Although in each conformer $H_{A'}$, $H_{A''}$, $H_{X'}$, and $H_{X''}$ are all nonequivalent, if conformational interconversion is rapid, $H_{A'}$ will become equivalent to $H_{A''}$ and $H_{X'}$ to $H_{X''}$. The additional peaks observed in the methylene region in the 100-MHz spectrum of $[Pd((\pm)dptn)_2]Cl_2$ may arise because $J_{A'X'} \neq J_{A'X''}$ in any particular chair conformation. If this conformational type is preferred, each methyl group would be in the required orientation for Pt–N–C–CH_3 coupling (*i.e.*, equatorial) for only 50% of the time, which could account for the absence of such coupling.

There are two different skew-boat conformations. In one of these (R_1, R_6 = CH_3, other R = H in Figure 8b) both methyl groups are equatorial and in the other (R_2, R_5 = CH_3) both are axial. The former would be expected to be favored over the latter, so that if the skew-boat conformation were preferred (*i.e.*, if the necessity of having one methyl group axial in the chair conformation sufficiently destabilizes it), the ring would be expected to exist almost exclusively in this conformation. Some complication of the spectrum of the methylene protons might be expected because coupling constants with the H_X protons would not all be equal.

Changes with Temperature.—The lack of significant change in the spectra on heating would be expected if conformational interconversion is already rapid at 30°. The behavior on cooling implies that conformational interchange in methanol and acetone has begun to slow down below −50°, but even at −100° it is not sufficiently slow for spectra of individual conformers to be detected. The temperatures at which broadening becomes noticeable are remarkably independent of the size of the chelate ring or the nature of the substituents, being similar for all of the complexes examined. In the glycol–water and DMSO–water mixtures the broadening at −35°, apart from that associated directly with increased viscosity of the solution, probably occurs because N–H protons interact strongly by H bonding with the solvent molecules. As the solvent becomes more rigid, conformational equilibrations will be slowed down.

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Multidentate Ligand Kinetics. XIV. Formation and Dissociation Kinetics of Rare Earth–Cyclohexylenediaminetetraacetate Complexes

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The rate of transfer of *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate (CyDTA) from rare earth ions to copper(II) is dependent on hydrogen ion concentration and independent of copper concentration. The acid dissociation rate constants, k_H^{MCy} (25°, 0.1 μ), vary from the value of 129 M^{-1} sec^{-1} for $La(CyDTA)^-$ to a value of 0.017 M^{-1} sec^{-1} for $Lu(CyDTA)^-$, decreasing in a regular fashion with decreasing ionic radii. All the rare earth 3+ ions (including Y^{3+}) follow this behavior but Sc^{3+} does not. The value for k_H^{ScCy} is 0.019 M^{-1} sec^{-1} which is several orders of magnitude larger than expected from comparison of ionic radii or of stability constants. In direct formation reactions the Sc^{3+} and CyDTA reaction is too fast to measure by stopped-flow methods at pH 4.2. On the other hand La^{3+} reacts at a measurable rate, rapidly forming a weak complex with $H(CyDTA)^{3-}$ followed by a slower first-order reaction in which La^{3+} is incorporated into the coordination cage of the ligand and displaces the proton. With the exception of Sc^{3+} all the ions are much slower in their formation rate constants than expected from their water exchange constants or their reaction with murexide.

Introduction

The rates of formation of complexes of many metal ions (M) with ligands (L) follow the general expression in eq 1 where K_{os} is the outer-sphere association con-

$$\text{rate} = K_{os}k^{M-H_2O}[M][L] \qquad (1)$$

stant and k^{M-H_2O} is the characteristic water exchange constant for the metal ion.[2,3] In the case of multidentate ligands eq 1 often is valid because the first water-substitution step is rate determining. However, the structure of the multidentate ligand can greatly alter the rate from that predicted if several coordination steps must occur simultaneously as is the case in some macrocyclic structures.[4] The reactions of CyDTA (*trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate) with divalent metal ions have been shown[5] to fall into two groups. One group including Co(II), Ni(II),

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Cu(II), and Zn(II) reacts with the monoprotonated form of CyDTA, HCy^{3-}, at rates consistent with eq 1. With these ions acetate coordination appears to occur prior to the rate-determining step of nitrogen coordination to the metal and K_{os} can be modified accordingly, but k^{M-H_2O} is essentially unaffected. A second group of metals including Mg(II), Ca(II), Sr(II), and Ba(II)[6] react with HCy^{3-} at rates as much as 1000 times slower than predicted by eq 1. The slower reactions can be attributed to the inability of the alkaline earth ions to form an intermediate with one CyDTA nitrogen coordinated to the metal ion if a proton is on the other nitrogen. As a result the proton must be transferred as the metal ion enters into coordination with both nitrogens. The CyDTA ligand provides a coordination cage which makes it difficult for the metal in the cage to be coordinated to only one nitrogen. Even the unprotonated ligand, Cy^{4-}, reacts with Sr^{2+} and Ba^{2+} at much slower rates than predicted from their characteristic water-exchange rate constants. Hence, with some metal ions the necessity for simultaneous desolvation steps coupled with proton transfer causes the effective k^{M-H_2O} values to be much smaller with CyDTA than in monodentate substitution reactions.

