The relatively high rate of reaction observed for reaction 24, when considered with the relative stability of copper(III) peptide complexes,[11] might explain in part the high selectivity in the copper-induced radiolytic deactivation of enzymes.[9,10] We are planning to extend this study to other copper complexes of biological importance.

Acknowledgments.—I am indebted to Dr. M. S. Matheson for his encouragement and discussions throughout this work. I also wish to thank Mr. W. A. Mulac and Miss C. Goldenberg for their invaluable assistance in all phases of these experiments and Mr. J. Ogdan and the Linac group at Argonne for their careful operation of the linear accelerators.

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Substituent Effects on the Kinetics of Ligand Substitution Reactions of Lead–Aminocarboxylate Complexes

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The rate constants for the ligand exchange reactions of CyDTA with the lead(II) complexes of *l*-PDTA, *d*-PDTA, and CyDTA and the exchange of *d*-PDTA with the lead(II) complex of *l*-PDTA have been measured by polarimetric techniques. Each reaction shows a pathway which is first-order in both entering ligand tetraanion and lead complex concentrations. It is found that one optical isomer of CyDTA exchanges more rapidly with optically active lead–PDTA than does the other. At high pH, the rate of exchange of CyDTA with lead–PDTA is increased and a parallel reaction pathway involving hydroxide ion is proposed. These rate constants are compared with those previously obtained for the exchange of EDTA with the lead(II) complexes of EDTA and PDTA and the steric effects of the alkyl substituents are discussed. The effect of potassium ion on the observed reaction rates is interpreted in terms of known stabilities of potassium complexes. The rate constants obtained are as follows: for *d*-CyDTA with lead–*d*-PDTA or lead–*l*-PDTA, 1.38 ± 0.02 M^{-1} sec^{-1}; for *l*-CyDTA with lead–*l*-PDTA or lead–*d*-PDTA, 2.86 ± 0.08 M^{-1} sec^{-1} for *d*-PDTA with lead–*l*-PDTA, 1.58 ± 0.07 M^{-1} sec^{-1}; for *d*-CyDTA with lead–*l*-CyDTA, (3.77 ± 0.33) × 10^{-2} M^{-1} sec^{-1}.

In a previous work[1] the ligand-exchange kinetics of EDTA[2] with lead–PDTA and with lead–EDTA were measured. In order to observe further the effect of a change in ligand structure on the rate of exchange, the kinetics of ligand exchange of CyDTA with lead–*l*-PDTA and lead–*d*-PDTA (eq 1, with protons omitted) and *d*-PDTA with lead–*l*-PDTA (eq 2) are measured by observing the change in optical rotation. Also, the exchange of CyDTA with lead–CyDTA (eq 3) is measured by polarimetric techniques.

$$\mathrm{Cy^{4-} + PbL^{2-} \longrightarrow PbCy^{2-} + L^{4-}} \quad (1)$$

$$\mathrm{L^{4-} + PbL^{2-} \longrightarrow PbL^{2-} + L^{4-}} \quad (2)$$

$$\mathrm{Cy^{4-} + PbCy^{2-} \longrightarrow PbCy^{2-} + Cy^{4-}} \quad (3)$$

Ionic charges represent the predominant species of reactants and products in the pH range studied. The pH dependencies of reactions 1–3 are analyzed and interpreted. Activation parameters for reaction 2 are measured. A comparison of reaction rates in potassium ion and cesium ion is interpreted in terms of recently measured stability constants of potassium complexes of CyDTA[3] and PDTA[4] and acidity constants of these ligands in the absence of potassium.

Experimental Section

A standard solution of CyDTA was prepared by dissolving doubly recrystallized CyDTA (Aldrich Chemicals Co., Inc.) by neutralization with KOH or CsOH as appropriate and titrating with a standard copper solution using SNAZOXS indicator.[5] Solutions of *l*-PDTA, *d*-PDTA, *dl*-PDTA, lead-*d*-PDTA, and lead-*l*-PDTA were prepared as previously described[1] and lead–CyDTA was prepared in the same manner as lead–PDTA. Optically active CyDTA was prepared by resolving *trans*-1,2-diaminocyclohexane with tartaric acid and subsequent reaction with potassium chloroacetate (see ref 6 for details).

Solution ionic strength was maintained at 0.5 with KNO_3 or $CsNO_3$ as appropriate. Solution pH was adjusted by adding HNO_3, KOH, or CsOH and was measured on a Corning Model 12 pH meter equipped with a Corning semimicro combination electrode. In many cases the potassium ion activity was measured after the kinetic reaction with an Orion potassium specific ion electrode.

Exchange reactions 1–3 were measured at 365 nm on a Perkin-Elmer Model 141 polarimeter with a Sargent Model SR recorder attached as previously described.[1] For the faster reactions a mixing device consisting of two 10-ml syringes and a countercurrent mixing block was used to fill the polarimeter cell, allowing measurement of optical rotation in less than 10 sec after mixing. Different initial reactant concentrations were used and in each case a 15- to 60-fold excess of entering ligand was present to force the reaction to completion. Solution pH was measured at the temperature of the kinetic run.

The rate of exchange of reaction 1 was followed polarimetrically by measuring the rates of the reactions

$$dl\text{-}\mathrm{Cy^{4-}} + \mathrm{Pb}\text{-}l\text{-}\mathrm{L^{2-}} \longrightarrow \mathrm{Pb}\text{-}d\text{-}\mathrm{Cy^{2-}} + \mathrm{Pb}\text{-}l\text{-}\mathrm{Cy^{2-}} + l\text{-}\mathrm{L^{4-}} \quad (4)$$

$$dl\text{-}\mathrm{Cy^{4-}} + \mathrm{Pb}\text{-}d\text{-}\mathrm{L^{2-}} \longrightarrow \mathrm{Pb}\text{-}d\text{-}\mathrm{Cy^{2-}} + \mathrm{Pb}\text{-}l\text{-}\mathrm{Cy^{2-}} + d\text{-}\mathrm{L^{4-}} \quad (5)$$

$$l\text{-}\mathrm{Cy^{4-}} + \mathrm{Pb}\text{-}l\text{-}\mathrm{L^{2-}} \longrightarrow \mathrm{Pb}\text{-}l\text{-}\mathrm{Cy^{2-}} + l\text{-}\mathrm{L^{4-}} \quad (6)$$

$$l\text{-}\mathrm{Cy^{4-}} + \mathrm{Pb}\text{-}d\text{-}\mathrm{L^{2-}} \longrightarrow \mathrm{Pb}\text{-}l\text{-}\mathrm{Cy^{2-}} + d\text{-}\mathrm{L^{4-}} \quad (7)$$

$$d\text{-}\mathrm{Cy^{4-}} + \mathrm{Pb}\text{-}l\text{-}\mathrm{L^{2-}} \longrightarrow \mathrm{Pb}\text{-}d\text{-}\mathrm{Cy^{2-}} + l\text{-}\mathrm{L^{4-}} \quad (8)$$

$$d\text{-}\mathrm{Cy^{4-}} + \mathrm{Pb}\text{-}d\text{-}\mathrm{L^{2-}} \longrightarrow \mathrm{Pb}\text{-}d\text{-}\mathrm{Cy^{2-}} + d\text{-}\mathrm{L^{4-}} \quad (9)$$

Reactions 4 and 5 were performed in the presence of cesium and

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[1] J. D. Carr, K. Torrance, C. J. Cruz, and C. N. Reilley, *Anal. Chem.*, **39**, 1358 (1967).

