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Ligand-Exchange Reaction of Ethylenediaminetetraacetate and Ethylenediaminetetraacetatocuprate(II)[1]

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The symmetric ligand exchange of EDTA with CuEDTA in deuterium oxide is measured by NMR line-broadening techniques from 7 to 94 °C. The ligand-exchange reaction is observed above ca. 56 °C; below this temperature, some other process causes the line width to increase. For the ligand-exchange reaction, $E_a = 10.8$ kcal/mol, $\log A = 9.6$, and the rate constant for unprotonated EDTA at 25 °C is 45 $M^{-1}\ s^{-1}$. In contrast to studies of other metal ions in analogous reactions, the rate constant of exchange of the monoprotonated EDTA is nearly equal to the value for the unprotonated ligand.

Introduction

Recently, several papers have appeared discussing the symmetric ligand-exchange reactions of EDTA (ethylenediaminetetraacetate ion or Y^{4-}) with a metal complex of EDTA (eq 1; the asterisk merely serves to distinguish the entering EDTA molecule from the leaving molecule), where M has been calcium,[2] cadmium,[3-5] lead,[6,7] strontium,[8] and nickel.[9] Nuclear magnetic resonance (NMR) line-broadening techniques were used to study the calcium, cadmium, lead, and strontium reactions. The nickel exchange reaction, a relatively slow reaction, was followed by NMR in which a deuterated ligand was exchanged with a nondeuterated complex.

$$\mathrm{EDTA}^{*4-} + \mathrm{M(EDTA)}^{2-} \rightleftarrows \mathrm{M(EDTA}^{*})^{2-} + \mathrm{EDTA}^{4-} \qquad (1)$$

In this work, NMR line-broadening techniques were used to follow the ligand-exchange kinetics of EDTA with the copper complex of EDTA. More elaborate experimental procedures were required to study the kinetics of reaction 1 with the paramagnetic copper(II) ion than had been the case with previously studied diamagnetic metal ions. The pH dependency and activation parameters for the exchange reaction are measured and parallel pathways for both the tetraanion and the monoprotonated anion as the entering ligand are observed.

Experimental Section

All exchange reactions were carried out in deuterium oxide to prevent the H_2O signal from obscuring the much weaker signals of the EDTA solute. A stock solution of potassium deuterioxide was prepared by slowly adding small pieces of reagent grade potassium metal to deuterium oxide (99.77% D_2O, Columbia Organic Chemicals Co., Inc.) and standardized by titration with standard nitric acid.

Solid D_4EDTA (the ionizable hydrogens replaced by deuterium) was prepared by dissolving reagent grade disodium ethylenediaminetetraacetate dihydrate in deuterium oxide and then stripping off the solvent. Fresh deuterium oxide was added and the procedure was repeated three times. Anhydrous phosphorus pentoxide was then added to the solution of EDTA (to increase the acidity without adding hydrogen ion) until precipitation of the D_4EDTA was observed. The solid tetra acid was filtered, dried in an oven for 2 h at 110 °C, and stored in a desiccator over P_2O_5. Stock solutions of the tetradeuterio acid were prepared by dissolving the D_4EDTA in deuterium oxide, neutralizing with potassium deuterioxide and standardizing with standard copper solution using Snazox indicator.[10]

The rate of reaction 2 was measured by recording the NMR spectra of different solutions of CuEDTA in the presence of a measured excess of EDTA. Each solution contained approximately the same total, or analytical, concentration of EDTA and CuEDTA, but since the pD of each solution was different, different concentrations of the tetraanion of EDTA were present. Working solutions were prepared with the aid of a Gilmont microburet. All pD measurements were made at 25 °C with a Corning Model 12 pH meter equipped with a Corning semimicro combination electrode. The appropriate ΔpD correction, 0.46, as described previously,[11] was applied to the meter reading to obtain the correct pD values.

$$\mathrm{EDTA}^{*} + \mathrm{Cu(EDTA)}^{2-} \rightleftarrows \mathrm{EDTA} + \mathrm{Cu(EDTA}^{*})^{2-} \qquad (2)$$

Relative concentrations of differently protonated species of EDTA were calculated from values of appropriate protonation constants. The pK_4 values used were measured in D_2O with the ionic strength controlled at 2.0 (KCl). The values at 25 and 35 °C were found to be 10.36 and 10.18, respectively. Values at higher temperatures were calculated using the reported ΔH of ionization of EDTA[12] and the measured pK_4. It was assumed that the ΔH of ionization of EDTA was the same in protium oxide and deuterium oxide. (The following pK_4 values were obtained: 9.36 (94 °C), 9.45 (85 °C), 9.72 (65 °C), 9.86 (56 °C), 10.25 (31 °C), 10.36 (25 °C), 10.70 (7 °C)).