In the present study the reactions of Sc^{3+}, Y^{3+}, La^{3+}, and the lanthanide(III) ions with CyDTA are studied. Geier[7] has measured the reaction rates of these ions in relaxation studies with murexide and suggests that the murexide rate constants provide good guide lines for their characteristic water-exchange constants.[8] Studies by $H_2{}^{17}O$ nmr with Gd(III)[9] and with Dy(III)[10] are in general agreement with Geier's results. Therefore, the effect of the ligand structure of CyDTA on the coordination rate constants can be determined and the rare earth ions permit a systematic study of the effect of metal ion size on the mechanism.

Experimental Section

The acid form of CyDTA (LaMont Laboratories) was recrystallized by dissolving in dilute NaOH followed by the addition of dilute $HClO_4$. Solutions were standardized by complexometric titration with copper nitrate using murexide indicator with ammonia buffer at pH 8.

The rare earth oxides, 99–99.9% pure (American Potash and Chemical Corp.), were dissolved in dilute $HClO_4$. The solutions were standardized by EDTA titration with murexide indicator in the presence of acetate buffer. The rare earth–CyDTA complexes were prepared in solution using 2% excess CyDTA and the pH was adjusted to about 5.

The ionic strength was adjusted to 0.1 *M* with $NaClO_4$. The hydrogen ion concentration was calculated from pH measurements using $-\log [H^+] = pH - 0.11$.

Thermostated (±0.1°) spectrophotometers were used for measurements of the dissociation rates of the rare earth–CyDTA complexes. The reactions were initiated by adding a small aliquot of the metal–CyDTA solution to solutions containing $NaClO_4$, buffer, and excess copper(II). The reaction observed is given in eq 2 and the absorbance of the $CuCy^{2-}$ was measured

$$MCy^- + Cu^{2+} \longrightarrow CuCy^{2-} + M^{3+} \qquad (2)$$

at 268 mμ (ϵ_{CuCy} 3.3×10^3 M^{-1} cm^{-1}). The rate of the reaction in eq 2 is independent of the copper concentration as shown in Table I and $d[CuCy^{2-}]/dt = k_0[MCy^-]$. However, the reaction rate depends on the hydrogen ion concentration in the same manner observed in the reactions of divalent metal ions.[5,6,11] The reaction mixtures contained acetate buffer (generally at 5×10^{-3} *M* total acetate). Table II shows that the acetate concentration does not significantly affect the observed first-order rate constants. This is in agreement with the results of Glentworth, *et al.*,[12] for the radiochemical exchange of Ce^{3+} and $CeCy^-$.

TABLE I

INDEPENDENCE OF THE RARE EARTH–CyDTA DISSOCIATION KINETICS WITH COPPER CONCENTRATION[a]

Metal	$10^4[Cu^{2+}]$, *M*	k_0, sec^{-1}
Gd	1.30	3.1×10^{-5}
	0.65	3.1×10^{-5}
Tb	1.30	1.4×10^{-5}
	0.65	1.6×10^{-5}
Ho	1.30	3.6×10^{-6}
	0.65	3.8×10^{-6}
Er	1.30	2.1×10^{-6}
	0.65	2.1×10^{-6}
Tm	1.30	1.2×10^{-6}
	0.65	1.0×10^{-6}
Lu	1.30	4.8×10^{-7}
	0.65	5.1×10^{-7}
Y	1.30	9.0×10^{-5}
	0.65	9.3×10^{-5}

[a] Initial $[MCy^-] = 1.27 \times 10^{-5}$ *M*, $[H^+] = 2.1 \times 10^{-5}$ *M*, μ 0.1, 25°.

TABLE II

INDEPENDENCE OF $LaCy^-$ AND $GdCy^-$ DISSOCIATION KINETICS WITH ACETATE CONCENTRATION[a]

CyDTA complex	$10^5[H^+]$, *M*	10^2[acetate], *M*	k_0, sec^{-1}
La	1.26	1.0	1.90
	1.29	2.0	2.02
	1.26	3.0	2.29
	1.29	4.0	2.14
	1.32	5.0	2.13
Gd	1.29	2.0	3.4
	1.29	4.4	3.2
	1.38	2.0	3.3
	1.38	4.4	3.0

[a] $[LaCy]_0 = 1.27 \times 10^{-5}$ *M*, $[Cu^{2+}]_0 = 1.30 \times 10^{-4}$ *M*, *T* = 25.0°.

The acidities of the reaction mixtures for eq 2 were sufficiently low to prevent appreciable formation of MHCy species.[13]

The rate of complex formation of $LaCy^-$ from aqueous La^{3+} and CyDTA solutions was measured at 240 mμ on a Durrum–Gibson stopped-flow spectrophotometer.

Results

Dissociation Reactions.—The exchange reactions in eq 2 depend on the hydrogen ion concentration and the reaction is first order in the dissociating MCy^- complex. The observed first-order rate constants for each metal and temperature are given in Table III. When k_0 is plotted against the $[H^+]$ for each set of data a straight line results which usually has a significant intercept in accord with eq 3. The acid dependent

$$k_0 = k_d{}^{MCy} + k_H{}^{MCy}[H^+] \qquad (3)$$

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TABLE III

EFFECT OF ACIDITY ON RARE EARTH–CyDTA DISSOCIATION KINETICS[a]

