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Interaction of Bivalent Metal Ions with Their Chelates of Ethylenedinitrilotetraacetic Acid (EDTA) and 1,2-*trans*-Cyclohexylenedinitrilotetraacetic acid (CDTA)

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An interaction of bivalent metal ions with their EDTA and CDTA complexes was established by means of spectrophotometry for Cu^{2+} and by means of nmr for Zn^{2+}. The competition between protons and metal ions in their reaction with metal chelates was demonstrated for Cu^{2+} and Zn^{2+} by aid of infrared spectroscopy and for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} by pH measurements. Evidence is presented for the formation of binuclear copper chelates of CDTA and it is proposed that the formation of binuclear chelates of bivalent metal ions with EDTA and CDTA is a general phenomenon. Whereas a symmetrical structure, with the metal ions in equivalent positions, may be achieved for binuclear EDTA complexes, this is obviously impossible for the CDTA complexes. From the known values of stability constants the formation of symmetrical binuclear EDTA complexes is, however, improbable except for Cu^{2+}. The intensity of the visible absorption band of the mononuclear EDTA complex of copper was found to be strongly temperature dependent. This is thought to reflect an equilibrium between complexes, differing in the number of water molecules, bound to the Cu^{2+} ion. Attention is drawn to the parallelism in spectral changes of CuEDTA observed on cooling and on protonation; both changes are imputed to a change in the number of coordinated water molecules. For the corresponding CDTA complex no temperature dependence of the light absorption was found, indicating the absence of a notable change in the coordination of the Cu^{2+} ion.

Introduction

On account of the preference for six-coordination of bivalent metal ions the bonding of more than one metal ion to one ligand molecule is not unexpected for ligands with more than six donor atoms. For example, binuclear complexes of diethylenetriaminepentaacetic acid (DTPA) or triethylenetetraminehexaacetic acid (TTHA) and ligands of the type $(CH_2COOH)_2N(CH_2)_nN(CH_2COOH)_2$ with $n \geq 3$ have been reported.[1-3] The formation of 2:1 bivalent metal–EDTA and –CDTA complexes is less obvious.

The existence of binuclear EDTA complexes in liquid solution has often been neglected or even denied.[4,5] However, the proposed formation of binuclear complexes of Ca^{2+} and Sr^{2+}, deduced from nmr experiments,[6] is an exception. A symmetrical configuration has been proposed for these complexes. In crystalline complexes symmetrical as well as asymmetrical configurations have been observed. In the symmetrical configuration as found for $Cu_2Y{\cdot}4H_2O$[7] (H_4Y represents EDTA) both metal ions are bound to an iminodiacetate fragment of the EDTA molecule; in the asymmetrical configuration as observed in $Sn_2Y{\cdot}4H_2O$[8] one metal ion is fully coordinated by the EDTA molecule whereas the second ion is bound to carboxylate oxygen atoms and water molecules.

The existence of heteronuclear 2:1 complexes of CDTA (H_4Cy) has been proposed by Margerum in explaining the rate-suppressing influence of Pb^{2+} or Cu^{2+} ions on proton-catalyzed exchange reactions.[9] For CDTA symmetrical binuclear complexes are very unlikely, owing to the rigidity of the ligand molecule.

Observations will be reported from which the interaction of a number of bivalent metal ions with their EDTA and CDTA complexes could be deduced. The formation of Cu_2Cy was established and of Cu_2Y made probable. Absorption spectra of binuclear, protonated, and normal copper chelates will be given and the structure of these chelates will be discussed.

