A New Chelating Cyclophane and Its Complexation with Ni^{2+}, Cu^{2+}, and Zn^{2+}: Spectroscopic Properties and Allosterism *via* Ring Contraction

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Received November 27, 1996[⊗]

A condensation reaction between ethylenediaminetetraacetic dianhydride and *p*-xylenediamine gave a new chelating cyclophane, 3,10,21,28-tetraoxo-5,8,23,26-tetrakis(carboxymethyl)-2,5,8,11,20,23,26,29-octaaza[12.12]paracyclophane, abbreviated as (32edtaxan)H_4, which has three types of electron-donor groups, *i.e.*, amine, carboxylate, and amide groups. The formation of the cyclophane has been confirmed by a single-crystal X-ray analysis of its Zn^{2+} complex, $[Zn_2(32edtaxan)]\cdot 7.5H_2O$, which crystallized in the monoclinic space group $P2_1/c$ with $a = 19.818(1)$ Å, $b = 13.169(1)$ Å, $c = 18.134(1)$ Å, $\beta = 104.491(6)°$, and $Z = 4$. Each cyclophane molecule coordinates two Zn^{2+} ions and results in the formation of a binuclear chelate molecule. The coordination geometry around each metal ion is distorted octahedral, the donor atoms being two carboxylate oxygen atoms, two amine nitrogen atoms, and two amide oxygen atoms. The new cyclophane exhibited a well-defined fluorescence band at 290 nm with 210 nm excitation. The emission intensity was markedly increased in the Zn^{2+} complex, in which the coordination of Zn^{2+} ions increases the rigidity of the cyclophane leading to a high fluorescence quantum yield. When the cyclophane was coordinated to Cu^{2+} ions, the molar absorptivity of a $\pi-\pi^*$ transition band observed at 260 nm was increased by a factor of about 10. Such a large spectral change was not observed for the Zn^{2+} and Ni^{2+} complexes. In the Cu^{2+} complex, the two phenyl rings of the cyclophane are expected to be brought closer, as a result of the coordination of deprotonated amide nitrogens to the central metal ion. This allosterism *via* ring contraction is responsible for the novel behavior of the absorption spectrum. The emission band of the cyclophane was weakened by coordination of copper and nickel as a result of fluorescence quenching caused by a photo-induced electron transfer.

Introduction

In a water-soluble cyclophane molecule that contains aromatic groups in the macrocyclic ring framework, intermolecular and/or intramolecular interactions of the π-conjugated systems confer novel supramolecular properties to the cyclophane molecule in aqueous media.[1] When coordinating groups such as amine and carboxylate groups are substituents in the cyclophane ring system, the resulting functionalized cyclophane is capable of forming stable metal chelates. The aromatic groups of a chelating cyclophane are brought closer by coordination with a metal ion.[2] This allosterism is expected to be reflected in the absorption spectrum and also in the emission spectrum of the chelated cyclophane, if the aromatic group is fluorescent.[2] Spectral changes induced by complexation with specific metal ions provide possible approaches to the development of sensing and switching devices *via* supramolecular photophysics.[3]

We have reported that condensation reactions between ethylenediaminetetraacetic (edta) dianhydride and aliphatic diamines give a new series of tetraaza macrocycles, dioxotetraazacycloalkanediacetic acids, that have amide groups in the ring framework and pendant carboxymethyl groups.[4] The resulting functionalized macrocycles have novel coordination and structural properties due to the unique arrangement of different types of donor groups.[4] A new class of chelating cyclophanes is obtained when aromatic diamines are used in condensation reactions with edta dianhydride. In this work, we have employed the aromatic diamine *p*-xylenediamine and obtained a chelating cyclophane (**1**), 3,10,21,28-tetraoxo-5,8,-23,26-tetrakis(carboxymethyl)-2,5,8,11,20,23,26,29-octaaza

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[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1997.

