDTA (trans-1,2-cyclohexanediaminetetraacetic acid), these latter ligands having been studied in part I of this series.[1]

EXPERIMENTAL

Materials

All chemicals were of reagent grade quality. Standard solutions were prepared by weight in all cases except for cobalt(II) nitrate which was standardized by titration with EDTA.[6] The ligand PDTA was prepared by the method of Dwyer and Garvan.[7]

Anal. Calcd. for $C_{11}H_{18}N_2O_8$: % C 43.1; % H 5.93; % N 9.15. Found: % C 43.5; % H 6.00; % N 9.16.

Measurements

All solutions were prepared to be at ionic strength, $I = 0.660$ and $p\text{H} = 5.00$ by adjustment with acetic acid, sodium acetate and sodium hydroxide. The Co^{II}PDTA solutions were prepared first neutralizing a weighed 10% excess of the ligand to the H_2PDTA^{2-} form followed by addition of an appropriate aliquot of cobalt(II) nitrate.

Measurements on the kinetics of decomposition of the intermediate were carried out under pseudo-first order conditions with [Co^{II}PDTA] in large excess over [$Fe(CN)_6^{3-}$]. Data acquisition and analyses were carried out as described previously.[1] Kinetic studies on the rapid formation of the intermediate were performed on an Aminco-Morrow Stopped Flow Apparatus. Spectral measurements were carried out as described previously.[1]

RESULTS

Kinetic measurements were carried out at four temperatures between 14.90° and 30.25°C, in which [Co^{II}PDTA] (3.40×10^{-3} to 2.00×10^{-2} M) $\gg$ [$Fe(CN)_6^{3-}$] (2.00×10^{-4} M). The results are reported in accordance with the reaction scheme above for which

$$\frac{1}{k_{3\mathrm{app}}} = \frac{1}{k_3 K_1[\mathrm{Co^{II}PDTA}]} + \frac{1}{k_3}$$

where $k_{3\mathrm{app}}$ is the observed first-order rate constant obtained from the kinetic plots.

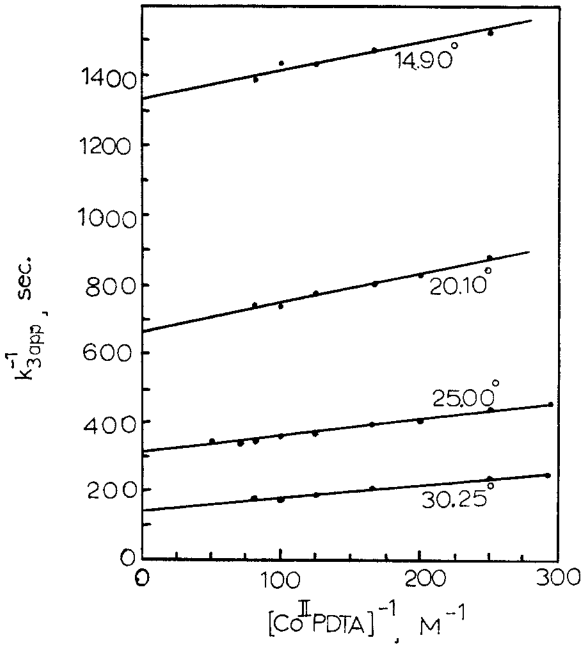

FIGURE 1 Double reciprocal plot for the decomposition of I_1 to Co^{III}PDTA and $Fe(CN)_6^{4-}$.

When the values of $k_{3\mathrm{app}}^{-1}$ are plotted versus [Co^{II}PDTA]$^{-1}$, linearity is obtained at each temperature, as shown in Figure 1. Values of k_3 and k_1, calculated from the intercepts and slopes of these double-reciprocal plots are listed in Table I. The activation parameters are $\Delta H_3^* = 26.5 \pm 0.8$ kcal/mole and $\Delta S_3^* = 14.5 \pm 1.5$ cal/deg-mole. A value of $\Delta H_1^\circ = 17.6 \pm 0.8$ kcal/mole is obtained from the temperature variation of K_1.