Experimental Section

All chemicals were reagent grade. Solutions of metal perchlorates were prepared by treating the basic carbonates $MCO_3{\cdot}M(OH)_2$ with perchloric acid (M represents a bivalent metal). The pH of the solutions was adjusted with NaOH or $HClO_4$. The ionic strength was controlled with $NaClO_4$. Deuterium oxide, which was used as a solvent in the infrared measurements, contained 99.75% D_2O. Solutions in D_2O were obtained by evaporation of the corresponding aqueous solutions and dissolution of the residue in D_2O. The evaporation followed by dissolution in D_2O was repeated twice. The pD of the solutions was obtained from a pH meter reading by employing the empirical equation[10]

$$pD = pH_{\text{meter reading}} + 0.40$$

Infrared spectra were recorded on a Hitachi EPI-G grating

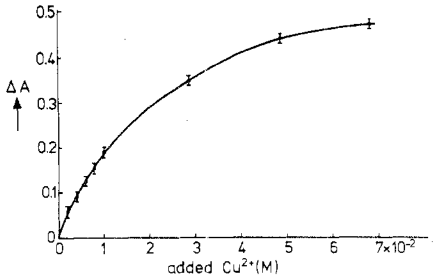

Figure 1. Excess absorbance of a 10^{-2} *M* $CuCy^{2-}$ solution to which $Cu(ClO_4)_2$ is added. Wavelength 640 nm; pH 4.0; temperature 25°; 1.25 *M* $NaClO_4$. Measured extinction coefficients of $CuCy^{2-}$ and Cu^{2+} at this wavelength are 78 and 3.4, respectively.

Table I. pH Observed after Mixing Solutions of $M(ClO_4)_2$ with Equal Volumes of Solutions of MHY^- or $MHCy^-$

[Metal], *M*	[Y], *M*	pH_{final}	[Cy], *M*	pH_{final}
1.00 (Cu^{2+})	0.1	1.3	0.1	1.4
1.00 (Ni^{2+})	0.1	2.0	0.1	2.0
1.00 (Co^{2+})	0.1	2.1	0.1	2.0
0.25 (Zn^{2+})	0.05	2.1	0.05	2.0
0.25 (Cd^{2+})	0.05	2.0	0.05	2.0

[a] Initial pH for all solutions 2.5; temperature 25°.

spectrometer, using cells having windows of calcium fluoride which were separated by Mylar spacers of 15 or 23 μm. Visible spectra were obtained by aid of a scanning Cary 16 spectrophotometer.

Nmr spectra were recorded on a Varian A-60 spectrometer. Chemical shifts were measured in ppm with respect to the sodium salt of 2,2,3,3-tetradeuterio-3-(trimethylsilyl)propionic acid (tdtp). The concentrations of the nmr solutions ranged from 0.2 to 0.4 *M*; no $NaClO_4$ was added.

Results

Formation of Cu_2Cy. Increased Light Absorption. The existence of an interaction between Cu^{2+} and $CuCy^{2-}$ is demonstrated by an increase in light absorption of a mixture containing $CuCy^{2-}$ with an excess of Cu^{2+} at pH 4.0 with respect to the sum of the absorbances of the components at the same pH (Figure 1). For solutions of pH ≤2.5 where CuCDTA exists mainly as the protonated complex $CuHCy^-$ (p*K* = 3) a similar, somewhat smaller increased light absorption was observed.

pH Effect and Ir Spectra. When solutions of CuCDTA in which the protonated species $CuHCy^-$ predominate (pH <3) are mixed with solutions of cupric perchlorate of the same pH, a notable decrease in pH is observed (Table I). This shows that there is a competition between protons and cupric ions, probably according to the equation

$$CuHCy^- + Cu^{2+} \rightleftharpoons Cu_2Cy + H^+ \qquad (1)$$

For CuCDTA solutions in which $CuCy^{2-}$ prevails (pH 4.0) no change in pH was observed.