[2] Abbreviations used: EDTA or Y, ethylenediaminetetraacetate; PDTA or L, propylenediaminetetraacetate; CyDTA or Cy, *trans*-1,2-cyclohexanediaminetetraacetate.

[3] J. D. Carr and D. G. Swartzfager, *Anal. Chem.*, **42**, 1238 (1970).

[4] J. D. Carr and D. G. Swartzfager, *ibid.*, **43**, 583 (1971).

[5] G. Guerrin, M. V. Sheldon, and C. N. Reilley, *Chemist-Analyst*, **49**, 36 (1960).

[6] P. E. Reinbold and K. H. Pearson, *Inorg. Chem.*, **9**, 2325 (1970).

potassium ions, whereas reactions 6–9 were performed only in cesium ion.

Values of molar rotations of CyDTA and PDTA were measured in cesium in the pH region 10–13 and are given in Table I.

TABLE I
MOLAR ROTATIONS OF *l*-CyDTA AND *l*-PDTA IN pH REGION 10–13[a]

pH	$[\alpha]_{l\text{-L}}$, l. deg/cm mol	$[\alpha]_{l\text{-Cy}}$, l. deg/cm mol	pH	$[\alpha]_{l\text{-L}}$, l. deg/cm mol	$[\alpha]_{l\text{-Cy}}$, l. deg/cm mol
10.0	−2.73	−5.77	12.0	+3.90	−5.80
10.5	−1.80	−5.80	12.5	+4.75	−5.76
11.0	−0.05	−5.83	13.0	+5.13	−5.75
11.5	+2.20	−5.83	13.5	+5.30	

[a] μ is 0.50 ($CsNO_3$), temperature is 25°, and λ is 365 nm.

The molar rotation of lead–*l*-CyDTA was found to be 70 l. deg/cm mol in the pH region 10–13.5.

Values of pK_{HCy} used were 13.17[3] and 12.05 (corrected from ref 7) in the presence of Cs^+ and K^+, respectively, and that of pK_{H_2Cy} was 6.15.[8]

In the cases that racemic CyDTA was used as a reactant (reactions 4 and 5) the reaction reached a pseudoequilibrium rotation (half-time ranging from 20 sec to 10 min) and then slowly (approximately 24 hr) attained a final equilibrium rotation. Values of observed pseudo-first-order rate constants (k_{obsd}) for reactions 4 and 5 (*i.e.*, those involving racemic CyDTA) were obtained from plots of $-\ln(\alpha - \alpha_e)$ *vs.* time. These data were treated as two separate consecutive reactions and the value of α_e for the faster reaction was taken as the pseudoequilibrium rotation (*i.e.*, the one occurring after 10 half-lives of the first reaction) whereas α_e for the slower following reaction was taken as the final equilibrium rotation (*i.e.*, the one occurring after at least 24 hr). Pseudo-first-order rate constants for reactions 6–9 were obtained from similar plots but without the difficulty of the pseudoequilibrium.

TABLE II
RESOLVED RATE CONSTANTS IN PRESENCE OF CESIUM AND POTASSIUM (25°, μ = 0.50)

Reaction[f]	k,[d] M^{-1} sec^{-1}	
	Cs^+	K^+
$EDTA^{4-}$ + lead–$EDTA^{2-}$		65[a] ($\mu \cong 3$)
$PDTA^{4-}$ + lead–$EDTA^{2-}$	(30)[e]	12[a] (estd from stability constants)
$CyDTA^{4-}$ + lead–$EDTA^{2-}$	(9)[e]	0.41[b]
$EDTA^{4-}$ + lead–$PDTA^{2-}$		1.2[a]
d-$PDTA^{4-}$ + lead–*l*-$PDTA^{2-}$	1.58 ± 0.07[c]	0.60[c]
l-$CyDTA^{4-}$ + lead–*l*-$PDTA^{2-}$ (or lead–*d*-$PDTA^{2-}$)	2.86 ± 0.08[c]	
d-$CyDTA^{4-}$ + lead–*l*-$PDTA^{2-}$ (or lead–*d*-$PDTA^{2-}$)	1.38 ± 0.02[c]	
$CyDTA^{4-}$ + lead–*l*-$PDTA^{2-}$	4.00 ± 0.14[c,g]	0.18[c,g]
d-$CyDTA^{4-}$ + lead–*l*-$CyDTA^{2-}$	$(3.77 \pm 0.33) \times 10^{-2}$ [c]	$(0.17 \pm 0.08) \times 10^{-2}$ [c]
$2OH^-$ + lead–*l*-$PDTA^{2-}$	1.06 ± 0.04[c] (M^{-2} sec^{-1})	
OH^- + lead–$CyDTA^{2-}$		$(9.0 \pm 0.6) \times 10^{-4}$ [c] $(10 \pm 2) \times 10^{-4}$ [c] (33°, μ = 1.3)

[a] Reference 1. [b] Reference 6. [c] This work. [d] Error quoted is one standard deviation. [e] Estimated in this work. [f] Rate constants for reactions including protonated PDTA and CyDTA are too small to be measured. [g] This rate constant is actually the sum of the rate constants of the two isomers of CyDTA.

The rate constants for reaction 2 were measured polarimetrically by exchanging both *d*-PDTA and *dl*-PDTA with lead–*l*-PDTA. When the *d*-PDTA was added as the optically pure reagent the rate constants were calculated in the manner of reaction 1. However, when the *d*-PDTA was added as the racemic mixture, the rate constants were calculated on the basis of a pseudo-first-order reversible reaction since a high, constant concentration of product (*i.e.*, *l*-PDTA) was present at time zero.

The rate of reaction 3 was measured by mixing *dl*-CyDTA with lead–*l*-CyDTA and monitoring the rotation as before. No slower following reaction was observed. These resulting rate constants are included in Table II.

Results

CyDTA + PbPDTA, Fast Reaction.—The results obtained in the presence of cesium ion are truly representative of eq 1 as written and will be described first.

The pseudoequilibrium and slow following reaction are shown in Figure 1 and observed no matter which method of mixing is used or whether cesium or potassium is used. The final equilibrium rotation agrees well with the value expected from molar rotations[1] (Table I) and reactant concentrations if reaction 1 proceeds totally to completion. Stability constants predict that the reaction will go to completion with the excess of entering ligand used. No such slow following reaction is observed when lead–PDTA reacts with EDTA, the latter having no sites of asymmetry, or when optically active CyDTA is used as reactant in reaction 1.

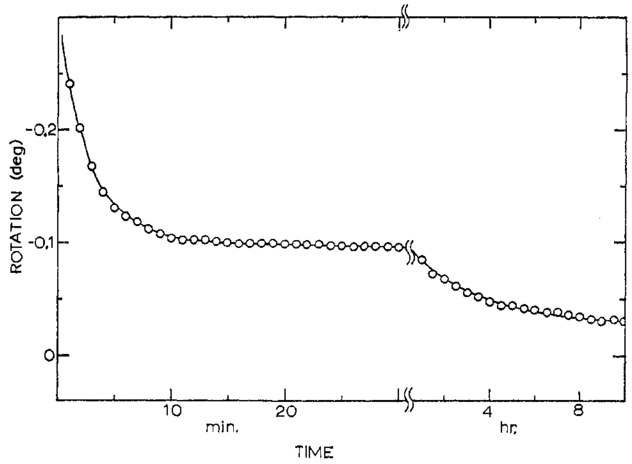

Figure 1.—Observed optical rotation; $[Cy]_0 = 2.04 \times 10^{-2}$ *M*, $[PbL]_0 = 5.33 \times 10^{-4}$ *M*, pH 12.47, μ = 0.5 ($CsNO_3$), and temperature 25°; pseudoequilibrium rotation −0.104° and true equilibrium rotation −0.022°.

