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Nuclear Magnetic Resonance and Infrared Spectral Studies of Structural and Kinetic Properties of Amino Polycarboxylate Chelates of Divalent Lead, Zinc, Cadmium, and Mercury in Acidic Aqueous Solutions^{1a,b}

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Solution properties of chelates of divalent Zn, Cd, Hg, and Pb with ethylenediaminetetraacetic acid (EDTA), 2-*N*-hydroxyethyl-ethylenediaminetriacetic acid (HEEDTA), and ethylene glycol bis(β -aminoethyl ether)tetraacetic acid (EGTA) have been examined in neutral and acidic solutions using infrared and nuclear magnetic resonance techniques. Of the complexes which were soluble in acidic solutions, all except ZnEGTA and PbEGTA appear to undergo primary protonation at carboxylate sites whereas ZnEGTA and PbEGTA appear to be primarily nitrogen protonated. Symmetrical exchange processes by which metal ions are transferred between ligands in acidic solutions were studied in the ZnEDTA, ZnHEEDTA, and CdEGTA systems. Exchange occurs through acid-assisted dissociation pathways with rate constants for the dissociation of the mono-protonated chelates of 0.9, 72, and $5 \times 10^{-2} \text{ sec}^{-1}$ for ZnEDTA, ZnHEEDTA, and CdEGTA, respectively. Proton-assisted dissociation of the monoprotated chelates of ZnEDTA and CdEGTA occurs with rate constants of 2×10^8 and $2 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$, respectively. Proton-assisted dissociation of the HgEGTA complex proceeds at an observable rate only in solutions containing complexing anions such as Cl^- , Br^- , I^- , and SCN^- .

Introduction

Acid catalysis of dissociation and ligand-exchange reactions involving metal-ethylenediaminetetraacetate (EDTA) complexes is well established.²⁻¹³ Metal-EDTA complexes in which one or more of the ligand dentates are protonated constitute a considerable fraction of the total complexed species in acidic solutions, and reduced metal-ligand coordination in the protonated species is undoubtedly responsible for part of the increased lability of the complexes in solutions of low pH. Various thermodynamic^{14,15} and spectral¹⁶ measurements as well as kinetic studies have provided insight into the structures of the protonated complexes. For kinetically inert complexes such as $\text{Co}^{\text{III}}\text{EDTA}$ ¹⁷ and $\text{Rh}^{\text{III}}\text{EDTA}$ ¹⁸ there is considerable evidence that a carboxylate group of the bound EDTA is protonated in acidic media. Although infrared spectra for solutions of EDTA complexes with several divalent ions¹⁶ in-

dicated the presence of protonated carboxylate groups, the possibility for a sizable fraction of nitrogen-protonated complexes remained. In the present work we have utilized nuclear magnetic resonance (nmr) and infrared spectral techniques to examine protonation of divalent Pb, Zn, Cd, and Hg complexes with EDTA, 2-*N*-hydroxyethylethylenediaminetriacetate (HEEDTA), and ethylene glycol bis(β -aminoethyl ether)-tetraacetate (EGTA). Kinetic properties of the complexes in neutral and acidic solutions have been examined using nmr line-broadening techniques.

Experimental Section

General Information.—Nmr spectra were recorded at 60 MHz with a Varian A-60A spectrometer operating at a probe temperature of $25 \pm 1^\circ$. Spectra at 100 MHz were recorded with a Varian HA-100 spectrometer at a probe temperature of $29 \pm 1^\circ$. Spectra for line width studies were recorded on the 50-Hz sweep width of the A-60A at sweep rates of less than 0.20 Hz/sec. Line widths for kinetic measurements represent the average of at least five individual spectral recordings, and uncertainty in the line widths is estimated to be less than 0.05 Hz which was the standard deviation for five measurements on the broadest lines of 5-Hz width. Tetramethylammonium ion (TMA) as the Cl^- or NO_3^- salt was employed as an internal chemical shift and field homogeneity standard.⁸ Chemical shifts were measured from the central component of the TMA triplet resonance.

Infrared spectra were recorded with a Perkin-Elmer Model 421 grating spectrometer. Spectra for D_2O solutions of the complexes were recorded in 0.025-mm BaF_2 cells.

pH measurements were made with a Corning Model 12 pH meter equipped with a Corning high-range glass electrode and fiber-tip saturated calomel reference electrode. The meter was standardized before each set of measurement with NBS buffer solution at three pH values. In the D_2O solutions for infrared studies, the pD was obtained from the expression $\text{pD} = \text{meter reading} + 0.40$.¹⁹

Chemicals and Solutions.—EDTA (J. T. Baker Chemical Co.) and HEEDTA (Geigy Chemical Co.) were obtained as the solid acids and were used without further purification. EGTA (Geigy Chemical Co.) was twice recrystallized from acid solution before use. D_2O (99.8%) was obtained from Bio-Rad Laboratories. All other chemicals were analytical reagent grade.

Solutions for nmr studies were prepared by dissolving the requisite quantities of the protonated ligand, metal oxide or metal nitrate salt, and KOH in triply distilled water and diluting to volume. The solution pH was adjusted with standard KOH or HNO_3 solutions. Large solution volumes (100–200 ml) and