The competition between cupric ions and protons was also studied by means of infrared spectroscopy. Sawyer and Tackett observed that upon acidification of solutions of CuY^{2-} the 1600-cm^{-1} carboxylate absorption band decreased in intensity and that a shoulder developed at approximately 1700 cm^{-1}. The band at 1600 cm^{-1} was interpreted as due to absorption by free or complexed carboxylate groups whereas the band at 1700 cm^{-1} was considered to be characteristic of deuterated carboxylate groups. We observed similar absorption bands in solutions of $CuCy^{2-}$ (pD 4.0) and $CuDCy^-$ (pD 2.3). Upon the addition of a large excess of cupric perchlorate to a solution of $CuDCy^-$ at a constant pD of 2.3 the deuteration shoulder disappeared completely.

Composition. The composition of the complex was obtained from a continuous-variation plot of the differential light absorption (Job's method). The plot, which was obtained for a total concentration of 5×10^{-2} *M*, showed a maximum at $[Cu^{2+}]:[CuCy^{2-}]$ = 1:1. Hence the complexation equilibrium is

$$Cu^{2+} + CuCy^{2-} \rightleftharpoons Cu_2Cy \qquad (2)$$

Stability Constant. The stability constant was obtained graphically from the measured excess light absorption data of Figure 1. Owing to the impossibility of performing accurate measurements of the free Cu^{2+} concentration, a careful analysis by means of a plot based on the formation function of the Cu_2Cy and the free Cu^{2+} concentration (a Scatchard plot for example) was impossible. Therefore we resorted to the generally less recommendable procedure described by Rossotti.[12] In this method the initial concentration of $CuCy^{2-}$ and the total concentration of Cu^{2+} added to the $CuCy^{2-}$ are used. A plot of $[Cu^{2+}][CuCy^{2-}]/\Delta A$ *vs.* $[Cu^{2+}] + [CuCy^{2-}]$ yielded a straight line. A least-squares fit of the data yielded $K = 80 \pm 16\ M^{-1}$. A *post hoc* justification for the use of this procedure is that six out of eight measuring points from Figure 1 correspond to formation fractions of Cu_2Cy between 0.2 and 0.8. According to Deranleau[23] it is necessary to perform measurements in this region of formation fractions in order to obtain reliable values of stability constants by graphical methods. Owing to the fact that all three species Cu_2Cy, $CuCy^{2-}$, and Cu^{2+} absorb in the spectral region of interest, it is difficult to obtain an accurate value of the stability constant from spectrophotometric measurements. The stability constant was also estimated by titration of the protons liberated in reaction 1 after a stepwise addition of Cu^{2+}. From the protonation constants of $CuCy^{2-}$ [13] the degree of formation of Cu_2Cy can in principle be calculated from the amounts of alkali required to restore the original pH of 2.5 after each addition of Cu^{2+}. This method yielded a significantly lower value of 30 M^{-1}. Since this value depends critically on the values of the protonation constants, the second of which is not accurately known, it must be considered as rather inaccurate. It is, however, of the same order of magnitude as the photometric result. Owing to experimental difficulties the value of the stability constant cannot be accurately determined. However, in view of the combined experimental results the formation of a species Cu_2Cy can be regarded as beyond doubt. In solutions containing no $NaClO_4$ a stability constant of approximately 300 M^{-1} was found optically.

Formation of Cu_2Y. Formation of Cu_2Y was inferred from the pH effect (Table I) and from the reduction of the infrared band at 1700 cm^{-1} upon addition of excess copper perchlorate to a solution of $CuDY^-$ (pD 2.1). The increase in light absorption upon the formation of this complex was smaller than for the corresponding CDTA complex. Therefore it was difficult to determine the composition and the stability constant of the complex from optical measurements. The titration method yielded, with the same limitations as for Cu_2Cy, a stability constant of 20 M^{-1}.