For reactions 6–9, the following pathways are considered

$$Cy^{4-} + PbL^{2-} \xrightarrow{k_{Cy^{4-}}{}^{PbL}} PbCy^{2-} + L^{4-} \qquad (10)$$

$$HCy^{3-} + PbL^{2-} \xrightarrow{k_{HCy^{3-}}{}^{PbL}} PbCy^{2-} + HL^{3-} \qquad (11)$$

and the rate of exchange is considered as

$$\text{rate} = k_{obsd}[PbL^{2-}] \qquad (12)$$

where

$$k_{obsd} = k_{Cy^{4-}}{}^{PbL}[Cy^{4-}]_0 + k_{HCy^{3-}}{}^{PbL}[HCy^{3-}]_0 \qquad (13)$$

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(7) G. Anderegg, *Helv. Chim. Acta*, **46**, 1833 (1963).

(8) G. Anderegg, *ibid.*, **50**, 2333 (1967).

TABLE III

RATE CONSTANTS FOR REACTION 1 (FAST REACTION) (25°)

pH	$10^2[\mathrm{Cy}]_0$,[a] M	$10^4[\mathrm{PbL}]_0$,[a] M	10^3k_{obsd},[b] sec^{-1}
μ = 0.50 ($CsNO_3$)			
l-CyDTA + Pb-*d*-PDTA			
11.82	1.71	6.00	1.29
12.56	1.81	6.34	9.66
12.65	1.81	6.34	11.2
12.82	1.80	6.28	16.1
l-CyDTA + Pb-*l*-PDTA			
11.52	1.71	9.84	0.928
12.30	1.76	10.1	6.08
12.59	1.81	10.4	10.5
d-CyDTA + Pb-*l*-PDTA			
12.30	0.638	2.58	0.968
12.53	1.63	10.0	3.88
12.68	0.675	2.73	2.03
12.73	1.64	10.1	6.07
d-CyDTA + Pb-*d*-PDTA			
12.39	0.678	3.34	1.29
12.72	0.679	3.34	2.13
dl-CyDTA + PbPDTA			
10.95	9.22	8.47	0.764
11.92	2.06	5.38	1.49
12.26	2.56	7.06	4.62
12.47	2.04	5.33	7.09
12.57	2.58	7.11	10.2
12.71	2.44	13.4	11.3
12.81	2.59	7.13	15.8
12.96	2.55	5.06	28.3
13.02	1.00	4.17	20.3
13.06	1.00	4.17	22.8
13.12	1.05	6.05	28.0
13.16	1.05	6.05	31.0
μ = 0.50 (KNO_3)			
dl-CyDTA + PbPDTA			
10.87	3.10	5.44	2.06
10.89	3.00	4.68	1.62
11.01	1.50	4.68	1.25
11.02	1.86	5.84	1.74 ± 0.01
11.18	3.00	4.68	2.98
11.32	3.00	4.68	3.79
11.37	1.43	4.68	2.15
11.38	1.43	4.68	2.28
11.42	1.86	5.84	4.00 ± 0.02
11.73	3.00	4.68	8.70
11.77	1.86	5.84	7.45
11.85	3.10	5.44	12.6
11.86	3.10	5.44	12.6
11.90	1.43	4.68	5.67
12.22	3.10	5.84	25.9
12.23	0.858	2.34	8.70 ± 0.02
12.25	1.86	5.84	19.1
12.34	1.14	4.68	10.6
12.34	3.10	5.44	31.4
12.35	1.50	4.68	13.0
12.37	1.43	4.68	16.9
12.40	1.86	5.84	23.5
12.42	1.43	4.68	16.1
12.49	1.14	4.68	16.0
12.50	3.10	5.44	35.9
12.56	1.20	4.68	18.9
12.56	2.49	4.17	40.9
12.56	2.01	4.18	31.7
12.70	2.86	9.36	41.5
12.73	1.50	9.36	24.0
12.89	1.50	9.36	40.0
13.05	3.10	5.44	125
13.06	1.50	9.36	77.7
13.17	3.00	5.44	159
13.19	0.901	5.44	116 ± 1.5
13.19	3.00	10.88	162
13.19	3.88	4.70	285 ± 4
13.19	3.88	4.70	280 ± 3
13.19	3.88	4.70	281 ± 3
13.19	3.88	4.70	286 ± 3

[a] The subscript zero indicates initial total concentration of all protonated species. [b] Standard deviations for representative runs are presented.

where the subscript zero indicates concentration at time zero.

If $HCyDTA^{3-}$ is not measurably reactive as shown for reaction 11 (*i.e.*, if $k_{\mathrm{HCy}^{3-}}{}^{\mathrm{PbL}} = 0$), then a plot of k_{obsd} *vs.* $[\mathrm{Cy}^{4-}]_0$ should yield a line of slope $k_{\mathrm{Cy}^{4-}}{}^{\mathrm{PbL}}$ and a zero intercept (Figure 2). It is apparent from Figure 2 that the rate of exchange of *l*-CyDTA is independent of which isomer of lead–PDTA is used but is different from the rate of exchange of *d*-CyDTA with the two isomers of lead–PDTA. The values of the rate constants obtained are given in Table II.

The faster preliminary portion of reaction 1 exhibits a complicated pH dependence and reactant order behavior and is much faster at a particular pH in cesium ion environment than in potassium. Over the entire pH range studied (pH 10.0–13.2) the reaction is first order in lead–PDTA. In the presence of cesium ion and absence of potassium ion at pH values below 12.8 it is also first order in the tetraanion of CyDTA, but at pH values greater than about 12.8 the reaction also shows a dependence on hydroxide ion. Table III shows the results of these experiments.

Resolved rate constants, $k_{\mathrm{Cy}^{4-}}{}^{\mathrm{PbL}}$ and $k_{\mathrm{HCy}^{3-}}{}^{\mathrm{PbL}}$, for reaction 1 were obtained from a plot of

$$\frac{2k_{\mathrm{obsd}}}{[\mathrm{Cy}]_{\mathrm{T}}} = \frac{K_{\mathrm{HCy}}}{[\mathrm{H}^+]} + 1 + \frac{[\mathrm{H}^+]}{K_{\mathrm{H_2Cy}}} \; vs. \; 1/[\mathrm{H}^+]$$

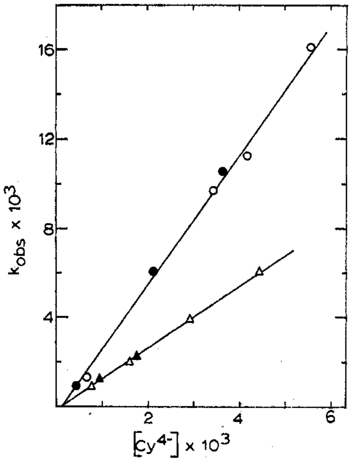

Figure 2.—Determination of $k_{l\text{-Cy}^{4-}}{}^{\mathrm{PbL}}$ and $k_{d\text{-Cy}^{4-}}{}^{\mathrm{PbL}}$ from reactions 6–9; μ = 0.50 ($CsNO_3$), temperature 25°: ○, from exchange of *l*-CyDTA with lead–*d*-PDTA; ●, from exchange of *l*-CyDTA with lead–*l*-PDTA; △, from exchange of *d*-CyDTA with lead–*l*-PDTA; ▲, from exchange of *d*-CyDTA with lead–*d*-PDTA.