	$10^5[\mathrm{H}^+]$, M	10^3k_0, sec^{-1}
La-15°	7.8	4.6
	5.8	3.3
	5.1	2.83
	3.24	2.04
	2.09	1.54
	1.15	0.74
	0.51	0.35
La-25°	12.3	17.0
	11.0	13.2
	9.6	11.5
	8.0	10.5
	6.0	7.4
	4.9	6.2
	3.24	4.2
	2.09	2.8
	1.07	1.19
	0.55	0.60
La-35°	8.5	26.0
	6.6	13.5
	5.1	14.9
	3.72	11.4
	2.24	5.9
	1.32	5.5
	0.58	1.46
Ce-25°	12.9	8.0
	10.7	5.7
	9.3	5.7
	8.1	5.5
	5.9	3.9
	5.0	3.7
	3.72	2.40
	1.26	0.95
	0.525	0.53
Pr-25°	13.8	5.0
	12.0	3.8
	11.0	3.8
	9.8	3.7
	7.2	2.7
	5.2	2.2
	3.31	1.14
	1.10	0.44
	0.49	0.27
	$10^5[\mathrm{H}^+]$, M	10^4k_0, sec^{-1}
Nd-25°	11.2	19.4
	10.2	17.3
	9.1	14.9
	6.8	12.5
	4.9	10.1
	4.36	8.3
	3.09	5.4
	2.00	3.9
	1.00	2.4
	0.38	1.63
	0.42	1.18
Sm-25°	12.6	6.9
	12.0	6.6
	10.5	5.6
	8.0	4.53
	6.5	3.5
	4.57	3.2
	3.02	1.77
	1.70	1.30
	1.21	0.94
	0.46	0.65
	$10^5[\mathrm{H}^+]$, M	10^4k_0, sec^{-1}
Eu-25°	13.5	3.5
	10.7	2.3
	9.9	2.3
	8.3	1.7
	6.0	0.9
	4.36	1.0
	3.32	1.0
	2.04	0.6
	0.54	0.2
Gd-15°	13.2	0.94
	12.6	0.88
	10.5	0.89
	10.0	0.57
	8.1	0.53
	6.0	0.43
	2.05	0.22
Gd-25°	13.2	2.16
	10.2	1.38
	8.7	1.15
	6.4	1.04
	4.9	0.82
	3.16	0.45
	1.91	0.39
	1.07	0.27
	0.72	0.18
	0.38	0.16
Gd-35°	11.0	3.21
	10.5	2.78
	9.1	2.27
	6.5	2.32
	6.2	1.80
	3.9	1.15
	$10^5[\mathrm{H}^+]$, M	10^5k_0, sec^{-1}
Tb-25°	14.8	8.8
	12.9	7.9
	10.8	6.5
	10.0	5.8
	7.3	4.9
	5.5	3.6
	4.08	2.9
	2.04	1.41
	1.35	1.01
	0.64	0.76
Dy-15°	10.7	1.54
	10.2	1.33
	9.6	1.16
	7.6	0.87
	6.2	0.74
	4.6	0.52
	3.16	0.45
Dy-25°	12.6	3.8
	12.0	3.5
	10.2	2.8
	8.1	2.19
	6.3	1.62
	4.8	1.30
	3.54	1.02
	2.04	0.68
	1.26	0.44
	0.54	0.27
	$10^5[\mathrm{H}^+]$, M	10^5k_0, sec^{-1}
Dy-35°	14.1	8.1
	13.2	7.2
	10.7	6.3
	9.8	5.3
	8.1	3.8
	6.2	3.3
	4.08	2.7
	$10^5[\mathrm{H}^+]$, M	10^6k_0, sec^{-1}
Ho-25°	12.3	17.1
	11.0	15.6
	10.2	15.2
	7.8	11.0
	6.2	8.5
	6.0	8.1
	3.47	5.6
	2.04	3.6
	1.26	2.5
	0.64	1.7
Er-25°	13.5	11.4
	11.2	7.0
	10.7	6.2
	8.5	5.3
	7.4	4.2
	5.1	3.06
	3.16	2.38
	2.14	2.10
	1.10	0.98
	0.58	1.01
Tm-15°	12.3	1.89
	11.2	1.66
	8.3	1.17
	6.4	1.02
	4.9	0.73
	3.55	0.49
Tm-25°	13.5	4.70
	12.3	4.43
	11.0	4.10
	8.3	3.56
	6.8	3.03
	4.8	2.34
	2.88	2.23
	2.14	1.19
	1.26	0.5
	0.63	0.44
Tm-35°	13.2	13.6
	13.2	14.0
	11.2	10.8
	10.0	10.4
	8.1	6.7
	6.2	5.5
	4.26	4.4
Yb-25°[b]	13.7	3.3
	8.4	2.0
	4.7	1.4
	3.9	0.89
	2.14	0.54
	1.35	0.39
	0.85	0.23
	0.51	0.18
	$10^5[\mathrm{H}^\dagger]$, M	10^6k_0, sec^{-1}
Lu-15°	12.3	0.67
	10.5	0.53
	9.8	0.46
	8.1	0.43
	5.9	0.37
	5.1	0.35
	3.47	0.21
Lu-25°	14.1	2.52
	11.5	2.17
	10.7	1.94
	9.3	1.63
	7.2	1.22
	5.1	0.93
	3.63	0.85
	2.14	0.48
	1.29	0.34
	0.56	0.19
Lu-35°	12.3	5.1
	11.0	5.0
	9.8	4.3
	8.0	4.0
	6.2	3.3
	4.7	2.3
	3.72	1.9
	$10^5[\mathrm{H}]$, M	10^6k_0, sec^{-1}
Y-15°	12.3	1.80
	11.5	1.61
	10.0	1.49
	8.3	0.99
	6.3	0.89
	4.9	0.72
	3.32	0.49
Y-25°	12.6	4.52
	11.5	4.45
	10.0	3.39
	8.9	3.24
	6.5	2.34
	5.2	1.92
	3.39	1.40
	1.95	0.90
	1.23	0.66
	0.54	0.33
	14.1	5.37
	8.3	3.42
Y-35°	12.3	11.9
	10.2	8.7
	9.1	8.1
	7.8	7.0
	6.0	5.1
	4.3	5.1
	3.16	3.8
	$10^4[\mathrm{H}^+]$, M	10^6k_0, sec^{-1}
Sc-25°[c]	12.3	28.1
	10.0	18.4
	8.1	17.8
	7.2	12.3
	5.0	10.0
	4.0	6.7
	2.51	5.3