At high pD, CuEDTA can also form a mixed deuterioxide complex, as shown in reaction 3. The formation constant (K = [Cu(OD)EDTA^{3-}]/[CuEDTA^{2-}][OD$^-$]) and ΔH of formation of the Cu–OD–EDTA complex were measured by standard spectroscopic techniques and found to be log K = 2.41 (molality units, 25 °C) and ΔH = −7.1 kcal/mol (see ref 13 for details). The relative concentrations of the different Cu–EDTA species at different temperatures were calculated using the formation constant and enthalpy of formation of the deuterioxy complex.

$$\mathrm{Cu(EDTA)^{2-} + OD^- \rightleftarrows Cu(OD)EDTA^{3-}} \qquad (3)$$

NMR spectra were recorded on a Varian XL-100 spectrometer over a temperature range from 7 to 94 °C using a 25-Hz sweep width and a sweep rate of 0.25 Hz/s. Different sweep rates were examined and the 0.25-Hz/s rate was chosen as optimum. It was experimentally verified that all measurements were carried out under the conditions of slow passage and negligible saturation. Data acquisition and reduction were accomplished with the aid of a Varian 620i 16K minicomputer interfaced to the spectrometer. A total of 1024 points could be sampled during each run, yielding a resolution of 0.025 Hz/point. At least three runs were made on the resonance of interest at every temperature, and the reported line widths are the average values at the respective temperatures. The line width is defined as the full width at half-height.

In the pD region studied (9.0–11.4), a solution of EDTA yields an NMR spectrum of two resonances corresponding to the acetate and ethylenic protons of the ligand. The two resonances are well separated and free of overlap. The Swift and Connick equations[14] in the slow-exchange limit relate the line width to the average lifetime in a particular environment, as given by eq 4 and 5. T_2' and T_2 are

$$1/T_2' = 1/T_2 + P_{\mathrm{CuEDTA}}/\tau_{\mathrm{CuEDTA}} \qquad (4)$$

$$W_{1/2}' = W_{1/2} + P_{\mathrm{CuEDTA}}/\pi\tau_{\mathrm{CuEDTA}} \qquad (5)$$

the transverse relaxation times in the presence and absence of exchange, respectively, $W_{1/2}'$ and $W_{1/2}$ are the line widths in the presence and absence of exchange, respectively, P_{CuEDTA} is a probability factor describing the fraction of all EDTA available which is complexed to copper (P_{CuEDTA} = [CuEDTA]$_{\mathrm{total}}$/[EDTA]$_{\mathrm{total}}$), and τ_{CuY} is the lifetime of the copper-coordinated EDTA. The line width in the absence of exchange was measured by recording the NMR spectrum of a solution of EDTA which contained no Cu(EDTA). The total concentration of CuEDTA was 4.52 × 10^{-3} m in all exchange measurements. A comparison of $W_{1/2}$ measurements at different pD values indicated that the line width in the absence of exchange was independent of pD.

The extent of broadening is observed to decrease with decreasing temperature from 97 to 56 °C and then to increase again on continued lowering of the temperature to 7 °C. The increase in the line width at low temperatures is roughly parallel to the increase in the natural line width of EDTA at low temperatures. This is an indication that the observed broadening at low temperatures is not due to any exchange process. The more likely explanation for the low-temperature broadening is that it is due to outer-sphere solvent-relaxation processes. The high-temperature broadening is regarded as due to ligand exchange and is the basis for rate constants measured in this series of experiments. Rate constants obtained on this basis correlate well with comparable values for ligand exchange of other, optically active, aminocarboxylates on copper(II) in which cases complete ligand exchange is unambiguous.[13]