as previously described[1] from data taken at pH values less basic than pH 12.8 and are given in Table II (see Figure 3). K_{HCy} and $K_{\mathrm{H_2Cy}}$ are the fourth and third acidity constants, respectively, of CyDTA. The value

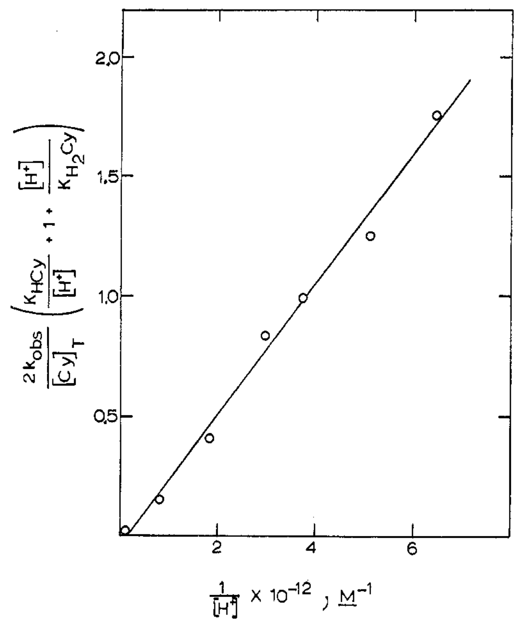

Figure 3.—Resolution of $k_{\mathrm{Cy}}{}^{\mathrm{PbL}}$ and $k_{\mathrm{HCy}}{}^{\mathrm{PbL}}$ from reactions 4 and 5, in $\mathrm{Cs^+}$; μ = 0.50 ($\mathrm{CsNO_3}$), temperature 25°.

obtained for $k_{\mathrm{Cy}^{4-}}{}^{\mathrm{PbL}}$ is actually the sum of the rate constants of the two isomers substituting lead–PDTA. The rate constant for the protonated CyDTA is immeasurably small.

The increase in slope at $1/[\mathrm{H^+}]$ greater than 7×10^{12} (pH 12.8) is attributed to a reaction involving hydroxide ion. A resolution plot obtained from data taken in the presence of potassium ion is shown in Figure 4 and the value of the rate constant obtained is given in Table II.

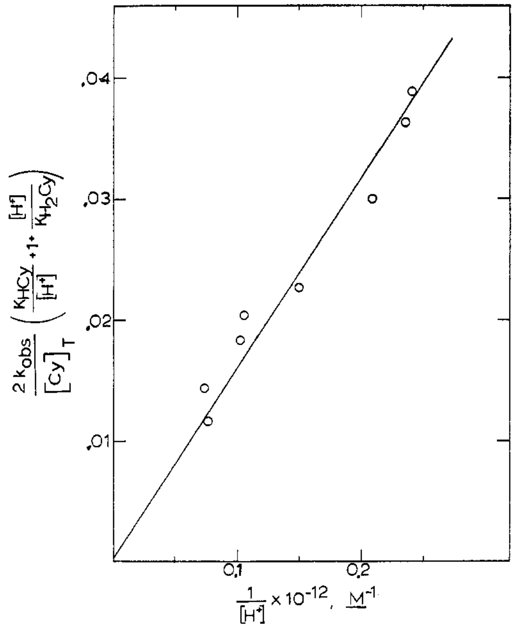

Figure 4.—Resolution of $k_{\mathrm{Cy}}{}^{\mathrm{PbL}}$ and $k_{\mathrm{HCy}}{}^{\mathrm{PbL}}$ in $\mathrm{K^+}$; μ = 0.50 ($\mathrm{KNO_3}$), temperature 25°.

If a reaction pathway parallel to eq 1 were considered as

$$\mathrm{PbL^{2-}} + n\mathrm{OH^-} \longrightarrow \mathrm{Pb(OH)}_n{}^{2-n} + \mathrm{L^{4-}} \qquad (14)$$

$$\mathrm{Pb(OH)}_n{}^{2-n} + \mathrm{Cy^{4-}} \xrightarrow{\text{fast}} \mathrm{PbCy^{2-}} + n\mathrm{OH^-} \qquad (14a)$$

then the rate of exchange would be given by the following equation, since both $\mathrm{Cy^{4-}}$ and $\mathrm{OH^-}$ would be in large excess over lead–PDTA

$$\text{rate} = k_{\mathrm{Cy}^{4-}}{}^{\mathrm{PbL_T}}[\mathrm{PbL^{2-}}][d\text{-}\mathrm{Cy^{4-}}] + k_{\mathrm{OH}^-}{}^{\mathrm{PbL_T}}[\mathrm{PbL^{2-}}][\mathrm{OH^-}]^n \qquad (15)$$

where

$$k_{\mathrm{Cy}^{4-}}{}^{\mathrm{PbL_T}} = k_{l\text{-}\mathrm{Cy}^{4-}}{}^{\mathrm{PbL}} + k_{d\text{-}\mathrm{Cy}^{4-}}{}^{\mathrm{PbL}} \qquad (16)$$

$$k_{\mathrm{obsd}} = k_{\mathrm{Cy}^{4-}}{}^{\mathrm{PbL_T}}[d\text{-}\mathrm{Cy^{4-}}] + k_{\mathrm{OH}}{}^{\mathrm{PbL_T}}[\mathrm{OH^-}]^n \qquad (17)$$

$$\log (k_{\mathrm{obsd}} - k_{\mathrm{Cy}^{4-}}{}^{\mathrm{PbL_T}}[d\text{-}\mathrm{Cy^{4-}}]) = \log k_{\mathrm{OH}}{}^{\mathrm{PbL}} + n \log [\mathrm{OH^-}] \qquad (18)$$

A plot of minus the left side of eq 18 *vs.* pOH (Figure 5) in which the value of $k_{\mathrm{Cy}^{4-}}{}^{\mathrm{PbL}}$ is that obtained from Figure 3 yields a slope of $n = 1.9 \pm 0.1$ and an intercept from which it is calculated that $k_{\mathrm{OH}}{}^{\mathrm{PbL}} = 0.8 \pm 1.0$. A more satisfactory value of $k_{\mathrm{OH}}{}^{\mathrm{PbL}} = 1.06 \pm 0.04\ M^{-2}$ sec^{-1} is calculated directly from eq 17 using $n = 2$, the measured value of $k_{\mathrm{Cy}^{4-}}{}^{\mathrm{PbL}}$, and each of the five observed rate constants included in Figure 5.

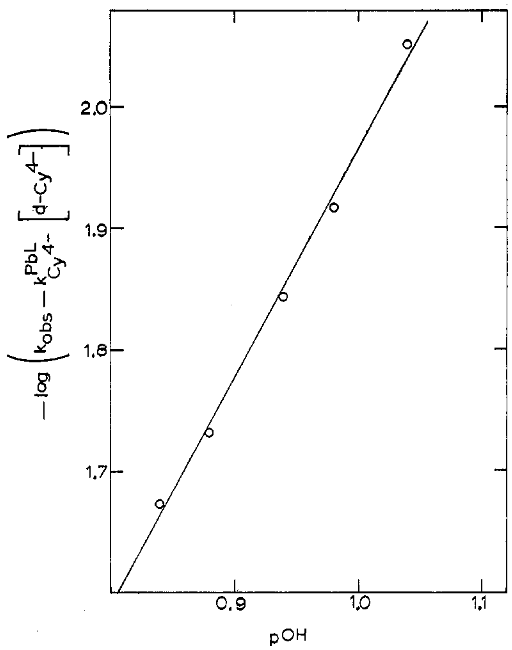

Figure 5.—Determination of $k_{\mathrm{OH}}{}^{\mathrm{PbL}}$ and reaction order dependence of hydroxide ion at pH greater than 12.8; μ = 0.50 ($\mathrm{CsNO_3}$), temperature 25°.