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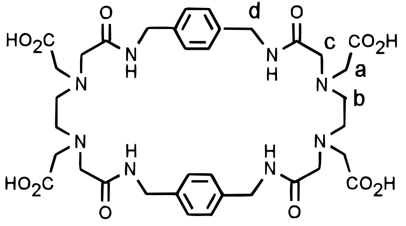
S0020-1669(96)01437-1 CCC: $14.00



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[12.12]paracyclophane, abbreviated as (32edtaxan)H_4, which incorporates two phenyl groups, four amide groups, and four amine nitrogens in the macrocyclic framework and four pendant carboxymethyl groups. The formation of the cyclophane has been confirmed by a single-crystal X-ray analysis of its Zn^{2+} complex. The new functionalized cyclophane is fluorescent, and its absorption and emission spectra vary upon complexation with transition metal ions.

Experimental Section

Synthesis of (32edtaxan)H_4. A dimethylformamide (DMF) solution (70 mL) containing 3.8 g of *p*-xylenediamine (Aldrich Chemical Co.) was added, through a dropping funnel in a period of 2 h, to 5 g of edta dianhydride (Aldrich Chemical) in 300 mL of DMF, with vigorous stirring at room temperature. After the resulting reaction mixture was left to stand overnight, any solid formed was removed by filtration and the filtrate was concentrated to a viscous liquid. Addition of water gave a colorless solid. When the crude product was dissolved in dilute NH_3, followed by adjusting the pH to 5 with dilute HCl, the pure cyclophane precipitated; this was suspended in dilute HCl at pH $\approx$ 2 so that NH_4^+ ions were completely removed. The product was washed well with water and dried in vacuum. Yield: 1.2 g (13%). Anal. Calc for $C_{36}H_{48}N_8O_{12}\cdot HCl\cdot H_2O$: C, 51.52; H, 6.12; N, 13.35; Cl, 4.22. Found: C, 52.08; H, 6.10; N, 13.29; Cl 4.26. (The elemental analyses were performed at Desert Analytics, Tucson, AZ.) ^1H NMR (D_2O, pD = 10.4, 250 MHz, referenced to DSS): $\delta = 2.59$ (s, 8H, H_b), 3.11 (s, 8H, H_a), 3.16 (s, 8H, H_c), 4.26 (s, 8H, H_d), 7.08 (s, 8H, H_e). ^{13}C NMR (D_2O, pD = 12, 62.9 MHz, DSS): $\delta = 45.1$ (C_d), 55.2 (C_b), 61.1 and 61.2 (C_a, C_c), 130.6 (C_e), 139.8 (phenyl *C*−CH_2), 176.6 (CONH), 181.8 (CO_2^-). MS (electrospray ionization) [*m/z* (relative intensity)]: 390.9 (12), $[M - 2H]^{2-}$; 783.3 (11), $[M - H]^-$; 122.7 (100).

X-ray Crystal Analysis of [Zn_2(32edtaxan)]·7.5H_2O. A reaction between Zn^{2+} nitrate and the Na salt of the cyclophane in a metal:ligand ratio of 2:1 in an aqueous solution immediately formed a colorless solid in an almost quantitative yield. Diffusion of acetone into an aqueous solution of the product at pH $\approx$ 8 gave colorless thin platelike crystals. A crystal of approximate dimensions 0.53 × 0.25 × 0.10 mm was sealed in a glass capillary together with the mother liquor; the crystal was highly efflorescent. Data collection was performed with monochromated Mo Kα radiation (λ = 0.710 73 Å) on an Enraf-Nonius CAD4 diffractometer. The crystallographic data are summarized in Table 1. A total of 8739 reflections ($+h,+k,\pm l$) with maximum 2θ of 50° were collected; 8060 reflections were unique, and 2657 reflections with $I > 3\sigma_I$ were used in the refinements. Many high-angle reflections were weak and could not be used in the calculation, as a result of the presence of two highly disordered water molecules. An empirical absorption correction based on a series of ψ-scans was applied by using the program PSICALC. The transmission factors ranged from 0.803 to 0.998. The Zn atoms were located by direct methods, and the remaining non-hydrogen atoms in succeeding difference Fourier syntheses. Hydrogen atoms of the ligand were included at the calculated positions with the riding model by assuming a bond length of 0.95 Å. Scattering factors were taken from Cromer and Waber.[5] All calculations were performed on a VAX computer with the program MolEn.[6]