Absorption Spectra of the Binuclear, Protonated, and Normal Copper Chelates. Once the stability constant is known, the visible absorption spectrum of Cu_2Cy can be obtained by subtraction of the absorbance of $CuCy^{2-}$ and Cu^{2+} from the total absorbance of solutions containing 10^{-2} *M* $CuCy^{2-}$ with a tenfold excess of cupric perchlorate. The result is shown in Figure 2, together with the spectra of solutions of $CuCy^{2-}$ and $CuHCy^-$. The latter was calculated by doubling the change in absorbance observed in going from pH 6 (only $CuCy^{2-}$) to pH 2.7 (the inflection point of the absorbance *vs.* pH curve which corresponds to $[CuCy^{2-}]/[CuHCy^-] = 1$). At pH 2.7 the contributions from CuH_2Cy and free Cu^{2+} are small, as follows from the values of the successive protonation constants of $CuCy^{2-}$ (pK_1 = 2.7 and pK_2 = 2.0 in 1.25 *M* sodium perchlorate solutions).[13]

The absorption spectrum of Cu_2Y (Figure 3) was calculated by assuming 100% conversion to Cu_2Y in a solution containing

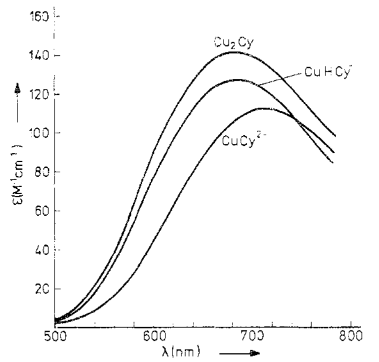

Figure 2. Absorption spectra of $CuCy^{2-}$, $CuHCy^-$, and Cu_2Cy. The last was calculated at pH 4.3, 25°, and 1.25 M $NaClO_4$. For $CuHCy^-$ and Cu_2Cy conditions see text.

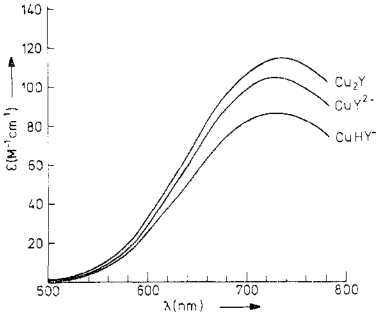

Figure 3. Absorption spectra of CuY^{2-}, $CuHY^-$, and Cu_2Y. The last was calculated at pH 4.3, 25°, and 1.25 M $NaClO_4$. For $CuHY^-$ and Cu_2Y conditions see text.

10^{-2} M CuY^{2-} and 10^{-1} M Cu^{2+}. Due to the strong similarity between the spectra of Cu_2Y and CuY^{2-}, the calculated extinction coefficient increases only by 6% if we assume 50% conversion to Cu_2Y corresponding to a value of K of only 10 M^{-1}.

The absorption spectrum of $CuHY^-$ was calculated in the same way as that of $CuHCy^-$.

Temperature Dependence of the Absorption Spectra of the Normal Chelates. We have also compared the temperature dependence of the absorption spectra of the normal complexes CuY^{2-} and $CuCy^{2-}$ (Figure 4). The light absorption of the latter complex shows hardly any temperature dependence after correction for thermal expansion whereas the former shows a considerable increase in absorption upon heating. The increases in bandwidths with temperature were small and the same for both complexes.

The different changes in the spectrum of CuY^{2-} as compared with that of $CuCy^{2-}$, which are observed upon heating as well as upon protonation, might well be due to a difference in rigidity of the ligand molecule: the flexible EDTA molecule is much more able to change its coordination to the central metal ion than is the rigid CDTA ligand.

Observations with Other Metal Ions. In order to establish whether the behavior of copper is normal or uncommon as compared with other bivalent metals, the interaction between a number of metal ions and their complexes was checked.

The pH effect was observed for Zn^{2+} and Cd^{2+} and for Ni^{2+} and Co^{2+} (Table I).

A differential light absorption as observed for $CuCy^{2-}$ with excess Cu^{2+} was also found for example for $CuCy^{2-}$ with Zn^{2+} and for $CuCy^{2-}$ with Ni^{2+}.