Results

For exchange reaction 2, in the pD region studied (9.0–11.4), the following reactions may be considered

$$\mathrm{Cu(EDTA)^{2-} + DEDTA^{*3-}} \xrightarrow{k_{\mathrm{DEDTA}}{}^{\mathrm{CuEDTA}}} \mathrm{Cu(EDTA^*)^{2-} + DEDTA^{3-}} \qquad (6)$$

$$\mathrm{Cu(EDTA)^{2-} + EDTA^{*4-}} \xrightarrow{k_{\mathrm{EDTA}}{}^{\mathrm{CuEDTA}}} \mathrm{Cu(EDTA^*)^{2-} + EDTA^{4-}} \qquad (7)$$

$$\mathrm{Cu(OD)EDTA^{3-} + EDTA^{*4-}} \underset{}{\overset{k_{\mathrm{EDTA}}{}^{\mathrm{Cu(OD)EDTA}}}{\rightleftarrows}} \mathrm{Cu(OD)EDTA^{*3-} + EDTA^{4-}} \qquad (7a)$$

and $1/\tau_{\mathrm{CuEDTA}}$ is related to the rate of exchange by

$$1/\tau_{\mathrm{CuEDTA}} = k_{\mathrm{obsd}} = k_{\mathrm{DEDTA}}{}^{\mathrm{CuEDTA}}[\mathrm{DEDTA}^{3-}]\alpha_{\mathrm{CuEDTA}} + k_{\mathrm{EDTA}}{}^{\mathrm{CuEDTA}}[\mathrm{EDTA}^{4-}]\alpha_{\mathrm{CuEDTA}} \qquad (8)$$

where α_{CuEDTA} is the fraction of the total CuEDTA in the nondeuterioxy form. Reactions involving $\mathrm{D_2EDTA^{2-}}$, $\mathrm{D_3EDTA^-}$, and $\mathrm{D_4EDTA}$ would not contribute significantly to the rate of exchange at pD values above 9.0. Exchange reaction 7a seems insignificant, in keeping with results of studies of related ligands with copper complexes.[13]

Table I. Solution Composition and Line-Broadening for the Reaction of EDTA with CuEDTA at Different Temperatures

pD	$\alpha_{\mathrm{DY}^{3-}}$	α_{CuY}	$[\mathrm{Y}]_{\mathrm{T}}$, m	$W_{1/2}' - W_{1/2}$, Hz
T = 94 °C; p$K_{\mathrm{D_2O}}$ = 12.949				
10.55	0.060	0.896	0.361	2.45
9.94	0.205	0.972	0.350	1.94
9.31	0.524	0.993	0.350	1.06
8.96	0.711	0.997	0.350	0.61
8.56	0.861	0.999	0.350	0.55
7.88	0.967	0.999	0.350	0.23
T = 85 °C; p$K_{\mathrm{D_2O}}$ = 13.180				
10.67	0.059	0.895	0.361	1.76
10.06	0.202	0.972	0.350	1.42
9.43	0.521	0.993	0.350	0.78
9.08	0.709	0.997	0.350	0.53
8.68	0.860	0.999	0.350	0.37
T = 65 °C; p$K_{\mathrm{D_2O}}$ = 13.694				
10.93	0.059	0.896	0.361	0.93
10.32	0.203	0.972	0.350	0.77
9.69	0.520	0.993	0.350	0.35
9.34	0.708	0.997	0.350	0.36
8.94	0.859	0.999	0.350	0.27
8.26	0.967	0.999	0.350	0.27
T = 56 °C; p$K_{\mathrm{D_2O}}$ = 13.952				
11.05	0.060	0.898	0.361	0.87
10.44	0.206	0.973	0.350	0.65
9.81	0.525	0.994	0.350	0.27
9.46	0.712	0.997	0.350	0.29
9.06	0.862	0.999	0.350	0.15
8.34	0.968	0.999	0.350	0.13
T = 31 °C; p$K_{\mathrm{D_2O}}$ = 14.748				
11.45	0.060	0.898	0.361	0.99
10.84	0.206	0.973	0.350	0.23
10.21	0.525	0.994	0.350	0.35
9.85	0.712	0.997	0.350	0.20
9.48	0.862	0.999	0.350	0.13
8.78	0.968	0.999	0.350	0.15
T = 25 °C; p$K_{\mathrm{D_2O}}$ = 14.955				
11.56	0.059	0.897	0.361	0.60
10.95	0.205	0.973	0.350	0.41
10.32	0.524	0.995	0.350	0.32
9.96	0.710	0.997	0.350	0.29
9.59	0.861	0.999	0.350	0.16
8.89	0.967	0.999	0.350	0.15
T = 7 °C; p$K_{\mathrm{D_2O}}$ = 15.646				
11.90	0.060	0.898	0.361	1.58
11.29	0.206	0.975	0.350	1.11
10.66	0.525	0.995	0.350	0.97