Table 1. Crystallographic Data for [Zn_2(32edtaxan)]·7.5H_2O

formula $Zn_2C_{36}H_{44}N_8O_{12}\cdot7.5H_2O$	fw = 1046.65
space group $P2_1/c$ (No. 14)	T = 23 °C
a = 19.818(1) Å	λ = 0.710 73 Å
b = 13.169(1) Å	ρ_{calcd} = 1.52 g cm^{-3}
c = 18.134(1) Å	μ = 11.5 cm^{-1}
β = 104.491(6)°	R^a = 0.066
V = 4582(1) Å^3	$R_w b$ = 0.074
Z = 4	

$^a R = \sum|F_o - F_c|/\sum F_o$. $^b R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

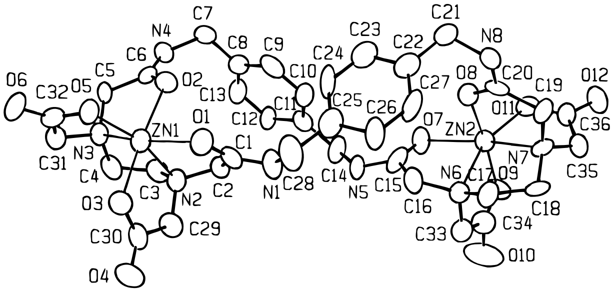

Figure 1. X-ray crystal structure of [Zn_2(32edtaxan)]^0. The atoms are shown at the 50% probability level.

Spectroscopic Measurements. The ^1H NMR spectra were obtained at 250 MHz and at a probe temperature of $\approx$23 °C on a Bruker AM 250 spectrometer. The internal reference was sodium 3-(trimethylsilyl)-propanesulfonate (DSS) for D_2O sample solutions. The pH of each sample solution was determined before and after the NMR measurement by using an Aldrich long-stem thin pH electrode, which was calibrated with standard aqueous buffers, and measured pH values were converted to pD values by pD = pH_{measd} + 0.4.[7] The electronic absorption and emission spectra were recorded at 25 °C on a Perkin-Elmer Lambda-2 UV−vis spectrophotometer and a Jasco 821-FP spectrofluorometer equipped with a microcell. Sample solutions of the metal complexes for the absorption and emission spectra were prepared from stock solutions of the cyclophane and appropriate metal chloride or acetate. The EPR spectra were obtained for the Cu^{2+} complex at liquid-nitrogen temperature on a Bruker ESP-300 spectrometer operating in the X band. Electron spin echo envelope modulation (ESEEM) experiments were performed on a laboratory-built X band ESE spectrometer at a temperature of about 20 K controlled with an Oxford ESR-900 helium flow low-temperature accessory.[8] Sample solutions for EPR and ESEEM experiments were prepared by dissolving $CuCl_2\cdot 2H_2O$ and the sodium salt of the cyclophane in 50% methanol; the sample concentrations were (2−10) × 10^{-3} M, and the ligand was in approximately 5% excess in order to minimize any dissociation of the complex.