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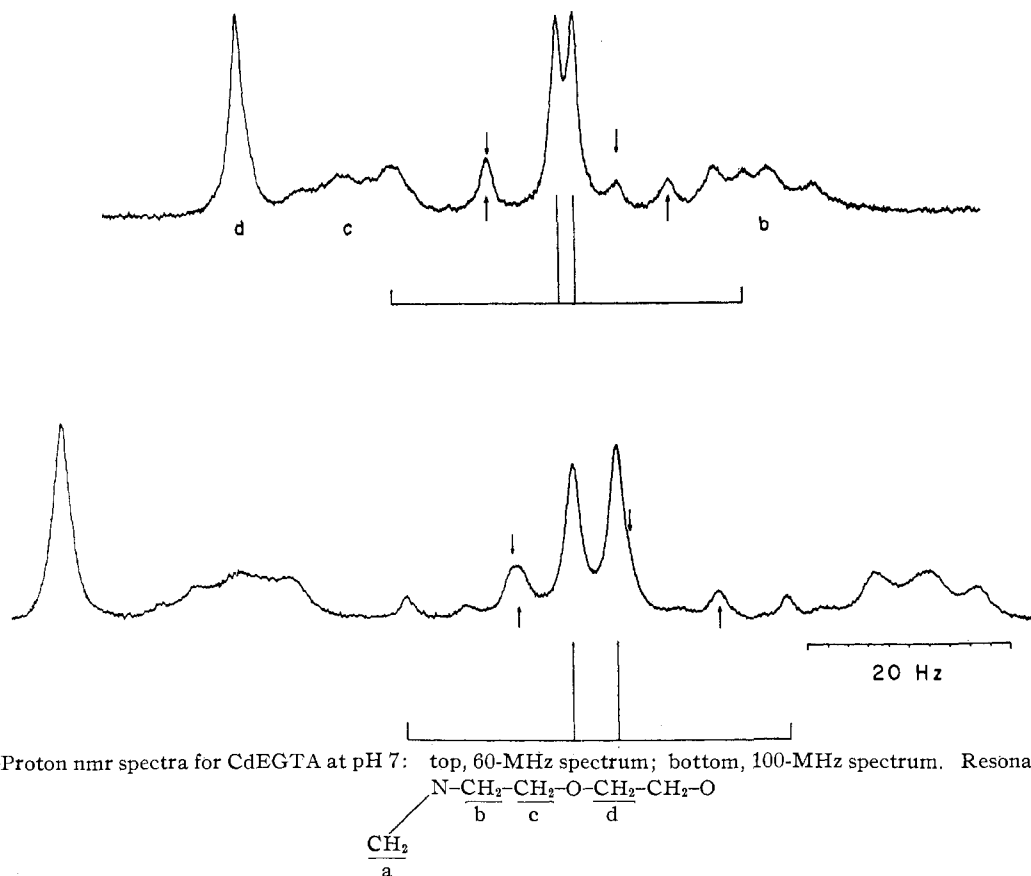


Figure 1.—Proton nmr spectra for CdEGTA at pH 7: top, 60-MHz spectrum; bottom, 100-MHz spectrum. Resonance assignments

J_{AB} for acetate protons, 16.5 Hz, $\nu_A - \nu_B = 0.13$ ppm; ^{111}Cd - and ^{113}Cd -coupled satellites of B protons, $J_{BX} = 20$ Hz; ^{111}Cd - and ^{113}Cd -coupled satellites of A protons, $J_{AX} = 11$ Hz. Arrows indicate metal-proton coupled satellites.

concentrated (5 *F*) standard base or acid were utilized to minimize sample removal and dilution effects. No additional electrolyte was added to control the ionic strength of the solutions (0.05–0.15 *F* in metal complex), and calculations do not include activity corrections.

Nmr Spectral Assignments.—Proton nmr spectra for solutions of EDTA,²⁰ HEEDTA, EGTA,²¹ ZnEDTA,²² PbEDTA, and CdEDTA²³ have been described in detail previously. In earlier nmr studies of metal-EDTA complexes the presence or absence of AB splitting patterns for the acetate protons of EDTA was construed as an indication of “inert” or “labile” metal-nitrogen bonding, respectively.²³ The latter conjecture has been particularly weak because the appearance of a discernible AB pattern requires a chemical shift difference, $\Delta\nu_{AB}$, for the geminal acetate protons of at least 6 Hz.²⁴ Recent nmr measurements at 220 MHz where $\Delta\nu_{AB}$ is enhanced have revealed AB patterns for the acetate protons of Zn²⁺, Pb²⁺, and Ca²⁺ complexes of EDTA.²⁵

At 60 MHz the spectrum for HgEDTA consists of a single, partially resolved AB pattern (~ 5 -Hz half-width for individual components) for the acetate protons and a singlet resonance for the ethylenic protons. Satellite peaks are present for both acetate and ethylenic protons coupled to the ^{199}Hg nucleus ($I = 1/2$, 16.86% natural abundance). The AB pattern is observed only between pH 4.5 and 8.0 in solutions free of halide ions.

Spectra at 60 MHz for the Zn²⁺ and Hg²⁺ complexes of HEEDTA resemble the spectrum for the free ligand,²¹ differing from the latter in line widths and chemical shifts of the resonances. Spectra for these two complexes at 220 MHz show partially resolved AB splittings for the acetate protons. AB splitting is apparent in acetate resonance at 60 MHz for Pb- and Cd-HEEDTA. At 100 and 220 MHz one can identify an AB pattern for each of the three acetate groups.

Spectra for the Zn²⁺ and Pb²⁺ complexes with EGTA at 60 MHz are similar to the spectrum of the free ligand.²¹ The spectra for Cd²⁺ and Hg²⁺ with EGTA at 60 and 100 MHz (see Figures 1 and 2) show a differential coupling of the geminal acetate protons with the spin $1/2$ isotopes of Cd and Hg. The chemical shift of the $-\text{OCH}_2\text{CH}_2\text{O}-$ protons of EGTA is relatively insensitive to the state of complexation of the ligand. The chemical shift of this resonance in the four complexes and the free ligand cover a range of only 4 Hz.

Nmr Rate Measurements.—Quantitative measurements of the rates of exchange of ligands between free and complexed forms were obtained for the CdEGTA, ZnEDTA, and Zn-HEEDTA systems. Nmr spectra for solutions containing an excess of ligand over metal ion exhibit two complete sets of resonances, one set for the complex and one set for the free ligand. The resonance separation between the free and complexed forms for at least one type of ligand proton is large compared with the reciprocal of the average lifetime, τ^{-1} of the ligand in each site, and, consequently, the lifetimes can be evaluated from the slow-exchange expression.²⁶ The average lifetime, τ , of the ligand in a given site is related to the resonance signal shape for a given type of proton in that site by the expression $W_{1/2,\text{obsd}} = W_{1/2} + 1/\pi\tau$, where $W_{1/2,\text{obsd}}$ and $W_{1/2}$ are the line widths at half-height in hertz with and without exchange, respectively.²⁶ For each of the systems, the value of $W_{1/2}$ was obtained from spectra for neutral solutions containing both the free ligand and chelate at the same concentration as that being studied. The absence of chemical-exchange contributions to line widths in neutral solutions was evidenced by values for $W_{1/2}$ of the free ligand resonances which were identical with values obtained for solutions containing no complexing metal ions.