Resolved rate constants, $k_{\mathrm{EDTA}}{}^{\mathrm{CuEDTA}}$ and $k_{\mathrm{DEDTA}}{}^{\mathrm{CuEDTA}}$, for reaction 2 were obtained from a plot of $k_{\mathrm{obsd}}/[\mathrm{EDTA}]_{\mathrm{T}}\alpha_{\mathrm{CuEDTA}}\alpha_{\mathrm{DEDTA}} = k_{\mathrm{DEDTA}}{}^{\mathrm{CuEDTA}} + k_{\mathrm{EDTA}}{}^{\mathrm{CuEDTA}}K_4/[\mathrm{D}^+]$ vs. $1/[\mathrm{D}^+]$ at 94, 85, 65, and 56 °C and from data less basic than pD 10.5 (25 °C) and are taken from Figure 1 as follows: $k_{\mathrm{EDTA}}{}^{\mathrm{CuEDTA}}$ = 1.39 × 10^3 (94 °C), 1.02 × 10^3 (85 °C), 3.23 × 10^2 (65 °C), 2.85 × 10^2 (56 °C); $k_{\mathrm{DEDTA}}{}^{\mathrm{CuEDTA}}$ = 1.4 × 10^2 (94 °C), 1.2 × 10^2 (85 °C), 1.8 × 10^2 (65 °C), 9.7 × 10 (56 °C). The subscript T represents

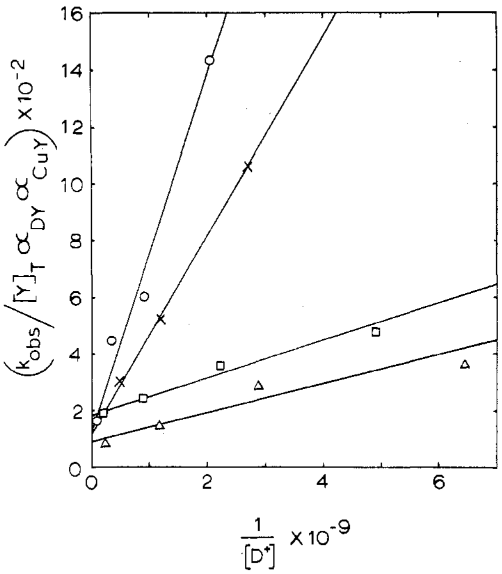

Figure 1. Resolution plot for $k_{EDTA}{}^{CuEDTA}$ and $k_{DEDTA}{}^{CuEDTA}$ at different temperatures: ○, 94 °C; ×, 85 °C; □, 65 °C; △, 56 °C.

the total concentration of EDTA and α_{DEDTA} is the fraction of the total EDTA in the monodeuterated form.

The broadening due to exchange becomes rather small at lower temperatures and the difficulty in accurately determining $1/\tau_{CuEDTA}$ becomes more pronounced. This is illustrated by the increased scatter in the resolution plots at lower temperature and the scatter in the intercepts (Figure 1).

An Arrhenius plot, Figure 2, yields an activation energy (E_a) for reaction 7 of 10.8 kcal/mol and a frequency factor of $10^{9.6}$ m^{-1} s^{-1}. Extrapolating the Arrhenius plot to 25 °C yields a rate constant for reaction 7 ($k_{EDTA}{}^{CuEDTA}$) of 45 m^{-1} s^{-1}. The rate constant for reaction 6, estimated from the intercepts in Figure 1, was estimated to be approximately 40 m^{-1} s^{-1} at 25 °C. The data were not sufficiently precise to estimate activation parameters for reaction 6. It is noteworthy that the values of $k_{EDTA}{}^{CuEDTA}$ and $k_{DEDTA}{}^{CuEDTA}$ are of approximately equal magnitude at 25 °C but that $k_{EDTA}{}^{CuEDTA} >> k_{DEDTA}{}^{CuEDTA}$ at higher temperatures.

A value of log K_{KY} of 0.70 (stability constant of potassium complex with EDTA) has recently been reported[16] at an ionic strength of 0.1 and at 25 °C. Thus, a significant amount of EDTA could exist as the potassium complex under the conditions of these experiments. The exact amount of EDTA existing as the potassium complex cannot be calculated because the value of K_{KY} at high ionic strength and high temperature is not known. However, if a sizable amount of the excess EDTA were associated as a potassium complex, the resulting rate constant would be smaller than in the absence of a K–EDTA complex.