Results and Discussion

Structure of [Zn_2(32edtaxan)]·7.5H_2O. Figure 1 shows the structure of a [Zn_2(32edtaxan)]^0 chelate molecule. The selected interatomic distances are collected in Table 2. Each ligand molecule is coordinated to two Zn^{2+} ions and forms a binuclear metal chelate with a Zn−Zn distance of 11.016(2) Å. The metal chelate molecule has no symmetry elements. Each Zn atom has a distorted octahedral coordination geometry in which two carboxylate oxygen atoms, two amide oxygen atoms, and two amine nitrogen atoms are coordinated to the Zn^{2+} atom. The two Zn atoms in the metal chelate molecule have a similar coordination geometry, but they are crystallographically independent. The dihedral angle between the two phenyl rings in

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Table 2. Selected Interatomic Distances (Å) for $[Zn_2(32edtaxan)]\cdot 7.5H_2O$

Zn−X Bonds			
$Zn1-O1_{amide}$	2.072(9)	$Zn2-O7_{amide}$	2.090(8)
$Zn1-O2_{amide}$	2.208(9)	$Zn2-O8_{amide}$	2.063(9)
$Zn1-O3_{carboxylate}$	2.10(1)	$Zn2-O9_{carboxylate}$	2.03(1)
$Zn1-O5_{carboxylate}$	2.006(8)	$Zn2-O11_{carboxylate}$	2.020(9)
$Zn1-N2_{amine}$	2.21(1)	$Zn2-N6_{amine}$	2.20(1)
$Zn1-N3_{amine}$	2.15(1)	$Zn2-N7_{amine}$	2.18(1)
Interatomic Distances between Two Phenyl Rings			
C9−C24	3.73(2)	C10−C23	3.93(2)
C10−C24	3.66(2)	C9−H(C24)	3.10(1)
C10−H(C24)	3.34(1)	C23−H(C10)	3.17(2)
C24−H(C9)	3.21(2)	C24−H(C10)	3.04(2)

a chelate molecule is 75.8(4)°. Some short C−C and C−H interatomic distances between the two phenyl groups are included in Table 2. The interatomic distance between C24 and H(C10), 3.04 Å, is close to the van der Waals C−H contact (the van der Waals radii of C and H are 1.7 and 1.2 Å); H(C10) is located only at 2.77 Å above the molecular plane of the second phenyl ring and has an H−π interaction. The geometrical relation between the two phenyl rings can be described by an edge-on (or edge-to-face) stacking. A calculation of the electrostatic interaction between two π-systems has shown that an edge-on stacking results in an attractive interaction whereas a face-to-face stacking without slip is repulsive.[9] The structure of $[Zn_2(32edtaxan)]^0$ is an example of a stable edge-on stacking, although the steric effect of the cyclophane framework is an additional factor that controls the geometrical relation between the phenyl rings. The C−N−CO−C atoms in each amide group are on the same plane within 0.03 Å. The planarity of the amide groups is one of the controlling factors that define the macrocyclic framework.

Characterization of Cyclophane 1, $(32edtaxan)H_4$. The electrospray ionization mass spectrum of the cyclophane and the X-ray analysis of $[Zn_2(32edtaxan)]\cdot 7.5H_2O$ confirm that the condensation reaction provides cyclophane **1**, $(32edtaxan)H_4$, in which two diamine units and two edta units are linked by four amide bonds. The edta chain length is too short to form a 1:1 condensation product in the reaction with *p*-xylenediamine; this differs from condensation reactions with aliphatic diamines, which give mainly 1:1 condensation products.[4] The difference can be attributed to the rigidity of the aromatic diamine.