Results

Equilibria.—Solution equilibria and their associated

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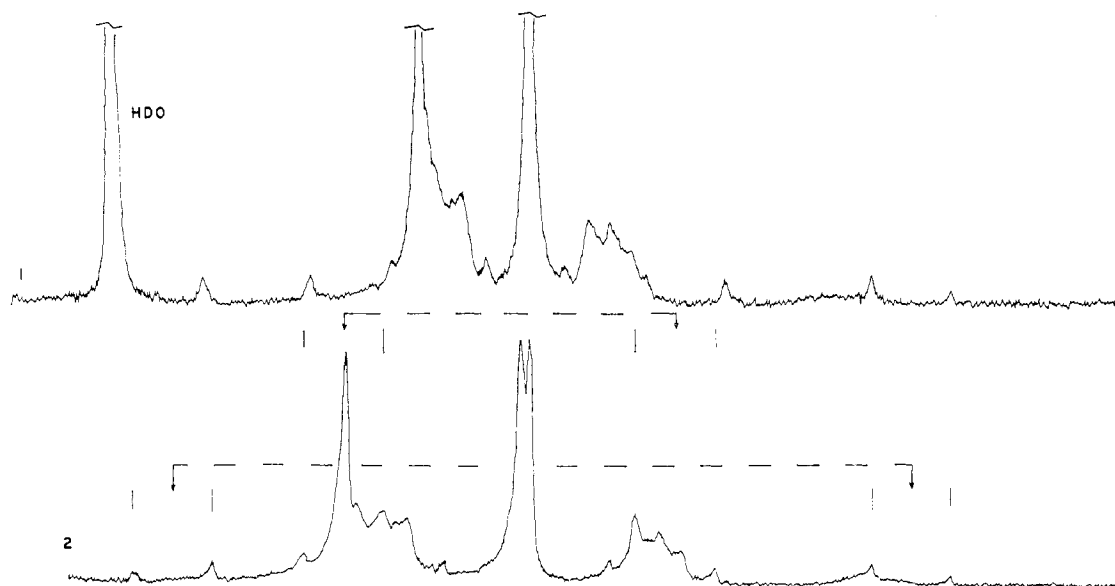
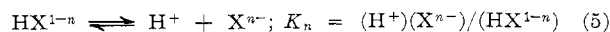
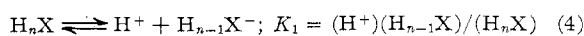
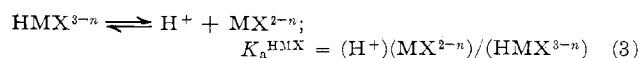
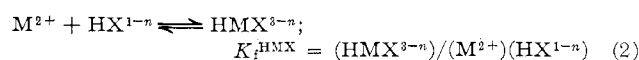
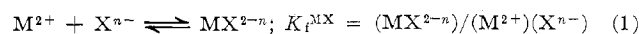


Figure 2.—(1) 60-MHz spectrum for HgEGTA. (2) 100-MHz spectrum for HgEGTA. $J_{AX} = 69$ Hz, $J_{BX} = 153$ Hz. Satellite assignments indicated by dashed lines.

constants which are important in this study are



where M^{2+} represents the central metal ion, and X^{n-} represents the totally ionized form of the ligand.²⁷ The constant for equilibrium reaction 2 is related to those for reactions 1, 3, and 5 by the expression

$$K_f^{HMX} = (K_f^{MX}K_n)/K_a^{HMX} \quad (6)$$

Values for the above constants are given in Table I.

TABLE I
EQUILIBRIUM CONSTANTS^a

Metal ion	EDTA		EGTA		HEEDTA	
	Log K_f^{MX}	Log K_f^{HMX}	Log K_f^{MX}	Log K_f^{HMX}	Log K_f^{MX}	Log K_f^{HMX}
Hg	22.1	14.6	23.8	3.17 ^b	16.8	20.1
Cd	16.6	9.1	16.7	3.20 ^b	10.7	13.0
Pb	18.0	10.6	14.6	5.25 ^b	10.3 ^b	15.5
Zn	16.5	3.05 ^b	9.3 ^b	14.5	5.05 ^b	10.5 ^b

	EDTA	EGTA	HEEDTA	EDTA	EGTA	HEEDTA
pK_1	1.99	2	2.04	pK_3	6.2 ^d	8.78 ^c
pK_2	2.7	2.68	5.4	pK_4	9.8 ^d	9.25 ^c

^a L. G. Sillén and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 17 (1964). ^b Determined potentiometrically at ionic strength of 1.5 M. ^c Reference 21. ^d Reference 8.

Infrared Spectra.—The antisymmetric carboxylate stretching frequency of amino polycarboxylate chelates depends on the physical state of the carboxylate group.^{16,28} For example, an unionized carboxylate group ($-COOD$) absorbs in the 1700–1750- cm^{-1} region of the spectrum, whereas the ionized ($-COO^-$) or metal-coordinated ($-COOM$) groups absorb at lower frequencies,

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generally about 1590–1650 cm^{-1} . This feature allows one to distinguish a protonated carboxylate group from other types of carboxylates which may be present in solution. The approach has been employed by Sawyer and Tackett¹⁶ in investigation of metal-EDTA complexes in acidic D_2O solutions. The infrared spectra for all of the chelates in neutral D_2O solutions show one broad band in the 1590–1650- cm^{-1} region of the spectrum indicative of metal-coordinated and/or ionized carboxylate groups. Table II summarizes the results of infrared studies in acidic D_2O solutions.

TABLE II
CARBOXYLATE ABSORPTION FREQUENCIES
FOR PROTONATED CHELATES^a

Metal ion	EDTA ^b		EGTA		HEEDTA	
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
Pb(II)	1720	1600	1605	1580	1685	1585
Hg(II)	1710	1545	1705	1590	1705 ^c	1580 ^c
Cd(II)	1720	1600	1695	1590		
Zn(II)	1720	1600	1620	1605	1740	1600

^a Values in cm^{-1} . ^b Reference 16. ^c Obtained from crystalline chelate in KBr pellet.

Nmr Spectra.—Two changes in the nmr spectra for the complexes are observed when neutral solutions of the complexes are acidified. (1) The resonances for the ligand protons shift to lower field, the shift being a linear function of the mole fraction of acid added to the solution. (2) The resonances broaden in acidic solutions, and where AB splitting patterns are present for acetate protons in neutral solutions, these partially or completely collapse in acidic solutions.