The competition of protons and metal ions in their reaction with the metal chelates was evidenced by the infrared spectra of the zinc complexes of EDTA and CDTA in the same way as for copper. Similar experiments on cadmium complexes failed owing to the formation of insoluble cadmium compounds upon standing of the solutions.

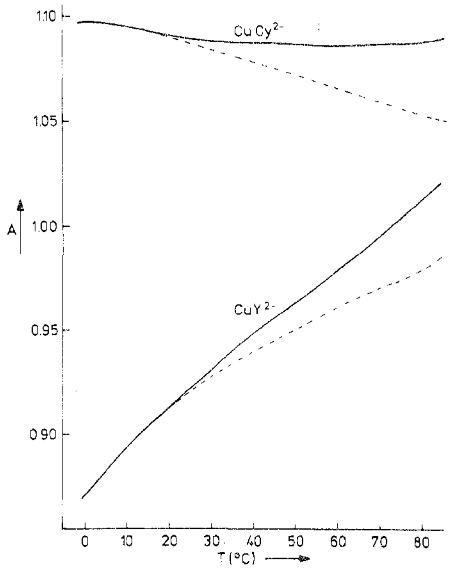

Figure 4. Temperature dependence of the absorbance of 0.98 × 10^{-2} M solutions of CuY^{2-} and $CuCy^{2-}$, recorded at 730 and 715 nm, respectively, pH 7.0, and 0.125 M $NaClO_4$. Dotted curves are uncorrected for thermal expansion.

Nmr Experiments with Zinc and Cadmium Complexes. Upon protonation of ZnEDTA (pH 8 → 1.5) the line widths of the acetate and ethylenic resonances increased from 1.4 and 1.2 Hz, respectively, to 2.0 and 2.5 Hz. After the addition of an equivalent amount of Zn^{2+} at pH 1.5, the line widths decreased again to 1.8 and 2.1 Hz, respectively. This is taken as indicative of an interaction of zinc ions with the $ZnHY^-$ complex.

The behavior of ZnCDTA is shown in Figure 5. Protonation causes a small broadening of the resonance lines. Heating of the protonated complex results in the almost complete collapse of the spectrum. Heating of the unprotonated complex (not shown in the figure) caused only a narrowing of the resonance lines. The addition of excess Zn^{2+} ions to the heated, protonated complex leads to reappearance of the lines.

The nmr behavior of the zinc complexes is in accord with the competition between H^+ and Zn^{2+} ions deduced from the infrared spectra and the pH measurements.

For CdEDTA a similar line broadening as observed for ZnEDTA was found upon protonation (Figure 6). It disappeared after heating. The broadening upon acidification followed by the subsequent narrowing upon heating with the complete disappearance of the isotopic splitting evidences a labilization of the complex. Line shape analysis according to the method of Gutowsky, *et al.*, cited in ref 14, yields a lifetime of the protonated complex of $\tau = 0.1$ sec at 30°.

Since no excess ligand was present, line-broadening caused by exchange reactions with free ligand molecules as observed by Sudmeier and Reilley[15] can be excluded. The chemical reaction, responsible for the line broadening is probably

$$CdHY^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cd^{2+} + HY^{3-} \qquad (3)$$

The observed dissociation rate constant $k_1 = 10$ sec^{-1} compares well with the value that is obtained from the equilibrium constant $K = k_2/k_1 = 10^{9.1}$ [16] and the rate of exchange of water molecules on $Cd^{2+}(H_2O)_6$ of 10^8 sec^{-1}.[17] It is also in agreement with a previously determined value.[15]

With CdCDTA no collapse of the spectrum was observed upon protonation. Heating of the protonated complex caused a similar change of the spectrum as found for ZnCDTA (Figure 5c).