[a] $[\mathrm{MCy}]_0 = 1.27 \times 10^{-5}$ M, $[\mathrm{Cu}^{2+}]_0 = 1.30 \times 10^{-4}$ M, [acetate] = 0.005 M, μ 0.1. [b] $[\mathrm{MCy}^-]_0 = 1.27 \times 10^{-4}$ M, $[\mathrm{Cu}^{2+}]_0 = 1.30 \times 10^{-3}$ M, [acetate] = 0.010 M. [c] Measured by initial rates.

TABLE IV

RESOLVED RATE CONSTANTS FOR DISSOCIATION OF RARE EARTH–CyDTA COMPLEXES 25.0°, μ 0.1, Cu^{2+} AS SCAVENGER

Metal	k_H^{MCy}, M^{-1} sec^{-1} [a]	k_d^{MCy}, sec^{-1} [a]
La	129 ± 3	$-(1.1 \pm 0.4) \times 10^{-4}$
Ce	60 ± 2	$(2.0 \pm 0.5) \times 10^{-4}$
Pr	35 ± 1	$(1.0 \pm 0.2) \times 10^{-4}$
Nd	16.2 ± 0.6	$(9.2 \pm 1.1) \times 10^{-5}$
Sm	5.0 ± 0.2	$(4.0 \pm 0.4) \times 10^{-5}$
Eu	2.2 ± 0.2	$(9.8 \pm 3.4) \times 10^{-6}$
Gd	1.3 ± 0.1	$(1.0 \pm 0.1) \times 10^{-5}$
Tb	0.58 ± 0.02	$(3.2 \pm 0.4) \times 10^{-6}$
Dy	0.26 ± 0.01	$(1.2 \pm 0.2) \times 10^{-6}$
Ho	0.132 ± 0.003	$(8.5 \pm 0.7) \times 10^{-7}$
Er	0.053 ± 0.004	$(6.1 \pm 1.0) \times 10^{-7}$
Tm	0.028 ± 0.002	$(2.3 \pm 0.4) \times 10^{-7}$
Yb	0.023 ± 0.001	$(5.4 \pm 1.4) \times 10^{-7}$
Lu	0.017 ± 0.001	$(1.1 \pm 0.1) \times 10^{-7}$
Y	0.36 ± 0.01	$(1.7 \pm 0.2) \times 10^{-6}$
Sc	0.019 ± 0.002	$-(1.1 \pm 1.0) \pm 10^{-7}$

[a] Uncertainties are standard deviations.

(k_H^{MCy}) and acid independent (k_d^{MCy}) rate constants in Table IV were resolved with a weighted least-square regression analysis computer program. The precision of the values for the k_H^{MCy} constants is much better than for the k_d^{MCy} constants. In the case of La and Sc the intercepts are slightly negative and their k_d^{MCy} values at 25° must be taken as zero within experimental error.

The values of k_H^{CeCy}, k_H^{NdCy}, and k_H^{LuCy} in Table IV are in fair agreement with the results of radioisotope exchange kinetic studies for $CeCy^-$,[12] $NdCy^-$,[14] and $LuCy^-$ [15] at 20°.

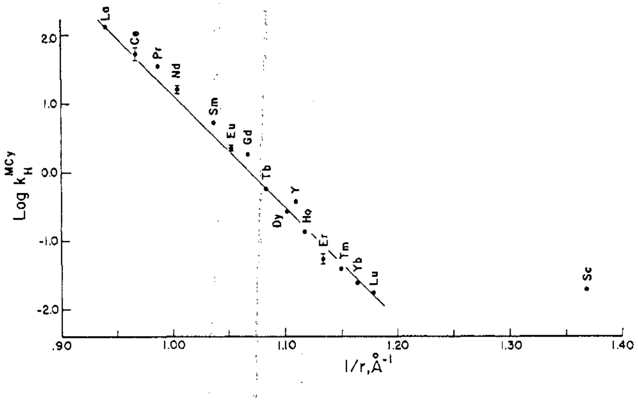

Figure 1.—Logarithmic rate constants for the acid dissociation of rare earth–CyDTA complexes, plotted *vs.* reciprocal +3 ion radius.

Figure 1 shows a regular change in k_H^{MCy} value with the reciprocal of the ionic radius[16] from La^{3+} to Lu^{3+}. The value for Y^{3+} falls on the curve but Sc^{3+} shows a markedly different behavior than would be expected from extrapolation of the plot.

The logarithmic acid-independent dissociation rate constants for yttrium and the lanthanides also plot fairly linearly *vs.* the reciprocal ionic radius, as seen in Figure 2. The ranges of log k_d^{MCy} and log k_H^{MCy} are about equal.