When data taken above pD 10.5 were used in the resolution plots for $K_{EDTA}{}^{CuEDTA}$ and $K_{DEDTA}{}^{CuEDTA}$ significant upward curvature is observed. This increase in slope is attributed to a parallel deuterioxy-catalyzed exchange reaction as given by reaction 9.

$$CuY^{2-} + nOD^- \xrightarrow{k_{nOD}{}^{CuY}} Cu(OD)_n{}^{2-n} + Y^{4-} \qquad (9)$$

This pathway, independent of EDTA concentration, is proposed instead of the ligand-exchange reaction shown in eq 7a based on the results of the kinetic study of other aminocarboxylate ligand-exchange reactions of copper(II).[13] An estimate of the magnitude of $k_{nOD}{}^{CuY}$ can be obtained from the difference between k_{obsd} and a calculated rate constant using $k_{EDTA}{}^{CuEDTA}$ and $k_{DEDTA}{}^{CuEDTA}$. The best estimate gives $k_{nOD}{}^{CuEDTA} \simeq 3 \times 10^5$ m^{-1} s^{-1} and $n = 1$.

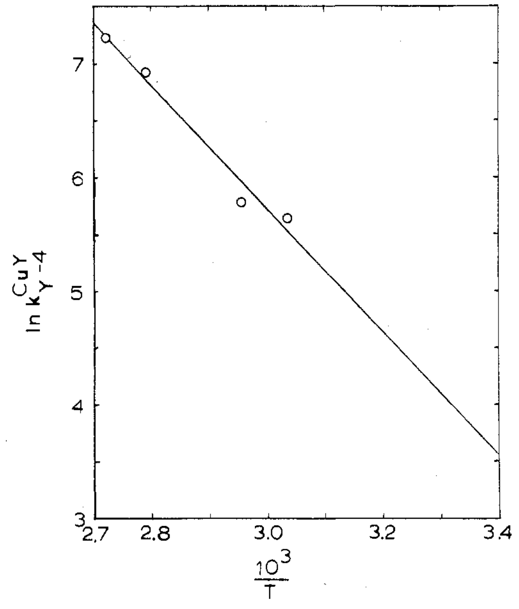

Figure 2. Arrhenius plot for $k_{EDTA}{}^{CuEDTA}$.

Discussion

It is inferred from the reaction that intermediates in this system involve two EDTA molecules, one breaking one bond at a time with its place being taken by a solvent water molecule and the other forming one bond at a time as the solvent water molecules are lost until the ligand substitution is complete. Examination of possible sequences of intermediates then shows structures with alternating n and $n + 1$ water molecules in the primary coordination shell. One can propose a reaction sequence with $n = 0$ as shown in Figure 3 if the following criteria are observed: an acetate group will be first to form a bond from an EDTA ion to copper because of steric problems of a nitrogen approaching the metal ion without prior acetate bond formation; subsequent bond formation will be only to ligand sites which will complete a five-membered chelate ring; and each bond rupture will destroy only a single chelate ring.

The observed rate constant of such a reaction is related to the rate constant of the rate-determining step and the stability constant of the intermediate prior to the rate-determining step as in eq 10.[9]

$$k_Y{}^{CuY} = k_{rds}\frac{K_{CuEDTA}{}^{Cu(EDTA)(EDTA*)}}{K_{Cu}{}^{CuEDTA}} \qquad (10)$$

The problem of estimating the stability constants of the proposed intermediates is to estimate the stability constant of species V, for example, as being the product of $K_2{}^{CuMeIDA}$ and $K_1{}^{CuGly}$, where MeIDA and Gly represent *N*-methyliminodiacetic acid and glycine, respectively, and is represented as $K_{CuEDTA}{}^{Cu(EDTA)(EDTA*)}$ in eq 10, the stability constant for CuEDTA is given by $K_{Cu}{}^{CuEDTA}$ in eq 10. The estimation of the stability constant of the intermediate is less straightforward for copper due to the differences in axial and equatorial sites. A proposed mechanism for the exchange of the tetraanion of EDTA with CuEDTA is given in Figure 3 and predicted rate constants for the various intermediates are given in Table II.