When racemic CyDTA is used, the pseudoequilibrium rotation (α_{pe}) is given by

$$\alpha_{\mathrm{pe}} = \alpha_{\mathrm{L}} = \alpha_{\mathrm{PbL}} + \alpha_{d\text{-}\mathrm{Cy}} + \alpha_{l\text{-}\mathrm{Cy}} + \alpha_{\mathrm{Pb}\text{-}d\text{-}\mathrm{Cy}} + \alpha_{\mathrm{Pb}\text{-}l\text{-}\mathrm{Cy}} \qquad (19)$$

where the rotation of each species is indicated by a subscript. Using the values of molar rotations of all substances and assuming total release of PDTA from lead-*l*-PDTA at pseudoequilibrium to form a total concentration of lead–CyDTA equal to the original concentration of lead-*l*-PDTA, the following relationship can be shown

$$[\mathrm{Pb}\text{-}d\text{-}\mathrm{Cy}]_{\mathrm{pe}} - [\mathrm{Pb}\text{-}l\text{-}\mathrm{Cy}]_{\mathrm{pe}} = \frac{\alpha_{\mathrm{pe}}/b - [\alpha]_{\mathrm{L}}[\mathrm{PbL}]_0}{[\alpha]_{l\text{-}\mathrm{Cy}} + [\alpha]_{\mathrm{Pb}\text{-}d\text{-}\mathrm{Cy}}} \qquad (20)$$

and the ratio of $[\mathrm{Pb}\text{-}l\text{-}\mathrm{Cy}]_{\mathrm{pe}}/[\mathrm{Pb}\text{-}d\text{-}\mathrm{Cy}]_{\mathrm{pe}}$ may be calculated. This ratio is proportional to the relative rate constants of *d*-CyDTA and *l*-CyDTA substituting lead–PDTA. It was observed that at pH less than 12.8 this ratio remains constant at ~1.5 but decreases at pH above 12.8. The value of the ratio of 1.5 is in fair agreement with the value of $k_{l\text{-Cy}}{}^{\text{PbL}}/k_{d\text{-Cy}}{}^{\text{PbL}} = 2.1$ (obtained from reactions in which optically active CyDTA was used). The value of this ratio determined *via* eq 20 is lower than the directly measured ratio because racemization of lead–CyDTA is occurring *via* eq 3 prior to pseudoequilibrium.

The decrease in the ratio $[\text{Pb-}l\text{-Cy}]_{\text{pe}}/[\text{Pb-}d\text{-Cy}]_{\text{pe}}$ at pH greater than 12.8 is consistent with the proposed hydroxide-dependent pathway in that a larger fraction of the reaction would proceed *via* the optically unselective hydroxide-dependent pathway at higher pH. Consequently, the ratio $[\text{Pb-}l\text{-Cy}]/[\text{Pb-}d\text{-Cy}]$ would be expected to approach unity as both isomers of CyDTA would be expected to attack the Pb(OH)_2 with equal probability.

In the presence of high potassium ion concentrations, much of the CyDTA is in the form of the potassium ion complex. No such complex is detectable with cesium ion. This complexation changes the apparent $\text{p}K_{\text{HCy}}$ to 12.05 and reduces the reactivity of CyDTA much as sodium ion has been shown to reduce the reactivity of EDTA.[1] Rate constants obtained from reactions performed in the presence of potassium ion are included in Table II. Attempts at their interpretation show a term first order in CyDTA^{4-} and in lead–PDTA^{2-} and a term requiring CyDTA attack on a postulated mixed intermediate, lead–$(\text{OH})_n$–PDTA. The high degree of complexation of potassium ion to CyDTA obscures observation of eq 14 in the presence of potassium ion.

Attempts to observe a Pb–$(\text{OH})_n$–PDTA species by polarimetry, uv spectroscopy, and potentiometric titration were unsuccessful, confirming Pearson's observations.[6] Stability constants for the lead–EDTA complex show that a protonated metal complex is only half formed at pH $\simeq$3.

CyDTA + Lead–PDTA (Slow Reaction).—The slow following reaction of reaction 1 was found to exhibit an apparent first-order dependence in lead–PDTA and a mixed-order dependence in CyDTA and hydroxide ion. It is proposed that the reaction of optically active lead–PDTA with one of the optical isomers of CyDTA in the fast reaction is more rapid than with the other. This results in a predominance of the slower reacting optical isomer of CyDTA and the lead complex of the rapidly reacting isomer when the rapid reaction is complete. Commercial CyDTA is the trans geometric isomer of which two optical isomers are possible. The kinetically favored product formed in the CyDTA-dependent pathway for the rapid reaction then slowly equilibrates to an equimolar mixture of lead complexes of the two optical isomers of CyDTA. The observed rotation at the completion of this slow reaction is equal to that expected for a racemic mixture of lead–CyDTA and the appropriate concentration of uncomplexed PDTA. Excellent agreement is observed between rate constants obtained from the slow following reaction of eq 1 and the direct exchange shown in eq 3. As before, the reaction is more rapid in the presence of cesium ion than in potassium.

The following parallel pathways are proposed for both the slow following reaction of eq 4 and the direct exchange in eq 3.

$$\text{Pb}(l\text{-Cy})^{2-} + d\text{-Cy}^{4-} \longrightarrow \text{Pb}(d\text{-Cy})^{2-} + l\text{-Cy}^{4-} \qquad (21)$$

and

$$\text{Pb}(l\text{-Cy})^{2-} + \text{OH}^- \longrightarrow \text{Pb(OH)}^+ + l\text{-Cy}^{4-} \qquad (22)$$

$$\text{PbOH}^+ + d\text{-Cy}^{4-} \xrightarrow{\text{fast}} \text{Pb}(d\text{-Cy})^{2-} + \text{OH}^- \qquad (23)$$

The rate of exchange may be considered as

$$\frac{-\text{d}[\text{PbCy}^{2-}]}{\text{d}t} = \text{rate} = k_{\text{Cy}^{4-}}{}^{\text{PbCy}}[d\text{-Cy}^{4-}][\text{Pb-}l\text{-Cy}^{2-}] + k_{\text{OH}}{}^{\text{PbCy}}[\text{OH}^-][\text{Pb-}l\text{-Cy}^{2-}] \qquad (24)$$

$$k_{\text{obsd}} = k_{\text{Cy}^{4-}}{}^{\text{PbCy}}[d\text{-Cy}^{4-}] + k_{\text{OH}}{}^{\text{PbCy}}[\text{OH}^-] \qquad (25)$$

A plot of k_{obsd} *vs.* $[d\text{-Cy}^{4-}]$ (Figure 6) for data from the direct reaction of *dl*-CyDTA and lead–*l*-CyDTA yields a value of $k_{\text{Cy}^{4-}}{}^{\text{PbCy}} = (3.77 \pm 0.33) \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$ with the hydroxide-dependent term entering only in cases of high pH and low CyDTA concentration. Figure 7 is an identical plot except that the data were ob-