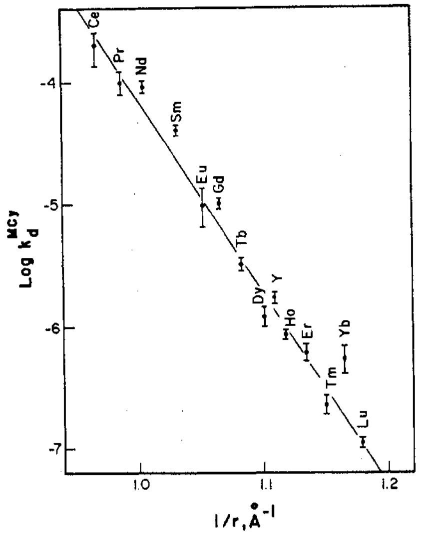

Figure 2.—Logarithmic rate constants for the acid-independent dissociation of lanthanide–CyDTA complexes, plotted *vs.* reciprocal +3 ion radius.

The temperature study of the dissociation rates gave the activation parameters in Table V. The values of $\Delta G^\ddagger$ for the systems closely parallel the difference in the standard free energies of the particular metal–iminodiacetate[17a] and the metal–CyDTA[17b] complexes. The transition state of the reactions may therefore contain a metal–iminodiacetate moiety, as was found for some divalent metal–CyDTA reactions.[5]

TABLE V

ACTIVATION PARAMETERS FOR THE ACID DISSOCIATION OF RARE EARTH–CyDTA COMPLEXES[a]

Metal	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal/deg mol	$\Delta G^\ddagger$, kcal/mol	$\Delta G^\circ_{MIDA} - \Delta G^\circ_{MCy}$, kcal/mol[b]
La	13.0 ± 0.3	−5.2 ± 1.1	14.6 ± 0.4	15.1
Gd	12.8 ± 1.0	−14.8 ± 3.5	17.2 ± 1.4	17.6
Dy	12.7 ± 0.2	−18.5 ± 0.8	18.2 ± 0.3	18.5
Tm	17.4 ± 0.1	−6.9 ± 0.5	19.4 ± 0.2	19.6
Lu	19.2 ± 2.3	−2.1 ± 7.8	19.8 ± 3.2	19.6
Y	14.7 ± 1.3	−11.0 ± 4.4	18.0 ± 0.8	17.8

[a] Calculated from data obtained at 15, 25, and 35°. Uncertainties are standard deviations. [b] The ΔG°_{MIDA} is the metal–iminodiacetate standard free energy from ref 17a. The ΔG°_{MCy} is the metal–CyDTA standard free energy from ref 17b.

Formation Reactions.—If the value of k_H^{MCy} and the stability constants K_{HCy} and K_{MCy} are known from the reaction

$$\mathrm{MCy^- + H^+ \underset{k_M^{HCy}}{\overset{k_H^{MCy}}{\rightleftarrows}} HCy^{3-} + M^{3+} \xrightarrow[\text{fast}]{Cu^{2+}} products} \qquad (4)$$

it is possible to calculate k_M^{HCy} from the relation

$$k_M^{HCy} = \frac{k_H^{MCy} K_{MCy}}{K_{HCy}} \qquad (5)$$

as is done for the CyDTA complexes of the divalent transition metals.[5,6] The lanthanum–, yttrium–, and

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lanthanide–CyDTA constants and the K_{HCy} values of Moeller and Hseu[13] (measured at 25°), as well as the K_{ScCy} value of Hiller and Powell (measured at 20°)[18] were used to calculate the $k_M{}^{HCy}$ values in Table VI.

Table VI

Calculated Metal–CyDTA Formation Rate Constants[a]

Metal	$10^{-7}k_M{}^{HCy}$, M^{-1} sec^{-1}	Metal	$10^{-7}k_M{}^{HCy}$, M^{-1} sec^{-1}
La	0.8 ± 0.1	Dy	3.4 ± 0.3
Ce	1.0 ± 0.2	Ho	2.7 ± 0.3
Pr	1.6 ± 0.2	Er	2.2 ± 0.3
Nd	2.1 ± 0.3	Tm	2.8 ± 0.3
Sm	5.6 ± 0.6	Yb	3.9 ± 0.5
Eu	3.4 ± 0.2	Lu	3.7 ± 0.6
Gd	2.2 ± 0.3	Y	2.4 ± 0.2
Tb	3.0 ± 0.3	Sc	600 ± 200

[a] The large uncertainties (standard deviations) come from the uncertainties in the K_{MCy} values, as well as the $k_H{}^{MCy}$ values.

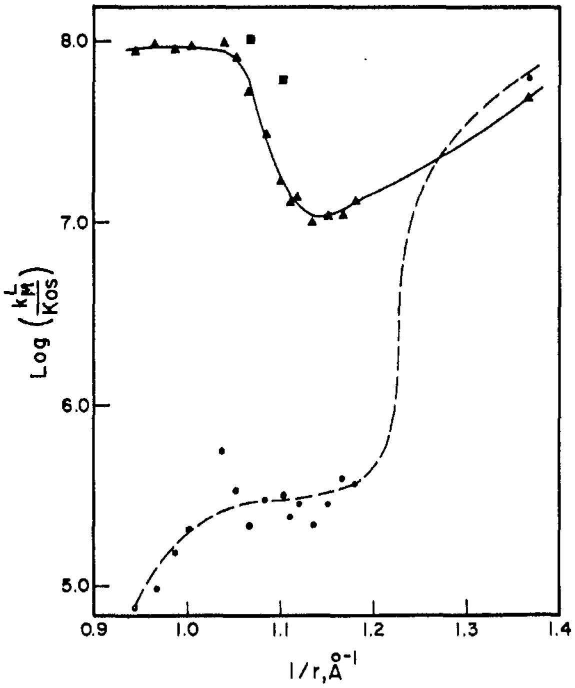


Figure 3.—Values of log ($k_M{}^L/K_{os}$) plotted *vs.* reciprocal +3 ion radius, comparing the results of this work with rate constants of metal ion–ligand reactions which take place by a water-loss mechanism: ●, this work, L = CyDTA, K_{os} = 100, T = 25°; ▲, ref 7, L = murexide, K_{os} = 1, T = 12°; ■, ref 9 and 10 (nmr studies), L = H_2O, K_{os} = 1, T = 25°.