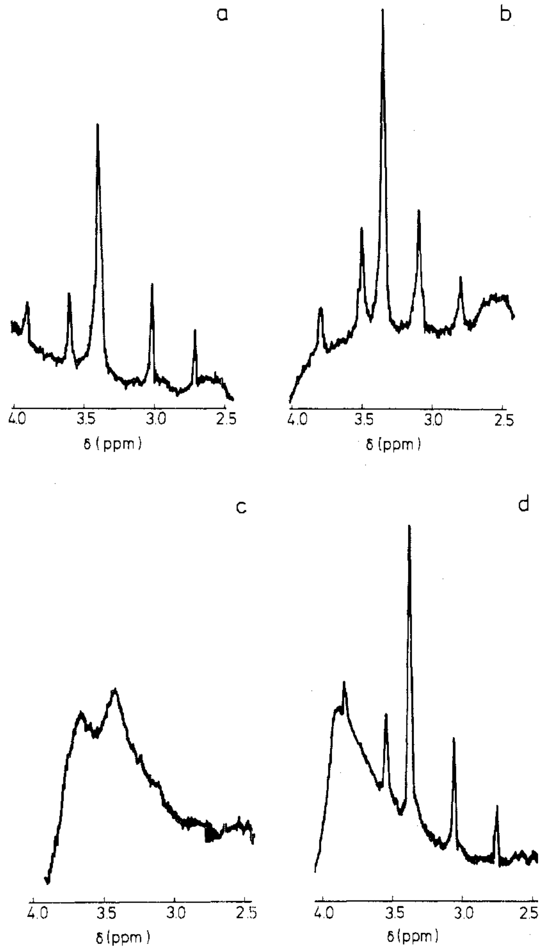

Figure 5. Proton nmr spectra of 0.2 *M* ZnCDTA. The signals of the ring protons have been omitted. Chemical shifts are in ppm from tdtp: (a) $ZnCy^{2-}$, pH 8.0, 30°; (b) $ZnHCy^-$, pH 2.5, 30°; (c) $ZnHCy^-$, pH 2.5, 90°; (d) Zn_2Cy, pH 2.5, 90° (0.2 *M* $ZnHCy^-$ + 0.2 *M* Zn^{2+}). The steep base line in the high-temperature spectra is caused by a temperature shift of the water signal.

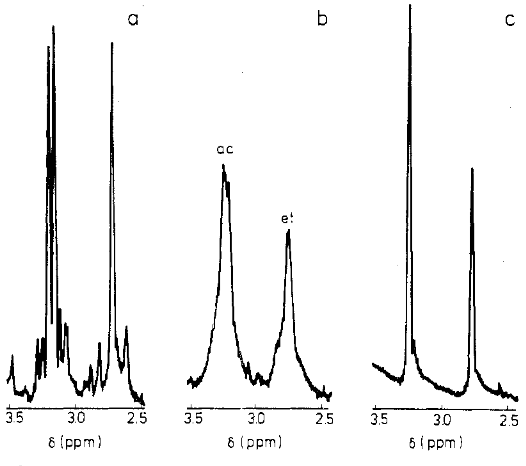

Figure 6. Nmr spectra of 0.4 *M* CdEDTA (ac, acetate protons; et, ethylenic protons): (a) CdY^{2-}, pH 8.0, 30°; (b) $CdHY^-$, pH 2.5, 30°; (c) $CdHY^-$, pH 2.5, 90°.

Discussion

Normal and Protonated Chelates. The structures of metal chelates in solution are rather uncertain. For example the number of bonds between a metal ion and a multidentate ligand is often unknown and so is the number of solvent molecules attached to the complexed cation. However, it has been shown that in protonated complexes of EDTA with copper,[18,19] nickel,[19,20] cobalt,[19] and lead[19] the protonated acetate arms are not bound to the cation. For neutral solutions, in which the unprotonated complexes of EDTA predominate, equilibria between species with six and five metal–ligand bonds have been proposed by Higginson and Samuel[19]