Chemical Shifts.—The downfield shift of the complexed ligand resonances in acidic media results from protonation of the complex. Exchange of acidic protons between basic groups on the chelates and between the chelates and solvent is sufficiently rapid so that no separate set of resonances appears for the protonated complexes. Rather, the observed spectra are an average over the unprotonated and protonated forms

of the complex. The chemical shift for a given type of ligand proton is thus given by the expression²⁶

$$\delta_{\text{obsd}} = P_{MX}\delta_{MX} + P_{HMX}\delta_{HMX} \quad (7)$$

where δ_{obsd} is the observed chemical shift, P_{MX} and P_{HMX} are the fractional populations of the simple complex and the protonated complex, respectively, and δ_{MX} and δ_{HMX} are the characteristic chemical shifts of the simple and protonated complexes. The above expression is valid provided that chemical exchange between the free and complexed forms of the ligand is slow and the free ligand does not contribute to the observed chemical shift changes. For all systems studied except PbEGTA, ZnEGTA, and HgEDTA, when an excess of ligand over metal ion was present in the solutions, the chemical shifts of the separate set of resonances for the free ligand followed a pH dependence identical with that observed in the absence of the metal complexes indicating no chemical-exchange contribution to chemical shifts for these systems. For solutions of PbEGTA, ZnEGTA, or HgEDTA the chemical-exchange contribution to the observed chemical shift brought about by rapid exchange between free and complexed ligands is related to the fractional population of the free ligand by the expression

$$\delta_{\text{obsd}} = P_{MX}\delta_{MX} + P_{HMX}\delta_{HMX} + P_X\delta_X \quad (8)$$

where P_X and δ_X are the fractional population and chemical shift of the free ligand at the pH of the measurement. However, calculations show that, in solutions where the mole ratio of metal to ligand is unity, the population of the free ligand amounts to less than 1% in the pH region investigated, and the free ligand makes a negligible contribution to the observed shift. Table III

TABLE III
CHEMICAL SHIFT CHANGES FOR LIGAND PROTONS UPON
PROTONATION OF THE METAL COMPLEX^a

Metal ion	EDTA		EGTA		HEEDTA	
	Acetate	Ethyl- enic	Acetate	Ethyl- enic ^b	Acetate ^c	Ethyl- enic
Zn	0.117	0.043	0.193	0.22	0.173	0.122
Cd	0.141 ^d	0.075	0.222 ^d	0.16		
Hg	0.155 ^d	0.080	0.150	0.05		
Pb	0.075	0.033	0.358	0.48	0.068 ^d	0.035

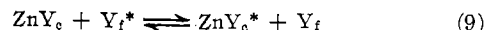
^a Values in ppm \pm 0.006 ppm for singlet resonances. ^b Values for N-CH₂-CH₂-O protons estimated from center of complex multiplet \pm 0.03 ppm. ^c Values for both types of acetate protons. ^d Center of AB multiplet.

contains the change in chemical shift, $\delta_{MX} - \delta_{HMX}$, for the various ligand protons upon protonation of the complexes. δ_{HMX} was taken as δ_{obsd} when P_{HMX} as determined from the equilibrium constants in Table I was unity.

Line Broadening.—The observed broadening of the chelate resonances in acidic solutions may be attributed to chemical-exchange processes. For the ZnEDTA, ZnHEEDTA, and CdEGTA systems the characteristics of the spectra for solutions containing both free ligand and metal complex were favorable for a quantitative evaluation of the exchange processes.

Spectra for solutions containing both ZnEDTA and free EDTA show broadening of both sets of resonances below pH 4. This broadening results from an exchange of Zn²⁺ ions between ligands, and several possible pathways for this transfer may be considered. For example, a direct, second-order reaction between the free

EDTA and ZnEDTA giving a reaction of the type



where $\text{ZnY}_e = \text{ZnY}^{2-} + \text{HZnY}^-$ ($\text{Y}^{4-} = \text{EDTA}$ tetraanion) and $\text{Y}_f = \text{Y}^{4-} + \text{HY}^{3-} + \text{H}_2\text{Y}^{2-}$ could account for the observed broadening. Such a process would lead to a rate expression of the form

$$1/\tau_{\text{ZnY}_e} = (\text{ZnY}_e)^{-1}d(\text{ZnY}_e)/dt = (\text{constant})(\text{Y}_f) \quad (10)$$

where τ_{ZnY_e} is the average lifetime of complexed EDTA. Table IV shows the line width of the ZnEDTA res-

TABLE IV
LINE WIDTHS OF RESONANCES IN THE ZnEDTA SYSTEM^a

(Y _f), F	W _{1/2}		(Y _f), F	W _{1/2}	
	ZnY	Y _f		ZnY	Y _f
0	1.17	...	0.075	1.18	1.05
0.025	1.18	1.27	0.10	1.18	1.03
0.050	1.17	1.17	0.15	1.18	1.02

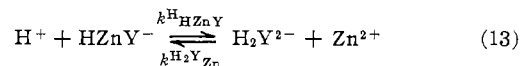
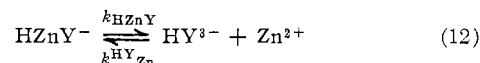
^a Values for acetate protons in cps \pm 0.01 cps at (ZnY) = 0.10 F, pH 3.14.

onances at various concentrations of free EDTA at constant pH, and the absence of a dependence on the free EDTA concentration shows that direct, second-order exchange makes a negligible contribution to the observed broadening.

Narrowing of the free ligand resonances with increasing free ligand concentration is consistent with the expression

$$1/\tau_{\text{Y}_f} = (\text{Y}_f)^{-1}[-d(\text{Y}_f)/dt] \quad (11)$$

Acid-assisted dissociation reactions of the type



can account for the observed broadening. The rate expression is of the form

$$1/\tau_{\text{ZnY}_e} = (\text{ZnY}_e)^{-1}[-d(\text{ZnY}_e)]/dt = (k_{\text{HZnY}})(\text{HZnY}^-)/(\text{ZnY}_e) + (k_{\text{H}^+\text{HZnY}})(\text{H}^+)(\text{HZnY}^-)/(\text{ZnY}_e) \quad (14)$$

Figure 3 shows an experimental plot of $(1/\tau_{\text{ZnY}_e})$.

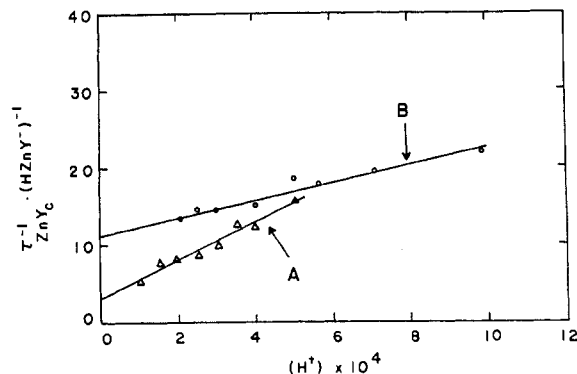


Figure 3.—Lifetime data for the ZnEDTA system from line broadening: (A) (ZnY) = 0.10 F, (Y_f) = 0.10 F; (B) (ZnY_e) = 0.20 F, (Y_f) = 0.10 F, temperature 25 \pm 1°.