TABLE I

Derived parameters for the interaction between $Co^{II}PDTA^{2-}$ and $Fe(CN)_6^{3-}$

Temperature, °C	$10^3 k_3$,sec^{-1}	$10^{-2} K_1$,M^{-1}
14.90 ± 0.01	0.743 ± 0.20	17.9 ± 1.70
20.10 ± 0.02	1.51 ± 0.04	8.89 ± 0.60
25.00 ± 0.03	3.17 ± 0.10	6.37 ± 0.60
30.25 ± 0.05	6.87 ± 0.20	3.82 ± 0.30

Kinetics of the rapid formation of the intermediate were carried out in the same manner as for the Co^{II}CyDTA complex.[1] The values of 10^{-4} k_1 are (number of runs and temperature in parentheses) 8.27 ± .25 (8; 18.6°), 8.81 ± 0.15 (9; 14.1°), 8.58 ± 0.20 (9; 12.9°), 8.98 ± 0.10 (18; 8.7°), 9.41 ± 0.15 (30, 3.0°) and 9.21 ± .10 (9, 2.6°). These values seem to be invariant with temperature, or, if anything, slightly decreasing with increasing temperature. This is indicative of a near zero or slightly negative activation energy much like the EDTA system.[4] For comparison purposes a value for k_1 at 25° is taken as $(8 + 1) \times 10^4$ M^{-1} sec^{-1}.

DISCUSSION

A summary and comparison of equilibrium and rate constants with associated thermodynamic parameters is presented for the Co^{II}EDTA, Co^{II}CyDTA and Co^{II}PDTA systems (at 25°) in Table II.

The equilibrium constant for the formation of the intermediate, K_1, follows the sequence: Co^{II}EDTA $\gtrsim$ Co^{II}PDTA $\gg$ Co^{II}CyDTA. The decreased magnitude of K_1 for CyDTA can be attributed to the steric restriction imposed on a displaced acetate group as discussed previously.[1] In the case of Co^{II}EDTA, an acetate group displaced by a bridging cyano group has considerable

TABLE II

Comparison of results at 25°C

	Co^{II}EDTA[a]	Co^{II}PDTA	Co^{II}CyDTA[a]
k_1,M^{-1} sec^{-1}	7×10^4 [b]	8×10^4	3.6×10^3
K_1, M^{-1}	831	637	43.6
$\Delta H_1{}^0$, kcal/mole	−16.7	−17.6	−17.5
k_3, sec^{-1}	5.40×10^{-3}	3.17×10^{-3}	22.1×10^{-3}
$\Delta H_3{}^*$, kcal/mole	+25.4	+26.5	+23.0
$\Delta S_3{}^*$, cal/deg-mole	+16.1	+14.5	+10.9

[a] Reference 1.
[b] Reference 4.

freedom to rotate away from the bridging site, whereas in Co^{II}CyDTA, the displaced acetate group encounters considerable hinderance to rotation by the axial proton in the 3-position of the cyclohexane ring.

A close examination of the Co^{II}PDTA complex reveals that there are two sites which differ a great deal in these regards (Figure 2). Considering only the in-plane acetate rings (*vide infra*), Co^{II}PDTA has one acetate ring (we shall call α) which has considerable freedom upon displacement and thus resembles Co^{II}EDTA planar acetate rings. The other acetate ring in Co^{II}PDTA (β) can be thought to resemble a planar Co^{II}CyDTA group in that there is a substituent in the equitorial position of the adjacent ethylenediamine ring. Thus, we might expect some degree of steric restraint to rotation upon displacement of this ring.

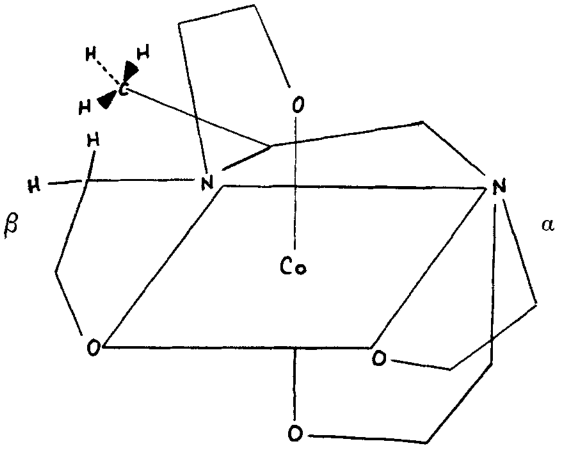

FIGURE 2 Structure of Co^{II}PDTA showing α and β acetate rings.