$$MY^{2-} + H_2O \rightleftharpoons M(H_2O)Y^{2-} \tag{4}$$

Since according to these authors neutral solutions contain about 60–80% of the hexadentate MY^{2-} species, protonation generally results in the rupture of an acetate–metal bond. Calorimetric studies by Nancollas, *et al.*,[21] are in accordance with this view; namely, the exothermic character of the protonation reaction

$$MY^{2-} + H^+ \rightarrow MHY^- \tag{5}$$

was attributed by these authors to a release of strain upon the opening of a chelate ring; the value of ΔH of approximately -2 kcal mol^{-1} compares nicely with the value of -2.9 kcal mol^{-1} found by Hunt for the hexadentate–pentadentate equilibrium in NiY^{2-} solutions.[20]

The temperature dependence of the intensity of the visible absorption band of CuY^{2-} (Figure 4) is in agreement with the proposed existence of an equilibrium between different complexes. The decrease in absorbance observed upon cooling parallels the decrease observed upon protonation (Figure 3). Since protonation results in a reduction of the number of ligand–metal bonds according to the exothermic reaction

$$MY^{2-} + H^+ + H_2O \rightarrow M(H_2O)HY^- \tag{6}$$

the effect observed on cooling might well be caused by a similar exothermic reaction

$$MY^{2-} + H_2O \rightarrow M(H_2O)Y^{2-} \tag{7}$$

The decrease in absorbance observed upon protonation of CuY^{2-} to $CuHY^-$ may be simply explained as follows. Rupture of an acetate–metal bond and the subsequent replacement of the acetate group by a water molecule in the first coordination sphere of the metal ion leads to a more symmetrical, pseudooctahedral environment of the metal ion. This, owing to the forbidden character of the ionic d → d transition, leads to a reduction of the intensity of the absorption band (Figure 3).

Study of molecular models shows that in CDTA complexes MCy^{2-} the presence of free, uncomplexed acetate arms is rather unlikely: the rotation of the acetate arms around the C–N bond is obstructed by the hydrogen atoms of the cyclohexane ring. Although protonation may still cause rupture of an acetate–metal bond, the subsequent insertion of a water molecule is improbable. This may explain the observed increase of the intensity of the $CuCy^{2-}$ visible absorption band upon protonation: the asymmetry around the cupric ion increases with respect to the unprotonated complex. The absence of a pronounced temperature dependence of the extinction coefficient of $CuCy^{2-}$ is in accord with the hindered rotation around the C–N bond, excluding water substitution in the case of $CuCy^{2-}$.

Binuclear Chelates. There is a similarity in the spectral changes observed on protonation of $CuCy^{2-}$ and the formation of Cu_2Cy: both reactions cause a blue shift of the visible absorption band from 720 to 690 nm and in both cases the molar extinction coefficient increases considerably (Figure 2). This suggests a similarity in the attachment of the proton and the second Cu^{2+} ion. Competition of protons and metal ions is illustrated by the change in the infrared spectra of protonated complexes upon the addition of excess metal ions (*cf.* ref 11) and by the observed pH effect (Table I).

In binuclear copper–carboxylate complexes it is often observed that two copper ions are linked by carboxylate groups. A coordination of the second copper ion with a peripheral

Table II. ΔG of 1:1 Complexation of Some Metal Ions M^{2+} with EDTA (Y), MIDA (L), and Acetate (Ac)[16] (in kcal mol^{-1})[a]

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
$-\Delta G(MY^{2-})$	11.5	14.5	11.7	10.5	21.8	24.9	25.1	22.1	22.0	24.3
$-\Delta G(ML)$	4.6	5.0	3.8	3.5	10.2	11.7	14.9	10.3	9.1	10.8
$-\Delta G(MAc^+)$	0.7	0.7	0.6	0.6	1.4	1.4	2.6	1.7	2.2	3.0
$-\Delta\Delta G$	3.0	5.2	4.7	4.1	2.8	3.1	−2.1	3.2	6.0	5.7

[a] Conditions: 20° and 0.1 *M* KNO_3 for EDTA and MIDA; 20 or 25° and ionic strength 0.1 or 0.2 for acetate.