$(\text{HZnY}^-)^{-1}$ vs. (H^+) from data at constant ZnY_e and Y_f but at varying pH which gives a straight line with an intercept of $k_{\text{HZnY}}/(\text{ZnY}_e)$ and slope of $k_{\text{H}^+\text{HZnY}}/(\text{ZnY}_e)$. From the equilibrium constants for reactions 12 and 13

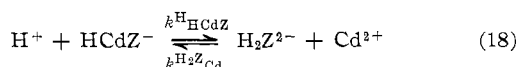
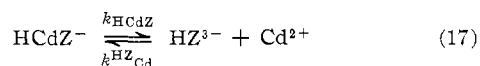
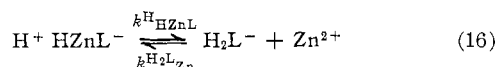
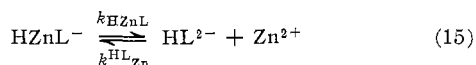
and the experimentally determined values of k_{HZnY} and k_{HZnY} , values for k_{HYZn} and $k_{\text{H}_2\text{YZn}}$ were obtained.²⁹ The constants are given in Table V.

TABLE V
RATE CONSTANTS FOR EXCHANGE PROCESSES^a

Chelate	Rate constant	Lit. values
ZnEDTA	$k_{\text{HZnY}} = 0.9 (\pm 0.4) \text{ sec}^{-1}$	$0.8 \text{ sec}^{-1} \text{ }^b$
	$k_{\text{HYZn}} = 2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$	10^9 ^c
	$k_{\text{HZnY}} = 2 (\pm 1) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$	$4.8 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1} \text{ }^b$
	$k_{\text{H}_2\text{YZn}} = 3 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$	
ZnHEEDTA	$k_{\text{HZnL}} = 7.2 (\pm 0.7) \times 10 \text{ sec}^{-1}$	
	$k_{\text{HLZn}} = 9 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$	
CdEGTA	$k_{\text{HCdZ}} \leq 5 \times 10^{-2} \text{ sec}^{-1}$	
	$k_{\text{HZCd}} \leq 1 \times 10^3 \text{ sec}^{-1}$	
	$k_{\text{HCdZ}} = 2 (\pm 1) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$	
	$k_{\text{H}_2\text{ZCd}} = 1.5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$	

^a Temperature $25 \pm 1^\circ$. ^b Reference 11. ^c R. G. Wilkins and M. Eigen, *Advan. Chem. Ser.*, No. 49, 61 (1965).

Line broadening in the ZnHEEDTA and CdEGTA systems follows the same pattern as that observed for the ZnEDTA systems with the line shapes of the complexed resonances being independent of the free ligand concentrations but dependent on pH. The observed broadening is attributed to acid-assisted dissociation reactions analogous to those for ZnEDTA



where L^{3-} and Z^{4-} are the trianion and tetraanion forms of HEEDTA and EGTA, respectively. Resonances for free HEEDTA and EGTA were used to evaluate the lifetimes in these systems, and equimolar concentrations of complex and free ligand were normally employed. Under conditions of equal concentrations of free and complexed ligand the expressions

$$1/\tau_{\text{ZnL}_0} = 1/\tau_{\text{L}_f}, \quad 1/\tau_{\text{CdZ}_0} = 1/\tau_{\text{Z}_f} \quad (19)$$

are valid, and the rate expressions take the identical form as that for the ZnEDTA system. Figure 4 shows an experimental plot of $(1/\tau_{\text{CdZ}})(\text{HCdZ}^-)^{-1}$ vs. (H^+) from which an upper limit of k_{HCdZ} and a value of k_{HZCd} are obtained from the intercept and slope, respectively. As indicated by the data in Table VI

TABLE VI
LIFETIME DATA FOR THE ZnHEEDTA SYSTEM^a

$10^{-2}(1/\tau_{\text{ZnL}_0}) \cdot (\text{HZnL})^{-1}$	$(\text{H}^+), \text{M}$	$10^{-2}(1/\tau_{\text{ZnL}_0}) \cdot (\text{HZnL})^{-1}$	$(\text{H}^+), \text{M}$
4.8	1.38×10^{-4}	4.6	8.50×10^{-4}
5.1	3.10×10^{-4}	4.8	1.0×10^{-3}
4.8	4.47×10^{-4}	5.1	2.3×10^{-3}
4.9	5.60×10^{-4}	4.8	11.5×10^{-3}
4.6	7.10×10^{-4}		

^a $(\text{ZnL}_0) = (\text{L}_f) = 0.15 \text{ F}$; temperature $25 \pm 1^\circ$.

the quantity $(1/\tau_{\text{ZnL}_0})(\text{HZnL})^{-1}$ was essentially constant over a considerable range of hydrogen ion concen-

(29) R. G. Wilkins and M. Eigen, *Advan. Chem. Ser.*, No. 4, 61 (1965).

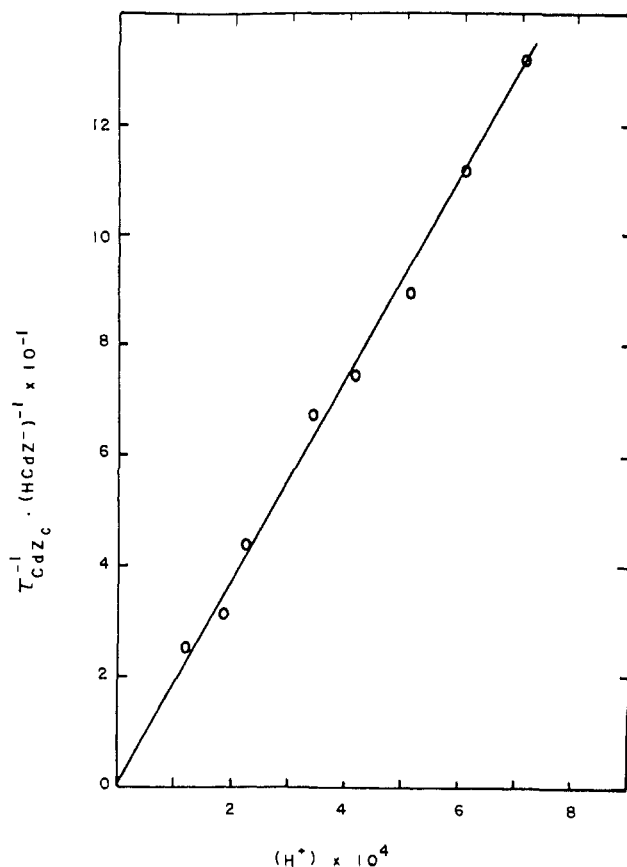


Figure 4.—Lifetime data for the CdEGTA system from line broadening. $(\text{CdZ}_0) = 0.10 \text{ F}$, $(\text{Z}_f) = 0.10 \text{ F}$, temperature $25 \pm 1^\circ$.