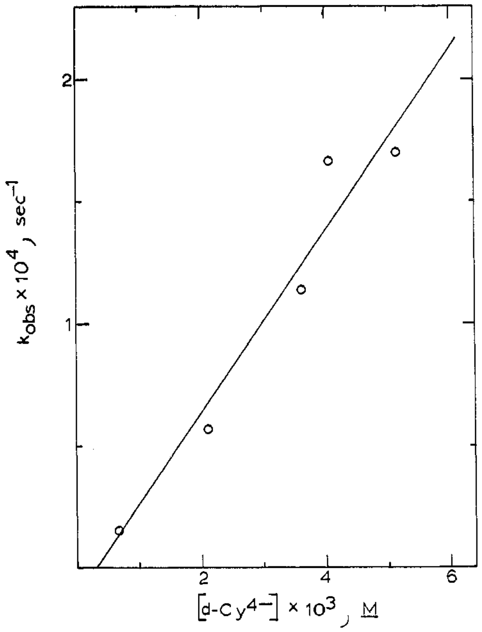

Figure 6.—Determination of $k_{\text{Cy}}{}^{\text{PbCy}}$ from the direct reaction of *dl*-CyDTA with lead–*l*-CyDTA; μ = 0.50 (CsNO_3), temperature 25°.

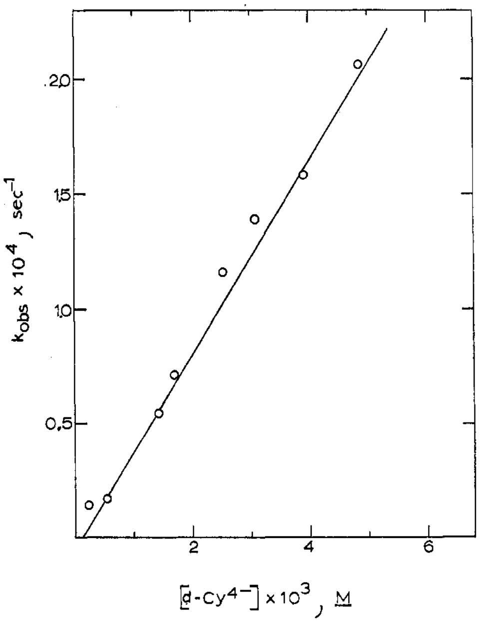

Figure 7.—Determination of $k_{\text{Cy}}{}^{\text{PbCy}}$ from the slow reaction of reaction 1; μ = 0.50 (CsNO_3), temperature 25°.

tained from the slow following reaction of reaction 1. The slope of Figure 7 yields a value of $k_{\mathrm{Cy}^{4-}}{}^{\mathrm{PbCy}} = (4.27 \pm 0.12) \times 10^{-2}\ M^{-1}\ \mathrm{sec}^{-1}$. Data for the reactions are given in Tables IV and V. A computer-aided weighted regression analysis[9] of data from reactions involving potassium ion yields $k_{\mathrm{Cy}^{4-}}{}^{\mathrm{PbCy}} = (1.7 \pm 0.8) \times 10^{-3}$ and $k_{\mathrm{OH}}{}^{\mathrm{PbCy}} = (9.0 \pm 0.6) \times 10^{-4}\ M^{-1}\ \mathrm{sec}^{-1}$. This hydroxide-dependent term is first order in hydroxide ion concentration in contrast to the second-order dependence found for reaction 1. The value of $k_{\mathrm{OH}}{}^{\mathrm{PbL}}$ should be unaffected by the presence of potassium ion but is more easily observed due to the depression of the ligand-dependent term of eq 25. Substitution of $k_{\mathrm{OH}}{}^{\mathrm{PbCy}} = 9.0 \times 10^{-4}$ and $k_{\mathrm{Cy}^{4-}}{}^{\mathrm{PbCy}} = 3.77 \times 10^{-2}$ into eq 25 gives relatively good agreement with experimental values of k_{obsd} obtained in cesium at high pH and low CyDTA concentration.

TABLE IV

OBSERVED RATE CONSTANTS FOR REACTION 3 FROM SLOW, FOLLOWING PORTION OF REACTION 1[a]

pH	$10^2[\mathrm{Cy}]_0$, M	$10^4[\mathrm{PbCy}]_0$,[b] M	10^5k_{obsd}, sec^{-1}
	25°, μ = 0.50 (CsNO$_3$)		
10.95	9.22	8.47	1.45
11.92	2.06	5.38	1.64
12.26	2.56	7.06	5.41
12.47	2.04	5.33	7.17
12.57	2.58	7.11	11.6
12.71	2.44	13.4	13.9
12.81	2.59	7.13	15.8
12.96	2.55	5.06	20.6
	25°, μ = 0.50 (KNO$_3$)		
12.56	2.00	4.68	4.63
12.73	1.50	9.36	5.60
12.89	1.50	9.36	7.60
13.05	3.10	5.44	13.0
13.06	1.50	9.36	12.8
13.17	3.00	5.44	14.8
13.19	0.901	5.44	14.7
13.19	3.00	10.88	16.0
	33°, μ = 1.3 (KNO$_3$)		
12.31	3.10	5.44	8.79
12.32	3.10	5.44	9.20
12.63	1.50	4.68	8.21
12.66	1.49	5.44	9.78
12.77	3.10	5.44	14.8
12.89	1.50	4.68	18.5

[a] The subscript zero indicates initial total concentration of all protonated forms. [b] This value assumes complete inversion from lead–PDTA in the rapid portion of reaction 1.

TABLE V

OBSERVED RATE CONSTANTS FOR REACTION 3, FROM DIRECT MIXING OF *dl*-CyDTA + Pb-*l*-CyDTA (25°, μ = 0.50 (CsNO$_3$))

pH	$10^2[dl\text{-Cy}]_0$,[a] M	$10^4[\mathrm{Pb}(l\text{-Cy})]_0$,[a] M	10^5k_{obsd}, sec^{-1}
11.89	2.94	7.62	1.53
12.40	2.92	7.46	5.67
12.40	5.60	7.26	16.6
12.69	2.95	7.54	11.4
12.90	2.97	7.59	17.0

[a] The subscript zero indicates initial total concentration of all protonated forms.

PDTA + Lead-PDTA.—Data for the rate of exchange of reaction 2 are given in Table VI. The rate constants $k_{\mathrm{L}^{4-}}{}^{\mathrm{PbL}}$ and $k_{\mathrm{HL}^{3-}}{}^{\mathrm{PbL}}$ were resolved as before (Figure 8) and are given in Table II.