CDTA oxygen atom may therefore be expected. Equivalent positions for the two Cu^{2+} ions seem very difficult to achieve owing to the rigidity of the molecule.

In crystalline $Cu_2Cy{\cdot}4H_2O$ the second Cu^{2+} ion links two neighboring $CuCy^{2-}$ complexes by coordination to one carboxylate group of each molecule. Its coordination polyhedron is completed by the four molecules of water of crystallization.[22]

In the case of CuY^{2-}, on the other hand, there is no similarity between the spectral changes on protonation and on formation of Cu_2Y (Figure 3), pointing to an attachment in nonequivalent positions of the proton and the second Cu^{2+} ion. For the binuclear complex a centrosymmetrical structure may be achieved in which the cupric ions occupy equivalent positions. Such a structure has been observed in crystalline $Cu_2Y{\cdot}2H_2O$.[6] The EDTA molecule then acts as two linked molecules of methyliminodiacetic acid (MIDA). Since the absorption spectra of Cu(MIDA) and CuY^{2-} both show a maximum near 730 nm, the absence of a pronounced wavelength shift for Cu_2Y as compared with CuY^{2-} is not unreasonable.

In the following discussion we will try to estimate the relative stabilities of symmetrical and asymmetrical complexes M_2Y. Since the binuclear complexes are formed spontaneously from M^{2+} and MY^{2-}, the free enthalpy of formation of M_2Y from $2M^{2+}$ and Y^{4-} must exceed that of MY^{2-}.

For the asymmetrical complexes, in which the second metal ion is supposed to be bound to an acetate group of the EDTA molecule, we estimate ΔG for complexation of the second metal ion to be in the same range as ΔG for complexation of a metal ion with an acetate ion, *i.e.*,[16] $-3.0 \leq \Delta G(MAc^+) \leq -0.5$ kcal mol^{-1}. Then the free enthalpy of formation of M_2Y exceeds that of MY^{2-} by a small amount (Table II).

For the symmetrical complexes the free enthalpy of formation may be approximated by doubling ΔG of formation of 1:1 metal–MIDA complexes. This approximation may be valid since the number and kind of metal–ligand bonds in 2ML (H_2L = MIDA) are the same as in symmetrical M_2Y and since the halves of symmetrical M_2Y are uncharged. It is rather unlikely that contributions of strain are very different in 2ML and M_2Y.

In Table II a comparison is made between the free enthalpies of formation of a number of EDTA, MIDA, and acetate complexes. Our own observations were generally made on solutions of a higher ionic strength (1.25 *M* $NaClO_4$) but the spontaneous formation of binuclear complexes, as gauged from differential light absorption and pH effect, did also occur at lower ionic strengths.

According to the assumptions made above, the quantity $\Delta\Delta G = \Delta G(MY^{2-}) + \Delta G(MAc^+) - 2\Delta G(ML)$ gives an indication of the relative stability of the two conformations. This quantity is listed in Table II. Although not too much weight should be given to the numerical values of $\Delta\Delta G$, the rather exceptional position of Cu^{2+} is obvious. The large difference between the positive $\Delta\Delta G$ for Cu^{2+} and the negative $\Delta\Delta G$ for other metal ions makes the formation of symmetrical binuclear chelates for the latter, as for example proposed for Ca^{2+} and Sr^{2+},[8] rather unlikely.

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Registry No. EDTA, 60-00-4; CDTA, 13291-61-7; Cu, 7440-50-8; Ni, 7440-02-0; Co, 7440-48-4; Zn, 7440-66-6; Cd, 7440-43-9; Mg, 7439-95-4; Ca, 7440-70-2; Sr, 7440-24-6; Ba, 7440-39-3; Pb, 7439-92-1.

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