Figure 3 shows that the values of $k_M{}^{HCy}$ divided by a K_{os} value of 100 are 10^2 to 10^3 lower than the $k_M{}^L/K_{os}$ values for the rare earth–murexide rate constants of Geier[7] and the water-exchange rates measured by ^{17}O nmr.[9,10] However for scandium the values are nearly the same. The K_{os} value of 100 is a reasonable estimate for the attraction between +3 and −3 ions. For the divalent metals a K_{os} value of 13 was found for +2 and −3 ions in 0.1 M ionic strength.

Table VII

$La(CyDTA)^-$ Formation Rates, μ 0.1, [Acetate] = 0.05 M

$10^3[La]_T$, M	$10^4[Cy]_T$, M	pH	k_0, sec^{-1} [a]
0.50	5.0	4.25	5.1 ± 0.2
1.00	10.0	4.25	6.3 ± 0.2
0.50	5.0	5.00	8.0 ± 0.9
0.50	5.0	5.50	9.3 ± 0.8
0.50	5.0	6.00	12.6 ± 1.6
2.50	5.0	4.25	6.7 ± 1.0
3.75	5.0	4.25	7.2 ± 0.8
5.00	5.0	4.25	9.3 ± 1.2
6.25	5.0	4.25	8.6 ± 1.4
7.50	5.0	4.25	9.7 ± 0.5
8.75	5.0	4.25	9.7 ± 0.3
10.00	5.0	4.25	9.2 ± 0.9
1.00	5.0	4.25	7.6 ± 0.3
1.50	5.0	4.25	8.3 ± 0.1
1.25	5.0	4.25	7.0 ± 0.1
0.85	5.0	4.25	6.9 ± 0.4
0.65	5.0	4.25	6.9 ± 0.3
0.40	5.0	4.25	4.4 ± 0.2
0.30	5.0	4.25	5.3 ± 0.3

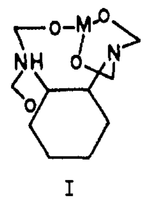
[a] Average and standard deviation for triplicate stopped-flow runs.

The rate of reaction of La^{3+} with CyDTA was measured in acetate-buffered solution in an attempt to directly determine $k_{La}{}^{HCy}$. The data are shown in Table VII. The reaction is first order at equal metal and ligand concentrations, indicating either a rate-determining deprotonation of H_2Cy^{2-}, which is the predominant CyDTA species at pH 4.25, or a rapid formation of LaH_nCy which then forms the stable product, $LaCy^-$. The latter process is shown to occur by allowing unbuffered solutions of lanthanum and CyDTA (5 × 10^{-4} M) to react in the stopped-flow spectrophotometer with brom phenol blue present. There is an instantaneous absorbance change which corresponds qualitatively to the release of acid given in eq 6 and is followed by a measurable reaction corresponding to the release of another proton (eq 7).

$$La^{3+} + H_2Cy^{2-} \longrightarrow La^*HCy + H^+ \qquad (6)$$

$$La^*HCy \longrightarrow LaCy^- + H^+ \qquad (7)$$

The species designated as La*HCy is not the same as the stable protonated form of lanthanum–CyDTA (*i.e.*, LaHCy) but rather is believed to be a complex in which the proton is on the nitrogen and the La^{3+} is coordinated to acetate groups but is outside of the coordination cage of CyDTA as depicted in structure I. On the other hand the stable protonated form of lanthanum–CyDTA must have the proton on a carboxylate oxygen as is the case with the corresponding EDTA compound of lanthanum.[19] In crystalline salts of Fe^{III}CyDTA[20] and of La^{III}EDTA the ligand is sexadentate with both nitrogens and all four carboxylate groups coordinated to the metal ion (the coordination number of the metal ion is greater



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than six and there are additional water molecules coordinated). By contrast only tridentate coordination of the ligand is suggested for La*HCy in structure I. The latter complex would not be expected to be as stable as LaHCy and indeed our estimated stability constant for $K^*_{\mathrm{LaHCy}} = [\mathrm{La^*HCy}]/[\mathrm{La^{3+}}][\mathrm{HCy^{3-}}]$ gives a value 25 times smaller than the stability constant $K_{\mathrm{LaHCy}} = [\mathrm{LaHCy}]/[\mathrm{La^{3+}}][\mathrm{HCy^{3-}}]$. Finally, the removal of a proton from a carboxylate oxygen in LaHCy would be expected to be extremely rapid compared to the measured rate for eq 7.

The first-order rate constants found for reaction 7 are given in Table VII. The k_0 values at pH 4.25 are nearly constant and approach a maximum value of about 9 sec^{-1} at the highest $\mathrm{La^{3+}}$ concentrations.