TABLE VI

SECOND-ORDER RATE CONSTANTS FOR REACTION 2 (25°)

pH	$10^2[dl\text{-L}]_0$,[a] M	$10^4[\mathrm{Pb}\text{-}l\text{-L}]_0$,[a] M	$10^2k_{\mathrm{L_T}}{}^{\mathrm{PbL}}$, M^{-1} sec^{-1}
	μ = 0.50 (CsNO$_3$) *dl*-PDTA + Pb-*l*-PDTA		
9.00	2.76	8.40	0.99
9.44	2.76	8.40	3.15
9.79	2.76	8.40	8.84
9.85	2.76	8.40	8.55
9.90	2.76	8.40	7.90
10.02	2.76	8.40	9.90
10.10	2.76	8.40	16.6
10.52	2.76	8.40	31.2
10.58	2.76	8.40	46.0
10.65	2.76	8.40	43.5
10.71	2.76	8.40	49.6
pH	$10^2[\mathrm{L}]_0$,[a] M	$10^4[\mathrm{PbL}]_0$,[a] M	$10^2k_{\mathrm{L_T}}{}^{\mathrm{PbL}}$, M^{-1} sec^{-1}
	μ = 0.50 (KNO$_3$) *dl*-PDTA + Pb-*l*-PDTA		
9.36	2.62	4.68	3.23
9.79	2.62	4.68	7.60
9.98	2.26	4.68	10.8
10.03	2.62	4.68	12.3
10.57	2.62	4.68	28.6
10.85	2.62	4.68	43.4
11.40	2.62	4.68	59.7
	d-PDTA + Pb-*l*-PDTA		
9.53	2.92	4.68	4.66
10.11	1.46	4.68	13.7
10.44	1.46	4.68	24.4
10.86	1.46	4.68	49.1

[a] The subscript zero indicates initial total concentration of al protonated forms.

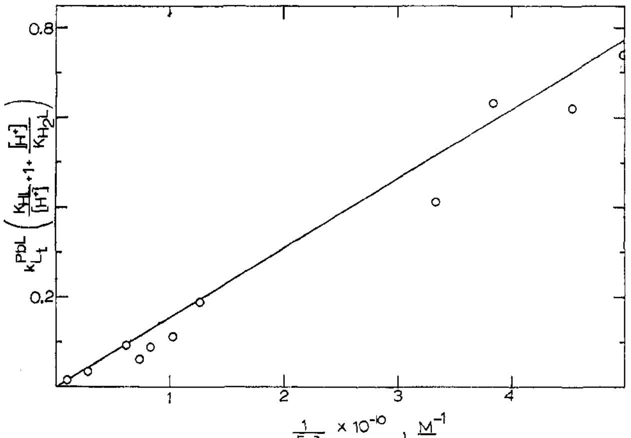

Figure 8.—Resolution of $k_{\mathrm{L}}{}^{\mathrm{PbL}}$ and $k_{\mathrm{HL}}{}^{\mathrm{PbL}}$ in the presence of Cs$^+$; μ = 0.50 (CsNO$_3$), temperature 25°.

In order to obtain values of K_{HL} in potassium ion, the fourth acidity constant of PDTA, at different temperatures, which were necessary for the resolution plots, it was assumed that the heat of ionization of PDTA is the same as for EDTA.[7] The value of pK_{HL} for PDTA at 25°[1] was then extrapolated to other temperatures. Values of log K_{HL} thus obtained are as follows: at 18°, log K = 10.73; at 30°, log K = 10.51; at 35°, log K = 10.42. The value of this content in cesium ion is taken from ref 4. Figure 9 shows the resolution of $k_{\mathrm{L}^{4-}}{}^{\mathrm{PbL}}$ at different temperatures in potassium ion.

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(9) R. F. Munn, "General Regression System for IBM System 360," Statistical Laboratory Report No. 1, The Statistical Laboratory, University of Nebraska, Lincoln, Nebr.

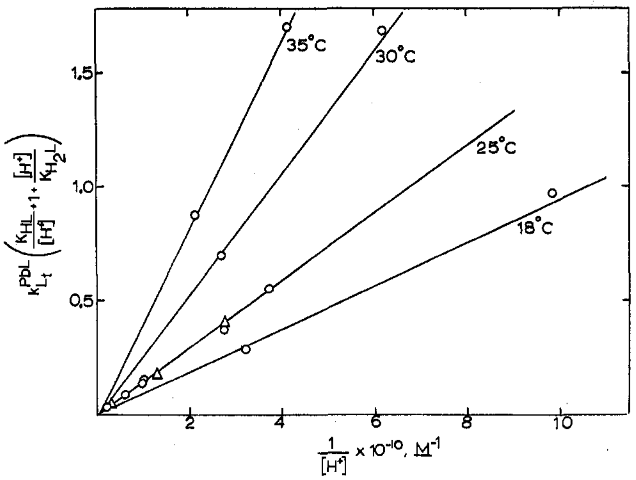

Figure 9.—Resolution of $k_L{}^{PbL}$ and $k_{HL}{}^{PbL}$ in the presence of K^+ and at different temperatures (μ = 0.50 (KNO_3)): ○, from exchange of *dl*-PDTA with lead–*l*-PDTA; △, from exchange of *d*-PDTA with lead–*l*-PDTA.

The activation energy for reaction 2 was then calculated to be 8.87 ± 0.69 kcal/mol and the frequency factor was $10^{6.33\pm1.03}$ M^{-1} sec^{-1}.

This rate constant is also resolved from data at 25° taken in the presence of cesium ion and found to be nearly 3 times the value taken in potassium (Table II).

Discussion

The stability of the potassium complexes of CyDTA and PDTA is considerable[3,4,10] (K_{KCy} = 33 (3) and K_{KL} = 8.06 (4)). In the presence of high potassium activities, only a small fraction of either ligand exists as the tetraanion. This causes an apparent decrease in the acidity constant of each ligand and a decrease in the rate of their ligand substitution reactions. This decrease is more severe when CyDTA, with its greater potassium stability, is the attacking ligand ($k_{Cy}{}^{PbL}$ = 4.00 (Cs^+) and 0.18 (K^+)). Ligand substitutions of PDTA are also depressed significantly ($k_L{}^{PbL}$ = 1.58 (Cs^+) and 0.60 (K^+)) but those of EDTA should be affected only slightly since the potassium stability constant of EDTA is probably less than unity. Cesium ion apparently forms no such complex ions with either CyDTA or PDTA. These kinetic problems with potassium ion are similar to those encountered previously with sodium ions in reactions with EDTA.[1]

Attempts to resolve the kinetics of eq 1 using data obtained from reactions performed in the presence of potassium ion require the postulation of stable mixed complexes of the stoichiometry $Pb(OH)_nL$ which are unobservable. Such conclusions are an artifact of the incorrect choice of ligand acidity constant (hence an incorrect tetraanion concentration) and a low reactivity of potassium–CyDTA in eq 1. Similar considerations should be applied to the substitution reaction of CyDTA and lead–EDTA described in ref 6.

If the exchange of EDTA with lead–EDTA is considered as having no substituent effects, it is concluded that added bulkiness due to alkyl substituents on the leaving ligand is effective in slowing the exchange reaction but that identical added bulkiness of the entering ligand has no steric effect. This can be seen by comparing appropriate rate constants presented in Table II. For the three reactions of EDTA, *d*-PDTA, and *d*-CyDTA attacking lead–*l*-PDTA, the rate constants are remarkably similar. For comparisons of a given ligand attacking a selection of lead complexes, the rate constant in cesium decreases with increased bulkiness of the leaving ligand. An example is CyDTA substituting lead–EDTA, lead–PDTA, and lead–CyDTA (rate constants of 9, 2.9 (1.4), and 0.038, respectively). This all implies that the rate-determining step in these reactions must come rather early in the stepwise substitution process in order that the bulky substituents of the entering ligand not have contacted the coordination sphere of the initial complex ion. Such contact would surely slow the reaction rate by lowering the stability of the intermediate prior to the rate-determining step. An early rate-determining step is consistent with the mechanism previously proposed for this class of reactions.[11] Also consistent with earlier studies is the observation that the rate constant of the protonated form of any of the ligands is immeasurably slow compared to that of the unprotonated ligand.