Qualitatively, it can be concluded that reaction occurs through the α acetate rings, as all rate and equilibrium constants resemble the EDTA system more closely than the CyDTA system. Furthermore, if we treat either the formation of I_1 or its decompostion as two parallel reactions proceeding through α and β sites, assuming that k_α or $K_\alpha = k_{EDTA}$ or K_{EDTA}, etc., we are led to the conclusion that (a) greater than 95% of the formation of I_1 should go through the α site and (b) the *rate* of decomposition of $I_{1\alpha}$ (the intermediate resulting from displacement of the acetate group at the α site) will occur five times faster than that for $I_{1\beta}$.

The results reported here are in agreement with the above conclusions. However, some points should be explored further. Statistically, one might expect k_1 (and K_1) to decrease by a factor of two since there are only half as many α positions in Co^{II}PDTA as in Co^{II}EDTA. It is seen (Table II) that k_1 (Co^{II}PDTA) $\cong k_1$ (Co^{II}EDTA) while K_1 (Co^{II}PDTA) $< K_1$ (Co^{II}EDTA).

Values for k_3 (the rate econstant for decomposition of the intermediate [YCo^{III}-NC-Fe^{II}(CN)$_5$]$^{5-}$) follow the sequence for Y : CyDTA > EDTA > PDTA. This is not in agreement with the qualitative predictions nor our own personal observations on other systems.[1, 2, 8] Thus, we now address ourselves to these differences.

The structures of the cobalt(II) and cobalt(III) complexes of these multidentate ligands have been discussed in a previous paper.[1] It was concluded that the in-plane acetate groups (coplanar with the nitrogen atoms of the en ring) experience more strain than the out-of plane acetate groups which render them more suceptible to displacement. It is reasonable to assume that the same holds true for Co^{III}PDTA and Co^{II}PDTA. In addition, steric interactions reported for Co^{III}CyDTA complexes have also been observed in Co^{III}PDTA complexes as well.[9,10] Thus, we believe that the β acetate rings in Co^{III}PDTA (and Co^{II}PDTA) are held more closely to the metal coordination site. This constraint produces internal crowding,[11,12] restricting the motion of and thus producing even more strain on the α-in-plane acetate groups. Thus, relative to the less strained EDTA system, ring opening at the α site will tend to occur at a faster rate and ring closure at a slower rate in the PDTA system.

The results on k_1 and K_1 obtained above support this argument when the statistical factor is considered. Data on the ring closure (decomposition of I_1) provides stronger support especially when compared with similar systems. Table III lists the rate constants for ring closure of several Co^{III}EDTAX and Co^{III}PDTAX complexes. It is interesting to note that if ring closure proceeded by an S_N1 process, the internal crowding would be expected to accelerate the rate of decomposition for the PDTA system.[11] However, it has been suggested that bond making occurs to the extent of 10–15% in the formation of the transition state in these ring closure reactions.[13] If true, this contribution would tend to decrease the rate of ring closure for the PDTA systems.

TABLE III

Rates of ring closure for $\text{Co}^{\text{III}}(\text{chelate})\cdot X$ complexes at 25°C

Complex	k_3, sec^{-1}	Reference
$\text{EDTACo}^{\text{III}}\cdot \text{OH}_2{}^{-}$	1.80×10^{-3}	14
$\text{PDTACo}^{\text{III}}\cdot \text{OH}_2{}^{-}$	2.00×10^{-3}	11
$\text{EDTACo}^{\text{III}}\cdot \text{Cl}^{2-}$	2.60×10^{-6}	13
$\text{PDTACo}^{\text{III}}\cdot \text{Cl}^{2-}$	2.24×10^{-6}	11
$\text{EDTACo}^{\text{III}}\cdot \text{Br}^{2-}$	2.00×10^{-5}	14
$\text{PDTACo}^{\text{III}}\cdot \text{Br}^{2-}$	1.16×10^{-5}	11
$\text{EDTACo}^{\text{III}}\cdot \text{NCFe(CN)}_5{}^{5-}$	5.40×10^{-3}	1
$\text{PDTACo}^{\text{III}}\cdot \text{NCFe(CN)}_5$	3.20×10^{-3}	this work

One feature of the PDTA system which is not different from previous systems studied is the value of the rate constant k_{-1} (reverse electron transfer and decomposition of I_1 back to products). A value of k_{-1} obtained from K_1 and k_1 is $1.8 \times 10^2\ \text{sec}_{-}{}^{1}$. Similar values have been obtained for EDTA ($1.4 \times 10^2\ \text{sec}^{-1}$) CyDTA ($1.3 \times 10^2\ \text{sec}^{-1}$) and DTPA ($1.5 \times 10^2\ \text{sec}^{-1}$).

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