The observation of the rapidly formed intermediate La*HCy is consistent with the steps in eq 8.

$$\begin{tikzcd}
\mathrm{La^{3+} + HCy^{3-}} \arrow[r, shift left, "K^*_{\mathrm{LaHCY}}"] \arrow[d, shift right, leftarrow, "K_{\mathrm{H_2Cy}}"'] \arrow[d, shift left, "\text{fast}"] & \mathrm{La^*HCy} \arrow[l, shift left, "\text{fast}"] \arrow[r, shift left, "k^*"] & \mathrm{LaCy^- + H^+} \arrow[l, shift left, "k_{\mathrm{H}}^{\mathrm{LaCy}}"] \\
\mathrm{H_2Cy^{2-}} \arrow[d, shift right, leftarrow, "K_{\mathrm{H_3Cy}}"'] \arrow[d, shift left, "\text{fast}"] & & \\
\mathrm{H_3Cy^-} & &
\end{tikzcd} \qquad (8)$$

With such a mechanism, the k_0 values in Table VII would approach a maximum value of k^* at high values of $[\mathrm{La^{3+}}]$ when all the CyDTA is converted to La*HCy.

Using this value for k^* and the $k_{\mathrm{H}}^{\mathrm{LaCy}}$ value of 129 sec^{-1}, as well as the equilibrium constant for the overall process (eq 9),[13] it is possible to calculate a value for the

$$K_{\mathrm{eq}} = \frac{K_{\mathrm{LaCy}}}{K_{\mathrm{HCy}}} = 5.9 \times 10^4 \qquad (9)$$

equilibrium constant, $K^*_{\mathrm{LaHCy}} = 8.4 \times 10^5\ M^{-1}$. The data at pH 4.25 in Table VII give mean values of $1 \times 10^6\ M^{-1}$ for K^*_{LaHCy} and 8.8 sec^{-1} for k^* but the precision is poor. Nevertheless they are in good agreement with the calculated values.

The formation of La*HCy (structure I) does not contradict the calculated values for $k_{\mathrm{M}}^{\mathrm{HCy}}$ given in Table VI but indicates that in order to have a second-order reaction the reactants should be less than $10^{-6}\ M$ at pH 4.25. Observation of the reaction at such low concentrations would be difficult.

A direct measurement of the rate of formation of ScCyDTA was attempted at the same conditions used for $\mathrm{La^{3+}}$. The $\mathrm{Sc^{3+}}$ reaction is much faster and is complete within the minimum observation time (5 msec) of the stopped-flow spectrophotometer.

Discussion

Acid-Dependent Reaction.—The regular change in the metal–CyDTA dissociation rates by a factor of nearly 10^4 throughout the lanthanide series corresponds to the regular change in the metal–CyDTA stability constants,[17b] which increases as $1/r$ increases for the lanthanide series.

As seen in Figure 3, the $k_{\mathrm{M}}^{\mathrm{HCy}}$ values for lanthanum, yttrium, and the lanthanides are slower by a factor of 10^2 to 10^3 than the rate constants predicted by a water-loss mechanism. The stopped-flow study of the lanthanum–CyDTA formation rate indicates that the formation of LaCyDTA takes place in a stepwise manner and not directly. The similar $k_{\mathrm{M}}^{\mathrm{HCy}}$ values in Table VI for La, Y, and the lanthanides indicate that these ions all react similarly with CyDTA.

Scandium ion, on the other hand, complexes with CyDTA at a rate which agrees well with the predicted water-loss value and is much faster than the rates for the larger ions.

The size of the rare earth aquo ion appears to be the main reason for the difference in behavior. The scandium ion, with a radius about 0.1 Å smaller than lutetium, may be small enough to enter the somewhat rigid CyDTA coordination cage and coordinate to one nitrogen without the necessity of transferring a proton from the other nitrogen. The larger ion can coordinate with some of the acetate groups of CyDTA outside of the coordination cage but must wait for the proton to be transferred from nitrogen to an acetate group of CyDTA before full coordination is achieved.

Acid-Independent Reaction.—Table IV indicates that significant acid-independent dissociation occurs with most of the rare earth–CyDTA complexes. This phenomenon cannot be explained by complete dissociation of $\mathrm{MCy^-}$, because the recombination rate would have to be several orders of magnitude greater than the diffusion-controlled limit of about $10^{10}\ M^{-1}$ sec^{-1}.

Glentworth, *et al.*,[12] have proposed that the acid-independent CeCy dissociation reaction proceeds by the mechanism

$$\mathrm{CeCyH_2O^-} \underset{\text{fast}}{\overset{K_1}{\rightleftarrows}} \mathrm{CeCyOH^{2-} + H^+} \qquad (10)$$

$$\mathrm{H^+ + CeCyOH^{2-} \longrightarrow CeOH^{2+} + HCy^{3-}} \qquad (11)$$

For this process the rate is given by eq 12. The K_1

$$\text{rate} = k_{\mathrm{H}}^{\mathrm{CeCyOH}} K_1[\mathrm{CeCyH_2O^-}] = k_{\mathrm{d}}^{\mathrm{CeCy}}[\mathrm{CeCy^-}] \qquad (12)$$

value must be less than $10^{-9.5}$,[21] so $k_{\mathrm{H}}^{\mathrm{CeCyOH}}$ must be at least $2.2 \times 10^5\ M^{-1}$ sec^{-1} in order for $k_{\mathrm{H}}^{\mathrm{CeCyOH}} K_1$ to equal Glentworth's observed value of 7×10^{-5} sec^{-1} for $k_{\mathrm{d}}^{\mathrm{CeCy}}$. It is very unlikely that $k_{\mathrm{H}}^{\mathrm{CeCyOH}}$ should be more than a thousand times greater than $k_{\mathrm{H}}^{\mathrm{CeCy}}$.