The rate of breakage of a copper–nitrogen bond of which the nitrogen forms part of a five-membered chelate ring with both ends of the chelate being amine nitrogens has been shown to be much slower[18] than the simple breaking of a nonchelated nitrogen.[19] Wilkins has measured the rate constant for the breakage of the first nitrogen to copper bond in diaquo-

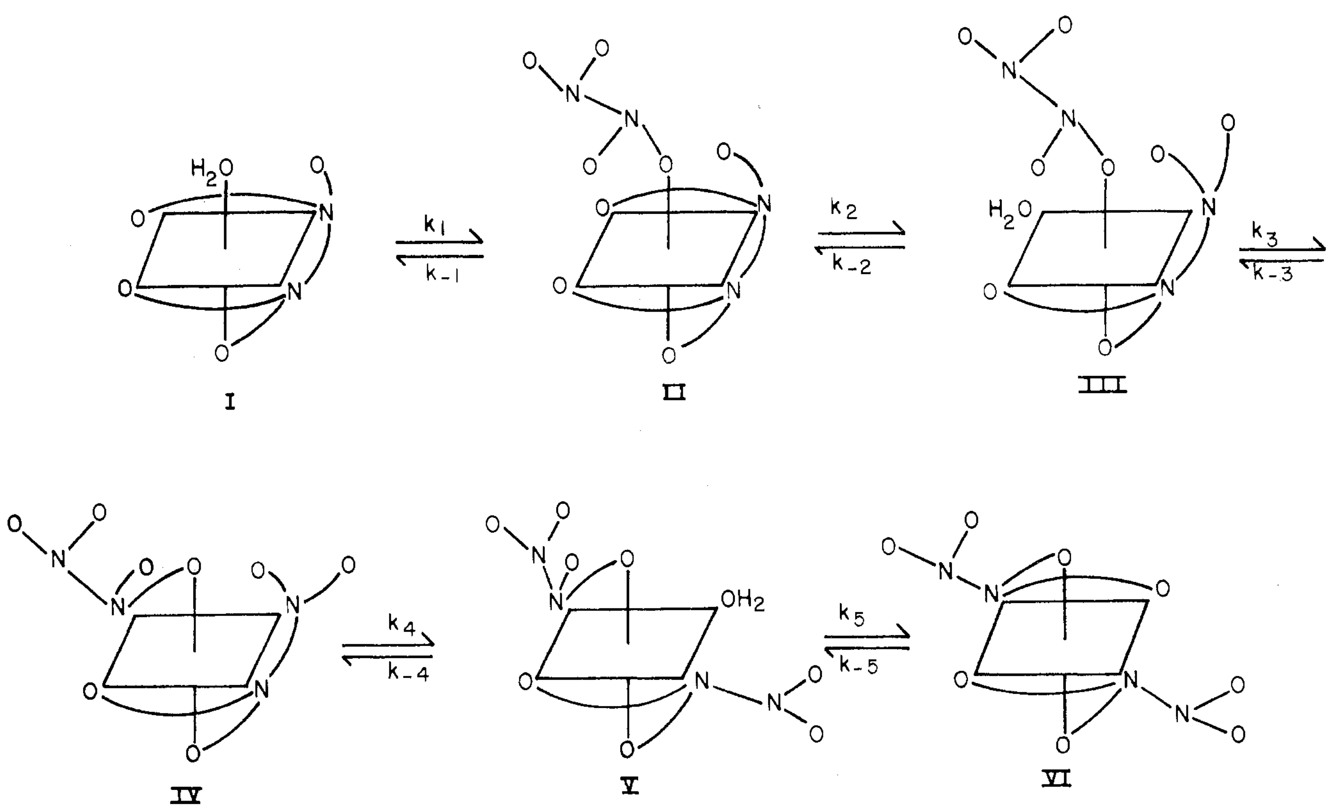

Figure 3. Proposed mechanistic pathway for EDTA exchange.

Table II. Values of Predicted Rate Constants for Possible Rate-Determining Steps

Structures	$K_{\mathrm{CuEDTA}}{}^{\mathrm{Cu(EDTA)(EDTA^*)}}/K_{\mathrm{Cu}}{}^{\mathrm{CuEDTA}}$ [a]	To form	k_{rds}, s^{-1}	$k_{\mathrm{Y}}{}^{\mathrm{CuY}}$(predicted), m^{-1} s^{-1}
II	$\cong 1$	III	$k^{-\mathrm{OAc}} = 10^4$	10^4
III	6.3×10^{-2}	IV	$k^{-\mathrm{H_2O}} = 2.5 \times 10^5$	1.6×10^4
IV	1.0×10^{-4}	V	$k^{-\mathrm{N}} = 3.2 \times 10^2$	3.2×10^6
V	1.4×10^{-4}	VI	$k^{-\mathrm{H_2O}} = 2.5 \times 10^5$	3.5×10