The ^1H NMR spectrum of the cyclophane showed five singlet peaks. The aliphatic protons, *a*, *b*, and *c*, were readily assigned by comparison with the spectra of dioxotetraazacycloalkanediacetic acids.[4e,f] Figure 2 shows the ^1H NMR chemical shifts at different pD values. The signals of the *a*, *b*, and *c* protons simultaneously shifted downfield in the pD range 7−9. These NMR shifts indicate that the amine nitrogen is protonated prior to the carboxylate oxygen.[4e,f] At pD below 5, the carboxylate oxygen is protonated gradually. The signals of the phenyl and benzyl protons also shifted in the pD ranges where the protonations occurred. These shifts are significant especially in the pD range corresponding to the protonation of the amine nitrogen. The phenyl and benzyl protons are remote from the protonation sites, and their electron densities are not directly affected by the protonation. The shifts of these protons can be attributed to the ring current effect[10] of the other group in the same molecule, as explained below. When the amine nitrogen in the cyclophane is protonated, an added proton is exchanged between the two amine nitrogen atoms in an edta moiety. The two nitrogen atoms are expected to be oriented so that the proton exchange favorably occurs, as predicted from X-ray structures of dioxopolyazacycloalkanepolyacetic acids.[4h] The geometrical relation between two *p*-xylene moieties is, therefore, dependent on the degree of the protonation, and the chemical shifts of the phenyl and benzyl protons of a phenyl ring are pH-dependent *via* the ring current effect of the other phenyl group. The succeeding protonation is expected to occur on the carboxylate group that is not adjacent to a protonated nitrogen atom so as to minimize the electrostatic energy, and weak hydrogen bonds are formed between the amine nitrogen and the carboxylate oxygen, as demonstrated for polyazacycloalkanepolyacetic acids.[4e,h,11] Thus the protonation of the carboxylate oxygen indirectly defines the geometry of the cyclophane ring, resulting in the small pH dependence of the phenyl and the benzyl proton signals in the pD range where the carboxylate oxygen is protonated. The chemical shifts of the phenyl and benzyl protons were independent of the sample concentration up to 30 × 10^{-3} M. At such a high sample concentration, the *a*, *b*, and *c* protons showed a small concentration dependence in the pH range where the amine nitrogen was protonated (Figure 2). This is probably because cyclophane molecules form aggregates as a result of intermolecular hydrogen bond formation at high concentrations.

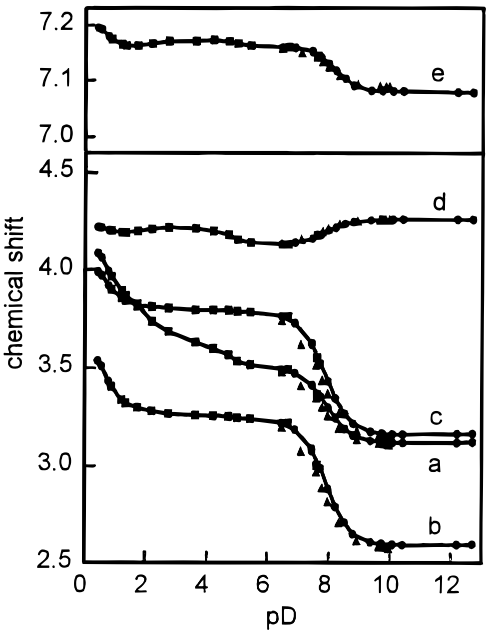

Figure 2. pD dependence of ^1H NMR chemical shifts (referenced to DSS) of $(32edtaxan)H_4$ in D_2O solutions with concentrations of 5 × 10^{-3} M (●) and 30 × 10^{-3} M (▲). The spectra between pD 1 and 6 were obtained at concentrations less than 2 × 10^{-3} M (■) because of the low solubility. For labeling, see formula **1**.

The absorption spectrum exhibited a $\pi-\pi^*$ transition band with some structural features at $\lambda_{max} = 261$ nm. The spectral shape and the molar absorptivity did not change significantly with pH in the range 4−11. A fluorescence band without any structure was observed at 290 nm. The emission intensity increased with decreasing pH, without any change in the spectral shape, in the pH ranges corresponding to the pD ranges where the ^1H NMR signals shifted downfield (Figure 3). The added protons define the conformation of the cyclophane frame *via* intramolecular proton exchange and/or intramolecular hydrogen bonds, as described above, and lead to an increase in the rigidity