trations, and from this quantity a value of k_{HZnL} was determined. Values for the rate constants for the reverse reactions 15–18 were obtained from their equilibrium constants and the experimentally determined forward rate constants. Rate constants for ZnHEEDTA and CdEGTA systems are included in Table V.

Line broadening in the CdEDTA system at low pH has been examined previously by Sudmeier and Reilly.⁹ Exchange effects on the nmr spectra of PbEDTA, HgEDTA, PbEGTA, and ZnEDTA complexes were observed in acidic solutions; however, problems of spectral overlap prevented a more quantitative evaluation of these effects.

For the HgEGTA system no exchange broadening was observed between pH 7 and 3 indicating an average lifetime for a given HgEGTA complex of greater than 6 sec. However, in solutions containing millimolar concentrations of Cl^- , Br^- , SCN^- , or I^- ions (HgEDTA present at 0.10 F) at pH values below pH 5, exchange of Hg^{2+} ions between EGTA ligands became quite rapid. Of the complexing anions studied, only I^- showed any effects on the nmr spectra at a solution pH of 7. The HgEDTA spectrum was broadened by 4 Hz at pH 7 by 5 mM KI ($(\text{HgEGTA}) = 0.10 \text{ F}$).

Discussion

Infrared spectra of the Pb, Hg, Cd, and Zn complexes of EDTA support the conclusions of Sawyer and Tackett¹⁶ that the complexes are primarily carboxylate protonated in acidic solutions. Infrared spectra for

acidic solutions of PbHEEDTA, ZnHEEDTA, CdEGTA, and HgEGTA show bands characteristic of an unionized carboxylate group, and, on this basis, these complexes appear to undergo protonation at carboxylate sites. However, spectra for PbEGTA and ZnEGTA under similar conditions do not show the unionized carboxylate band, indicating that carboxylate protonation does not occur to any significant extent. It seems probable that these two complexes undergo nitrogen protonation.

Chemical shift changes for the ligand protons in the chelates upon protonation result from a decrease in the extent of metal-ligand coordination and from protonation of the freed dentate groups of the ligand. A comparison of the chemical shift changes for various types of protons within the same complex should reflect relative distances of the protons from the actual site or sites of protonation in the complex. Protonation at carboxylate sites would result in a larger change in the shielding of the protons immediately adjacent to these sites (*i.e.*, the acetate protons) than for protons more distant, since these effects normally attenuate rapidly through bonds. Protonation at nitrogen sites should result in approximately equal changes in the shielding of all the protons on carbons adjacent to the nitrogen atoms (*i.e.*, the acetate and ethylenic protons). An examination of Table III reveals that for all of the EDTA complexes and for PbHEEDTA, ZnHEEDTA, HgEGTA, and CdEGTA the changes in chemical shift for the acetate protons upon protonation of the complex are greater than the changes observed for the ethylenic protons, and this order suggests that the protonation is primarily at a carboxylate site. However, for the ZnEGTA and PbEGTA complexes the opposite order is observed; ethylenic protons, adjacent to the nitrogens, undergo a larger shift upon protonation than do the acetate protons of the complexes. This behavior suggests nitrogen protonation for ZnEGTA and PbEGTA. Conclusions regarding the primary protonation site from nmr and infrared data are identical. Substantial changes in the chemical shifts of the ethylenic protons in those complexes which appear to be carboxylate protonated could represent contributions from nitrogen-protonated fractions.

The protonation pattern for the EGTA complexes and their nmr spectra warrant additional comment. If the ether oxygen atoms participated in binding to the metal ions, one would expect a significant change in the electronic environment of the methylene protons adjacent to these atoms. The absence of any significant change in the chemical shifts of these protons when the ligand is complexed to Pb^{2+} , Cd^{2+} , Hg^{2+} , or Zn^{2+} suggests that the ether oxygens do not participate in coordinate bonding. Two possible structures for EGTA complexes which do not involve metal-ether oxygen bonding incorporate either cis or trans metal-nitrogen bonds. Both of these structures have an 11-member chelate ring, and molecular models indicate that both are feasible. The trans nitrogen configuration would be especially favorable for the Hg^{2+} complex because of the tendency for Hg^{2+} to form two strong 180° bonds.³⁰ The differential protonation patterns of Pb- and Zn- and Cd- and Hg-EGTA com-

plexes may reflect the relative abilities of these ions to accommodate the large chelate ring. The presence of a single AB pattern for the Hg- and Cd-EGTA complexes suggests that either the cis or the trans configuration dominates (*i.e.*, a mixture of cis and trans could lead to two distinct sets of AB patterns). In addition, the single AB pattern (and single set of satellites) for these two complexes indicates that the metal-carboxylate bond may be sufficiently labile effectively to average possible chemical shift differences for the two types of acetate groups present in either the cis or the trans configuration.²⁴

In addition to the AB splitting for the acetate protons in the nmr spectra for CdEGTA and HgEGTA the coupling of the acetate protons to the spin $1/2$ isotopes of Cd and Hg provide additional information about the complexes. The observed J_{BX} ($X = {}^{111}Cd, {}^{113}Cd$) is 20 Hz and J_{AX} is 11 Hz for the A and B protons on each acetate group of the ligand. Differences between AX and BX coupling of acetate protons have been observed in the nmr spectra for Co(III) and Mo(VI) complexes of iminodiacetic acid (IDA) where the X nucleus was the N-H proton.^{31,32} These effects can be attributed to the differences in the dihedral angle that the A and B protons make with the X nucleus.^{31,32} Thus the conformation of acetate chelate rings in Cd- and HgEGTA is such that the dihedral angle which the B protons make with the Cd or Hg nucleus is more favorable for coupling than the corresponding angle for the A protons. In the spectrum for HgEGTA the differential coupling of the geminal acetate protons to ${}^{199}Hg$ lifts their approximate chemical shift degeneracy and the splitting pattern is almost first order. Similar effects have been observed for mercury dialkyls.³³