[a] Estimated stability constants for intermediates are obtained as follows: $K_{\mathrm{II}} = K_{\mathrm{Cu}}{}^{\mathrm{CuEDTA}} = 6.3 \times 10^{18}$; $K_{\mathrm{III}} = K_{\mathrm{Cu}}{}^{\mathrm{CuEDDA}}K_{\mathrm{Cu}}{}^{\mathrm{CuOAc}} = (7.9 \times 10^{15})(5.0 \times 10)$; $K_{\mathrm{IV}} = K_{\mathrm{Cu}}{}^{\mathrm{CuEDDA}}K_{\mathrm{CuGly}}{}^{\mathrm{Cu(Gly)_2}} = (7.9 \times 10^{15})(8.3 \times 10^6)$; $K_{\mathrm{V}} = K_{\mathrm{CuMIDA}}{}^{\mathrm{Cu(MIDA)_2}}K_{\mathrm{Cu}}{}^{\mathrm{CuGly}} = (6.8 \times 10^6)(1.3 \times 10^8)$. EDDA = ethylenediamine-*N*,*N*-diacetate; OAc = acetate; Gly = Glycine; MIDA = methyliminodiacetate. Stability constants are taken from ref 21.

Table III. Comparison of Predicted Ligand-Exchange Rate Constants for Various Metals

		$k_{\mathrm{y}}{}^{\mathrm{MY}}$, m^{-1} s^{-1}	
Metal	$k^{-\mathrm{H_2O}}$, s^{-1}	Predicted	Obsd
Cu	2.5×10^5	35	45
Ni	1.5×10^4	3×10^{-3}	1.95×10^{-3} [9]
Ca	3×10^8	800	120[2]
Cd	4×10^8	320	130[3]
Sr	3.5×10^8	6000	1100[8]
Pb	7.5×10^9	25	65[6,7]

bis(ethylenediamine)copper(II) to be 43.3 s^{-1} at 0.8 °C.[18] If an activation energy of 13 kcal/mol, the value for tetraaquoethylenediaminecopper(II),[18] is assumed, a rate constant of 3.2×10^2 s^{-1} is obtained at 25 °C. This number is taken as the best approximation of the rate constant for breakage of the first EDTA nitrogen to copper bond although electrostatic and steric effects are also operable.

Hunt and co-workers have recently reported the rate of equatorial water loss from copper β,β',β''-triaminotriethylamine to be 2.5×10^5 s^{-1} at 25 °C.[20] This is in excellent agreement with the value predicted by Rorabacher and Margerum of 2×10^5 s^{-1} for the rate of equatorial water loss.[17] The value of 2.5×10^5 s^{-1} is taken as the best estimate for the rate of water loss from CuEDTA since, in each step involving water loss in Figure 3, the loss takes place from an equatorial position.

Apparently the rate of equatorial copper–acetate bond breaking has not been measured. However, the rate of bond breakage must be less than the rate of water loss or else copper would not form a stable complex with acetate ion. Considering the relative stabilities of copper acetate and copper monoammine one would also expect the rate of copper–acetate bond breakage to be much greater than the rate of copper–nitrogen bond breakage. Using the rough rule $\Delta \log K_{\mathrm{d}} = \Delta \log k_{\mathrm{d}}$ one then estimates a value of $\simeq 10^4$ s^{-1} for the rate of acetate bond breakage in CuEDTA. This value is taken as a lower limit. The stability constants for $\mathrm{Cu(NH_3)^{2+}}$ and $\mathrm{Cu(OAc)^+}$ and $K_{\mathrm{d}} = 3.2 \times 10^2$ s^{-1}, the rate for chelated nitrogen to copper bond breakage, were used in determining the rate of acetate bond breakage.