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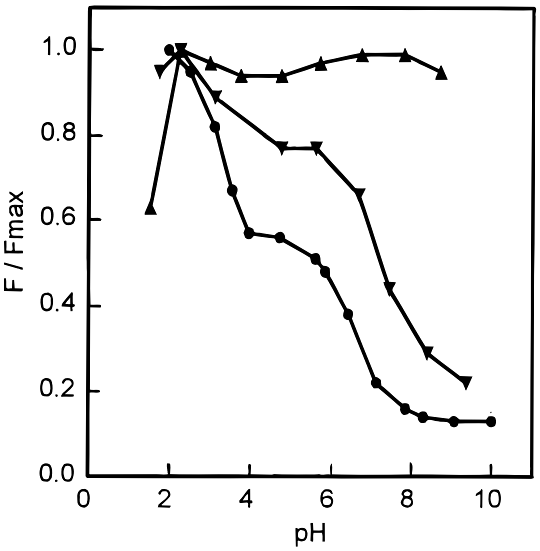

Figure 3. pH dependence of the relative fluorescence intensity F/F_{max} of the 290 nm emission band for solutions (0.2×10^{-3} M) of (32edtaxan)H_4 (●), Zn−(32edtaxan)H_4 (▼), and Zn_2−(32edtaxan)H_4 (▲). F_{max} is the fluorescence intensity of each compound at a pH where the most intense emission was observed. The pH values of the sample solutions were adjusted with a minimum amount of a dilute HCl or a dilute NaOH solution. For Zn_2(32edtaxan)H_4, a precipitate was formed at pH above 9. The excitation wavelength was 210 nm.

Table 3. Relative Intensity $F(M_nL)/F(L)$ of the 290 nm Fluorescence Band for the M_n−(32edtaxan)H_4 Systems, with Reference to the Intensity F(L) of the Uncoordinated Cyclophane Ligand under the Same Conditions[a]

		$F(M_nL)/F(L)$	
M	pH	$n = 1$	$n = 2$
Zn^{2+}	6.0	3.4	5.0
	8.6[b]	8	50
Cu^{2+}	5.5	0.30	0.02
	10.9	0.29	0.12
Ni^{2+}	5.5	0.40	0.06
	10.7	0.67	0.42

[a] The concentration of the ligand was $(0.19-0.20) \times 10^{-3}$ M. An CH_3CO_2H (0.2 M)−CH_3CO_2Na (0.2 M) buffer was used for the acidic solutions, and a $NaHCO_3$ (0.05 M)−NaOH (0.1 M) buffer for the basic solutions. The excitation wavelength was 210 nm. [b] A precipitate was formed at higher pH.

of the ring framework and consequently the fluorescence quantum yield.[12]

Fluorescence Spectra of Zn−(32edtaxan)H_4. The nature of the $\pi-\pi^*$ band of the Zn^{2+} chelate was identical with that of the free ligand and independent of pH. On the other hand, the 290 nm emission band was markedly strengthened by the coordination of Zn^{2+} ion; fluorescence intensities of solutions containing Zn and the cyclophane in 1:1 and 2:1 mole ratios are shown in Table 3, with reference to the intensity of the uncoordinated cyclophane. The shape of the emission band was unchanged, and no new emission band was observed upon complexation with Zn; the proximity between two phenyl groups that may occur in $[Zn_2(32edtaxan)]^0$ gives no significant effect on the emission spectrum. The increase in the emission intensity is, therefore, attributable to an increase in the rigidity of the cyclophane ring upon complexation.[12] The fluorescence intensity of $[Zn_2(32edtaxan)]^0$ was practically independent of pH between 2 and 9 (Figure 3). In this complex, all donor atoms are coordinated to the metal ions, and hence, the conformation of the ligand is unchanged with pH so that the fluorescence intensity is independent of pH except at very low pH. At pH below 2, the fluorescence was weakened (Figure 3); in such a strongly acidic solution, the protons present in high concentration cause a partial dissociation of the metal chelates. The resulting $[Zn(32edtaxan)H_n]^{n-2}$ and/or liberated ligand molecules have a lower quantum yield than $[Zn_2(32edtaxan)]^0$. In a solution containing equimolar amounts of Zn and the cyclophane, the ZnL type complex is in equilibrium with the Zn_2L type complex and the uncoordinated ligand. The rigidity of the ZnL type complex increases with decreasing pH, similar to that of the uncoordinated ligand, because uncoordinated donor atoms in the metal chelate can be protonated. The overall intensity of emissions from the three species in the 1:1 solution, therefore, increases with a lowering of the pH, as observed in Figure 3.