The exchange of Zn ions between EDTA ligands in acidic solutions proceeds *via* acid-assisted dissociation of the complex followed by an association of EDTA with the hydrated Zn^{2+} ion. Thus, the rate expression for the exchange reaction is identical with that found for the exchange reaction of Zn^{2+} ions with Zn^*EDTA ($Zn^* = {}^{65}Zn$) in a study by Jervis and Krishnan.¹¹ The agreement between the rate constants obtained from the nmr and radiolabeling techniques for the dissociation of the protonated complex, k_{HZnY} , is excellent (see Table V). However, there is an order of magnitude discrepancy between the values for the rate constant k^H_{HZnY} . The reason for this discrepancy is not clear. The value of k^H_{HZnY} obtained in the isotopic exchange study would require a 2.1-Hz broadening of the proton nmr resonances of ZnEDTA at pH 3.50 where the total line width is actually less than 1.2 Hz ($0.10 F ZnY, 0.10 F Y_i$).

Association rate constants, k^{HY}_{Zn} and $k^{H_2Y}_{Zn}$, for the reaction of Zn^{2+} with monoprotonated EDTA and diprotonated EDTA, respectively, differ by three orders of magnitude, and this difference reflects a change in the rate-determining step for association reactions with changes in the extent of protonation of the ligand. The value for k^{HY}_{Zn} is in the region of rate constants for which the rate of water loss from Zn^{2+} is the rate-determining step in the reaction.²⁹ The three order of magnitude difference in k^{HY}_{Zn} and $k^{H_2Y}_{Zn}$ cannot be accounted for from a decrease in the outer-sphere association constant

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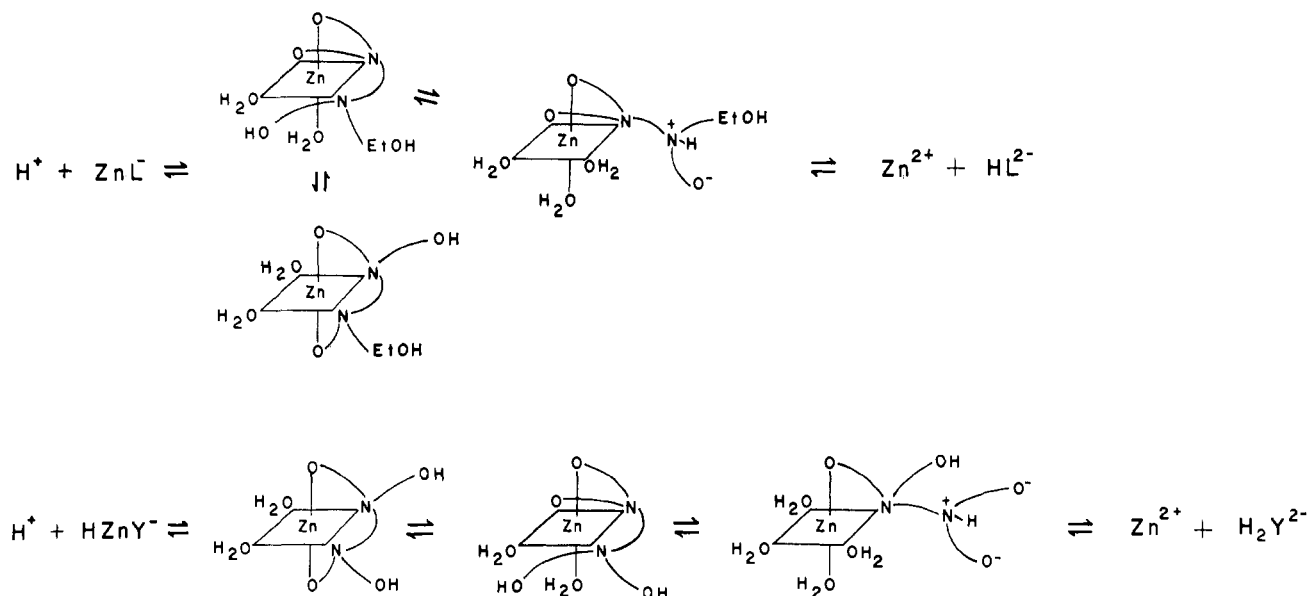
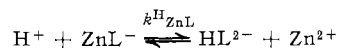


Figure 5.—Possible stepwise mechanisms for acid-assisted dissociation reactions for ZnHEEDTA and HZnEDTA.

in the two reactions, and the rate of water loss from Zn^{2+} is not the rate-limiting step in the reaction of Zn^{2+} with H_2Y . The rate-limiting step in this reaction may be the transfer of an acid proton from one of the nitrogens of EDTA. Proton transfer would be required before a Zn–N bond could form, and such proton-transfer reactions in amino acids have been shown to proceed at a relatively slow rate.³⁴ Protonation of the nitrogen nitrilotriacetate ion (NTA) slows the rate of formation of the Zn complex with this ligand, and a proton-transfer step has been suggested as the slow process in this reaction.³⁵ Decreases in the association rates of metal ions with diprotonated EDTA have been observed in other systems.²⁹

The rate constant for the dissociation of protonated ZnHEEDTA, k_{HZnL} , is almost two orders of magnitude greater than the rate constant k_{HZnY} for the dissociation of protonated ZnEDTA. This difference may be attributed, in part, to the lower number of ligand dentates available for coordination in the ZnHEEDTA complex. In fact, the extent of coordination in the protonated ZnHEEDTA complex should be analogous to that of EDTA in the diprotonated ZnEDTA complex. When the dissociation reaction of ZnHEEDTA is expressed as



where $k_{ZnL}^H = k_{HZnL}(K_a^{HZnL})^{-1}$, the process can be compared to the acid-assisted dissociation of protonated ZnEDTA which is characterized by the constant k_{HZnY}^H . Since the same number and types of coordinate bonds are involved in both reactions and there are no overall electrostatic differences, the two reactions could be expected to proceed at equal rates. However, k_{ZnL}^H is an order of magnitude greater than k_{HZnY}^H . The observed difference in the rates of dissociation in the two complexes may, in fact, be related to the positions of coordinate bonds in the protonated intermediates as illustrated in Figure 5. Nmr spectra for ZnHEEDTA in acidic solutions show that both types of acetate protons

are deshielded to the same extent upon protonation of the complex so that protonation of the carboxylate group on the unsymmetrical (monoacetate) end of the ligand does occur. The intermediate in the ZnHEEDTA system with the acidic proton on the carboxylate of the monoacetate end of the ligand would undergo "half-unwrapping" readily with a rupture of the adjacent Zn–N bond. On the other hand, in the diprotonated ZnEDTA intermediate the presence of an acidic proton on a carboxylate group at one end of the ligand could make a simultaneous protonation of the adjacent carboxylate groups less favorable, on electrostatic grounds. Thus, the more predominant form of the diprotonated ZnEDTA complex would exist in a state which would require both a zinc–nitrogen and zinc–carboxylate bond rupture before the complex would reach the "half-unwrapped" condition. An alternate explanation for the more sluggish dissociation in the ZnEDTA system would involve a slow addition of the second proton to the complex.