Application of eq 10 to the microscopic reactions shown in Figure 3 indicates that the most probable rate-determining step is V → VI. The assignment of step V → VI as rate determining gives good agreement with data for calcium, cadmium, strontium, lead, and nickel,[9] as shown in Table III. The remarkable agreement between predicted and observed rate constants implies a common mechanism for these complexes although the rate constants vary over a range of 10^6. In an earlier article,[9] the stability constants of these intermediates were estimated in a slightly different manner for the nickel, calcium, cadmium, and strontium reactions. The approach employed here causes only small changes in these values but gives a much better fit between experimental and predicted rate constants for the lead and copper reactions than would the previous estimation method.[9]

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Polarized Optical Absorption Studies on Copper and Silver Diethyldithiocarbamates

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Polarized optical absorption measurements are reported for bis(*N*,*N*-diethyldithiocarbamato)copper(II) and -silver(II) diluted in the corresponding zinc complex. The measurements have been made at room, liquid nitrogen, and helium temperatures. The results for the copper complex are at variance with those reported earlier by Reddy and Srinivasan. The electronic transition energies are used in conjunction with the previously reported spin-Hamiltonian parameters to derive the molecular orbital coefficients for the two complexes.

I. Introduction

N,*N*-Diethyldithiocarbamate (detc), $[(C_2H_5)_2NCS_2]^-$, is a rare case of a nonreducing sulfur-containing ligand which is able to coordinate with copper and silver in their formal oxidation state of 2+. In fact Ag(detc)$_2$ is one of the few known silver(II) complexes. Earlier reports on the optical absorption studies on Cu(detc)$_2$[2–4] seem to have completely missed the low-energy bands in the visible region, which is well resolved even in solution. In the case of Ag(detc)$_2$ only a broad band has been reported[3,4] in the visible region. Recently van Rens[5] has reported the EPR results on Ag(detc)$_2$. No attempt has been made so far to study in detail the optical absorption of the silver complex in a single crystal. It was thought worthwhile to undertake such a study for both the copper and the silver complexes, because the complete assignment of the electronic transitions will lead to a better understanding of the electronic structure of the complexes in the light of the spin-Hamiltonian parameters obtained earlier by the EPR studies.

II. Experimental Section

The diethyldithiocarbamates of Cu(II), Ag(II), and Zn(II) were prepared by the methods reported in the literature.[3,6] Single crystals were grown by slow evaporation of a solution of Zn(detc)$_2$ in benzene containing about 1–2% of the corresponding Cu(II) or Ag(II) complex. Large (4 mm × 2 mm) crystals in the form of parallelepipeds or hexagonal plates were obtained. The *a* axis of the crystal was identified as one of the crystal edges based on the morphology reported earlier.[2]

Optical absorption measurements were made using a Carl-Zeiss DMR-21 recording spectrophotometer, modified to accommodate polarizer prisms and a liquid nitrogen cryostat, and a Cary Model 17 spectrophotometer. For measurements below liquid nitrogen temperature the crystal was cooled by controlled boil-off from a liquid helium storage Dewar located underneath the Cary sample compartment. The polarization is referred to the *a* axis of the crystal with light incident on the (011) face.

III. Crystal Structure and Polarization of Absorption Bands

The crystal structures of Cu(detc)$_2$ and Zn(detc)$_2$ belong to the space group $P2_1/c$ with two pairs of centrosymmetrically related molecules per unit cell.[7] The copper and zinc compounds are isomorphous, though not exactly isostructural.[8] EPR results for Cu(detc)$_2$–Zn(detc)$_2$[9] and Ag(detc)$_2$–Zn(detc)$_2$[5] suggest that in mixed crystals, the copper and silver complex molecules assume a configuration more similar to that of pure Cu(detc)$_2$ rather than that of Zn(detc)$_2$. However, their principal axes remain identical with those of Zn(detc)$_2$. The complex molecules belong to a local symmetry of C_{2v} with the metal ion slightly raised above the plane of the sulfur atoms. The x axis is chosen as the one bisecting the projection of the shorter S–Zn–S angle as shown in Figure 1.

The relative orientations of the two molecular units have been discussed earlier.[2] The tetragonal axis of one of the molecules is in the (011) plane while that of the other is 50° out of this plane. The *a* axis bisects the projection angle which is also 50°. The usual analysis of polarization amplitudes leads to the following expressions for the intensity of absorption of the light polarized parallel and perpendicular with respect to the tetragonal axis of the complex molecule

$$I_\parallel = \frac{1.16 I_\parallel{}^a - 0.25 I_\perp{}^a}{1.28} \qquad (1)$$

$$I_\perp = \frac{1.16 I_\perp{}^a - 0.25 I_\parallel{}^a}{1.28} \qquad (2)$$

Here the superscript "*a*" refers to the polarization with respect