The observed decrease in rate constant as substituents are added to the leaving ligand must be due to slower breaking of metal–ligand bonds and a greater barrier to rotation after breaking the first lead–nitrogen bond.

The apparent decrease in reaction rate with additional alkyl substituents on the entering ligand in the presence of potassium ion is due only to a corresponding increase in the potassium ion stability constant and hence a smaller fraction of each ligand actually present as the tetraanion. This apparent decrease in rate constant does not reflect differing steric requirements of the entering ligands.

If it is assumed that the potassium complexes of CyDTA and PDTA are unreactive in substitution reactions (much like the protonated ligands) and that the rate decrease is due solely to decrease in tetraanion concentration, the rate constants in the two media are interrelated as shown in

$$k_{Cy(K^+)}{}^{PbCy} = k_{Cy(Cs^+)}{}^{PbCy}[1/(1 + K_{KCy}[K^+])] \qquad (26)$$

Using the referred values of potassium stability constants with PDTA and CyDTA and 0.5 M K^+, the ratio of rate constants calculated from eq 26 in cesium to potassium medium is 17 for CyDTA and 5 for PDTA substituting lead complexes. These ratios are in fair agreement with the observed ratios of 22 and 2.5, respectively. The two cases in which CyDTA substitutes both lead–PDTA and lead–CyDTA give the identical rate constant ratios. Similar calculations for systems not measured in cesium lead to values included as estimates in Table II. No major changes are expected for reactions in which EDTA is the attacking ligand.

The alkyl substituents also demonstrate an inductive effect and increase the basicity of the ligand nitrogen atoms as measured by acid–base titrations in which, presumably, steric blocking is of minimal importance.

Ligand	pK_4	Ligand	pK_4	Ligand	pK_4
EDTA	10.0	PDTA	11.01	CyDTA	13.17

The relative basicities of the ligands and linear free energy relationships would predict that the order of rate constants for the exchange of the three ligands with lead–PDTA would be $k_{Cy}{}^{PbL} > k_L{}^{PbL} > k_Y{}^{PbL}$. This

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[10] J. L. Sudmeier and A. J. Senzel, *Anal. Chem.*, **40**, 1693 (1968).

[11] J. D. Carr and C. N. Reilley, *ibid.*, **42**, 51 (1970).

order is not observed, the conclusion being that basicity of the entering ligand does not determine the magnitude of the rate constants. Rather, the leaving ligand is of the most importance in this regard.

It was observed that there is a kinetic preference for one optical isomer of CyDTA in attacking the optically active lead–PDTA. This is in partial agreement with recent observations by Pearson, *et al.*,[12] in which different rates for the exchange of *l*-CyDTA with the two isomers of lead–PDTA were reported. The product of this reaction then slowly exchanges with the other isomer to give as final product the racemic mixture of the two CyDTA complexes with lead ion.

The exchange of *d*-PDTA with lead–*l*-PDTA shows the same rate constant when the *d*-PDTA is added as an optically pure reagent and when it is added as the racemic mixture of *d*- and *l*-PDTA. This demonstrates only that the exchange of *l*-PDTA with lead–*l*-PDTA does not remove an appreciable fraction of lead complex as a reaction intermediate at any given time. The concentration of any mixed-ligand intermediate Pb-$(PDTA)_2^{6-}$ is less than 1% of the total lead complex concentration.

The structure of the intermediate prior to hydroxide-dependent dissociation of lead–PDTA is visualized to have one nitrogen–lead bond broken and an iminodiacetate segment rotated away from the lead ion. The lead ion then is coordinated to the remaining iminodiacetate group and two hydroxide ions. The analogous intermediate for lead–CyDTA contains only a single hydroxide ion which is sufficient to block the much more rigid ligand from rebonding the lost iminodiacetate group. Both intermediates are subject to rapid loss of the remainder of the original ligand, without help from the substituting ligand.

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[12] K. H. Pearson, W. R. Howell, and P. E. Reinbald, Anachem Conference, Detroit, Mich., Oct 1970.

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The Chemistry of Sodium Bis(borane)dimethylamide(1−)

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In monoglyme solution μ-dimethylaminodiborane and sodium borohydride reversibly form sodium heptahydrodiborate(1−) and sodium bis(borane)dimethylamide(1−), $Na(CH_3)_2N(BH_3)_2$. The latter compound cannot be isolated by solvent removal owing to the volatility of μ-dimethylaminodiborane but may be prepared quantitatively by reaction of sodium hydride with μ-dimethylaminodiborane in monoglyme. Sodium bis(borane)dimethylamide(1−) reacts with diborane to form μ-dimethylaminodiborane and sodium heptahydrodiborate(1−); boron exchange does not occur. Treatment of a monoglyme solution of sodium bis(borane)dimethylamide(1−) with hydrogen chloride results in chlorination and solvent cleavage. Sodium bis(borane)dimethylamide(1−) reacts with ammonium chloride and mono-, di-, and trimethylammonium chloride to form ammonia or amine adducts of μ-dimethylaminodiborane. At lower than ambient temperature the intermediate salt $[(CH_3)_2NH_2][(CH_3)_2N(BH_3)_2]$ can be isolated.

Introduction

Very few examples of compounds with two equivalent borane groups bonded to the same donor atom have been reported. The first to be characterized was the bis-borane adduct of the dihydrogenphosphide(1−) ion, $H_2P(BH_3)_2^-$.[1] Subsequently the sulfur compound $[(C_2H_5)_4N][HS(BH_3)_2]$[2] and another phosphorus complex $Li(CH_3)_2P(BH_3)_2$[3] have been described. Recent studies in this laboratory on the reaction of diborane with $Na(CH_3)_2NBH_3$[4,5] led to the discovery and preliminary description of the first example of a nitrogen complex $Na(CH_3)_2N(BH_3)_2 \cdot 0.5diox$ (I).[6] This paper details the preparation and characterization of I and discusses some of its chemical reactions.

Experimental Section

General Information.—Conventional high-vacuum and glove bag techniques were used in this investigation. The pure solvents diethyl ether, monoglyme (1,2-dimethoxyethane), diglyme (bis(2-methoxyethyl) ether), and dioxane were stored in evacuated bulbs over lithium aluminum hydride and, when needed, were condensed directly into the reaction vessel. Boron-11 nmr spectra were obtained with a Varian HA-100 spectrometer operating at 32.1 MHz equipped with standard variable-temperature accessories; proton nmr spectra were obtained with Varian HA-100 and A-60 instruments. Boron-11 and proton chemical shifts are reported in ppm relative to diethyl ether–boron trifluoride and tetramethylsilane, respectively. Signals at lower field than the standard have negative chemical shifts. Infrared spectra were obtained using Perkin-Elmer 137 and 337 spectrophotometers. A KBr matrix was used for solids; a 5- or 10-cm cell with NaCl windows was used for gases.

Boron-10 diborane was prepared by the lithium aluminum hydride reduction of $(C_2H_5)_2O \cdot {}^{10}BF_3$ (96% ^{10}B; $^{10}BF_3$ obtained as $CaF_2 \cdot {}^{10}BF_3$ from Oak Ridge National Laboratory). The μ-dimethylaminodiborane was prepared from the reaction of diborane with $Na(CH_3)_2NBH_3$.[4] Sodium hydride was freed of mineral oil by repeated washing with cyclohexane under a blanket of dry nitrogen. Other reagents used in this work were purchased

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