The rate of association of Zn^{2+} with HL^{2-} appears to be governed by the rate of water loss from the outer-sphere association complex of aquo Zn^{2+} and HL^{2-} . The water loss rate also appears to limit the association of Cd^{2+} and HZ^{3-} . However, as in the association reaction of Zn^{2+} with H_2Y , the association rate of Cd^{2+} with H_2Z^{2-} is slowed by the presence of acidic protons on both nitrogens of the ligand. Thus, in the association of Cd^{2+} and H_2Z^{2-} a proton transfer from a nitrogen of the ligand may be the rate-limiting step.

Spectral properties of the HgEGTA complex in acidic solutions were extremely sensitive to relatively small concentrations of monovalent anions which form rather strong complexes with Hg^{2+} . In the absence of such anions the HgEGTA complex is not particularly susceptible to acid-dissociation reactions or second-order exchange with the free ligand, whereas in concentrations of the anions as low as 2% of the HgEGTA concentration, exchange of Hg ions between EGTA ligands becomes observable. Margerum and Janes³⁶ have examined an acceleration in the rate of acid dissociation of

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the mercury(II)-cyclohexanediaminetetraacetate (Hg-CyDTA) complex brought about by complexing anions. These workers concluded that the anions, coordinated to Hg ions in ternary Hg-anion-CyDTA complexes, facilitate the formation of a nitrogen-protonated intermediate and thus accelerate the overall acid dissociation of the complex. Hydrogen ion and anion dependencies of the line broadening in the HgEGTA spectrum suggest that the anions play a similar role in the dissociation

of the HgEGTA complex. However, more quantitative information on the ternary complexes in the EGTA system would be necessary before the detailed mechanism and the rate constants for the dissociation reaction can be established.

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Transition Metal Eight-Coordination. II. Synthesis and Characterization of Several Tetrakis(8-quinolinolato)tungsten(IV) Chelates^{1a}

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A series of tungsten(IV) 8-quinolinol complexes of the type WL_4 (where L = 8-quinolinol or a derivative thereof) has been synthesized and spectrally and magnetically characterized. For L = 5-chloro-, 5-bromo-, 5,7-dichloro-, and 5,7-dibromo-8-quinolinolato, synthesis is feasible from sealed-tube melt reactions between either $K_3W_2Cl_9$ or $W(CO)_6$ and the appropriate quinolinol derivative. For the parent complex, salts of $W_2Cl_9^{3-}$ are required. Synthesis in high-boiling basic organic solvents is also feasible as shown by the synthesis of the L = 5-acetyl-8-quinolinolato derivatives from $W(CO)_6$ and the ligand in pyridine. Chemical investigation indicates inertness to alcoholic KOH. Electronic spectra (5–36 kK) of these complexes display low-energy charge-transfer bands ($14\text{--}15\text{ kK}$, $\epsilon > 10^4$) plus the ligand transitions usually observed in 8-quinolinol complexes with other metal ions. The dihalo derivatives also show two low-intensity bands in the near-infrared region (9.9–11.2 kK) which are absent in the other derivatives. Magnetic measurements indicate that the complexes are spin paired. Together the observations constitute evidence for the first unequivocal series of inert, completely chelated eight-coordinate complexes of d^2 spin-paired electronic configuration.

Introduction

Although hundreds of octahedral complexes are known which are inert to substitution reactions, the octacyano ions were the only substitution-inert eight-coordinate complexes known prior to this study.² Whereas most eight-coordinate complexes of transition elements are d^0 or easily oxidized d^1 complexes,³ we have synthesized a series of completely chelated, spin-paired d^2 eight-coordinate complexes which are inert to alcoholic KOH.

A stereochemical rule regarding the geometry in transition metal eight-coordinate species was formulated by Orgel in 1960.⁴ He suggested that eight-coordinate systems of the type MA_4B_4 (M = d^2 metal ion; A = ligand without π -acceptor properties; B = π -acceptor ligand) should adopt a dodecahedral stereochemistry

with the π -acceptor B ligands forming a flattened tetrahedral array to give maximum overlap with the filled metal $d_{x^2-y^2}$ orbital, while nonacceptor A ligands should occupy the elongated tetrahedral positions of the dodecahedron. Hoard and Silverton⁵ later designated these positions as B and A dodecahedral sites, respectively. The proposal by Orgel was based on the reported stoichiometries of $Mo(CN)_4(OH)_4^{4-}$,⁶ $W(CN)_4(OH)_4^{4-}$,⁶ $Mo(CN)_4(OH)_3H_2O^{3-}$,^{6,7} and $ReCl_4(diars)_2^{+}$.⁸ Recent crystallographic and infrared evidence⁹ has disproved the formulation of the molybdate and tungstate species, and the $ReCl_4(diars)_2^{+}$ structure is unknown. The steric bulk of the diars and chloride ligands may preclude electronic structure control; therefore, other MA_4B_4 complexes appeared necessary if Orgel's postulate were to be checked.

The preparation of MA_4B_4 complexes of d^2 electronic configuration with four π -acceptor ligating atoms and four other donors should allow an evaluation of Orgel's postulate. The ligand 8-quinolinol appeared ideal because the unsaturated nitrogen atoms are σ donors

(1) Taken in part from the Ph.D. dissertation of W. D. B., University of Massachusetts, 1970. Abbreviations: HQ, 8-quinolinol; HQCl, 5-chloro-8-quinolinol; HQCl₂, 5,7-dichloro-8-quinolinol; etc. $1\text{ kK} = 1000\text{ cm}^{-1}$. Part I: R. D. Archer and W. D. Bonds, Jr., *J. Amer. Chem. Soc.*, **89**, 2236 (1967).

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