A more reasonable mechanism is a slow, rate-determining distortion of the complex, followed by a rapid attack of a second metal ion, $(\mathrm{M'})^{n+}$, or a proton.

$$\mathrm{MCy} \underset{k_{\mathrm{f}}^{\mathrm{MCy}}}{\overset{k_{\mathrm{d}}^{\mathrm{MCy}}}{\rightleftarrows}} \{\mathrm{MCy^-}\}^* \qquad (13)$$

$$\{\mathrm{MCy^-}\}^* + \{(\mathrm{M'})^{n+} \text{ or } \mathrm{H^+}\} \xrightarrow{\text{fast}} \text{products} \qquad (14)$$

This can explain the observed lack of $\mathrm{Cu^{2+}}$ catalysis, and gives reasonable values for all the constants. For $\mathrm{CeCy^-}$, $k_{\mathrm{d}}^{\mathrm{MCy}}$ is about 10^{-4} sec^{-1}. The maximum $k_{\mathrm{f}}^{\mathrm{MCy}}$ value for Ce would be about 10^8 sec^{-1}, the characteristic water-exchange rate constant of that ion.[7] Therefore K', the equilibrium constant for eq 13, must be greater than 10^{-12} (eq 15). From the $\mathrm{CeCy^-}$ stabil-

$$\frac{\{\mathrm{MCy^-}\}^*}{[\mathrm{MCy^-}]} = K' = \frac{k_{\mathrm{d}}}{k_{\mathrm{f}}} \geqq \frac{10^{-4}}{10^8} = 10^{-12} \qquad (15)$$

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[21] $K_{\mathrm{CeOH}} = 10^{-9.5}$, from T. Moeller, *J. Phys. Chem.*, **50**, 242 (1946). The negative charge of the CyDTA makes removal of a proton from CeCyDTA$^-$ even less likely, so K_1 is even smaller.

ity constant of $10^{17.5}$ [17b] the value of the stability constant of $\{MCy^-\}^*$ formed from M^{3+} and Cy^{4-} must be greater than $10^{5.5}$ M^{-1}. This is close to the values for rare earth–citrate complexes,[22] so the intermediate may be a metal atom coordinated to several of the acetate groups of CyDTA, outside the coordination cage. This would be similar to structure I without a proton on the nitrogen. For La^{3+} the value of K^*_{LaHCy} was 10^6 M^{-1} and therefore the association of Ce^{3+} and Cy^{4-} would be expected to be at least this large.

Glentworth and coworkers have observed a slight cerium ion catalysis of the radiocerium–CeCy⁻ exchange reaction. This phenomenon cannot be observed with our experimental method. His reaction may proceed by way of the $\{MCy^-\}^*$ intermediate proposed here.

Both metal ions cannot simultaneously be in the coordination cage, but one may be inside the cage and the other metal ion could coordinate with an acetate group outside the cage. Such a complex is known to inhibit the acid exchange reaction,[23] however, so an intermediate with both metal ions outside the coordination cage is more likely.

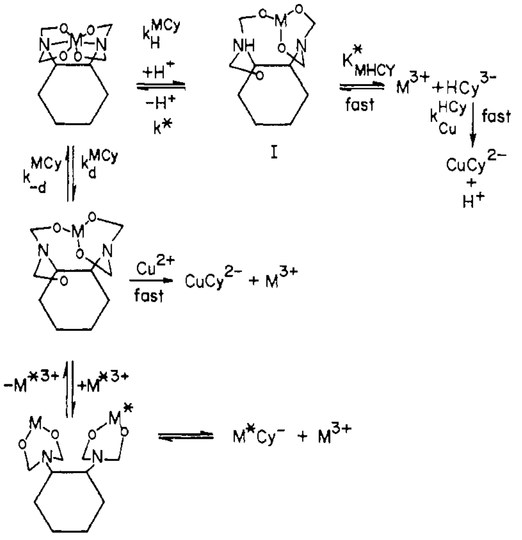

Figure 4.—Mechanism of formation and dissociation of CyDTA complexes of the rare earths.

Mechanism.—The CyDTA complexes can therefore form and dissociate according to the scheme given in Figure 4. The pathway through which the reaction proceeds depends on the complexed metal, the scavenger metal, and the experimental conditions. The acid path is shown at the top of the figure and this pathway predominates for most experimental conditions. The intermediate I is observed with La^{3+} formation reactions because k^* is slow but with Sc^{3+} this intermediate is not observed. The structure of the ligand, the location of protons, and the size of the coordinating metal can have a large influence on the reaction rate.

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The Preparation of Bis(trifluoromethyl)-1,2-diselenetene and Some 1,2-Diselenolene Transition Metal Complexes

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The synthesis and properties of the heterocycle $Se_2C_2(CF_3)_2$ are described. Various attempts to prepare related compounds formally derived from ethylene-1,2-diselenol are discussed. The preparation and properties of a representative series of bis(trifluoromethyl)-1,2-diselenetene transition metal complexes are reported. The complexes are similar in behavior to the corresponding dithiolene species, though they are much less stable.

Introduction

Relatively few transition metal complexes having ligands with selenium as the donor atoms have been reported. However, work in this area is being actively pursued. Summaries of the earlier studies have been included in two recent reviews.[2,3] The most recent studies have dealt with the synthesis of seleno ligands and their complexes such as diselenocarbamates,[4–6] diselenoxanthates,[5] diselenophosphinates,[7] and diselenoacetylacetonates[8] and complexes of 1,2-bis(isopropylseleno)ethane[9] and of but-3-enyl selenides.[10] A number of mixed-donor set ligands involving selenium have

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