Absorption, Emission, and EPR Spectra of Cu−(32edtaxan)H_4. The 261 nm ($\epsilon = 720$ M^{-1} cm^{-1} at pH = 10.2) band of the cyclophane was markedly strengthened and also slightly shifted when Cu^{2+} is coordinated: $\lambda_{max} = 264$ nm ($\epsilon = 4600$ M^{-1} cm^{-1}) and 266 nm (8400) for [Cu]/[cyclophane] = 1 and 2, respectively, at pH = 10.2. The molar absorptivity of the $\pi-\pi^*$ transition for the concentration ratio [Cu]/[cyclophane] = 2 is approximately 12 times as large as the value of the uncoordinated ligand at the same pH. It is not plausible that the coordination of copper affects the electronic state of the conjugated system *via* a direct electronic interaction, such as electron back-donation, because the π-system is isolated from the coordination sites by benzyl carbon atoms. It has been reported that the electronic absorption spectra of [*m.n*]paracyclophanes are sensitively dependent on the length of the bridging groups.[13] The absorption spectra show a red shift for the short bridges, and a new long-wavelength band appears for $m = n = 2$; the spectra of paracyclophanes with long bridging groups closely resemble those of noncyclic *p*-substituted benzene derivatives.[13] The novel absorption spectrum of [2.2]paracyclophane has been explained by the proximity of the two π-systems and by the distortion of the aromatic rings.[14,15] A similar effect is expected to cause the spectral change observed for (32edtaxan)H_4 upon coordination of copper.

The $\pi-\pi^*$ band observed for the Cu_2(cyclophane) complex showed a marked pH dependence: $\epsilon = 7200$ M^{-1} cm^{-1} at $\lambda = 260$ nm (shoulder) at pH = 7.5; $\lambda_{max} = 264$ nm (7900 M^{-1} cm^{-1}) at pH = 9.5; $\lambda_{max} = 268$ nm (9500) at pH = 11.6. A similar spectral behavior was observed for a 1:1 mixture of Cu-(cyclophane), although the shift and the enhancement of the molar absorptivity occurred to a lesser extent. The pH dependence of the $\pi-\pi^*$ transition of the Cu^{2+} complex suggests that the mode of coordination of copper is changed with pH.

The coordination mode of copper can be clarified by examination of the electronic and EPR spectra of the Cu^{2+} complex. The d−d transition band showed a large blue shift and an increase in intensity with increasing pH: $\lambda_{max} = 708$ nm (70 M^{-1} cm^{-1}) at pH = 6.2; 670 nm (130) at pH = 9.6; 660 nm (165) at pH = 11.7. This type of spectral change is commonly observed when coordinated oxygen atoms are

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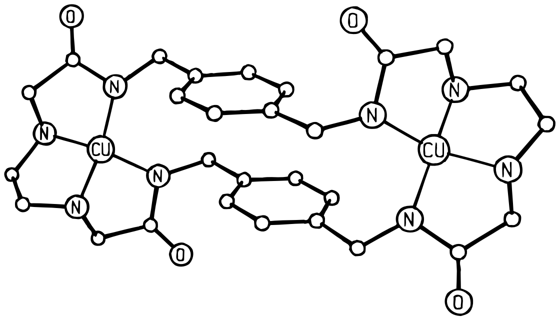

Figure 4. Possible coordination of amide nitrogens in [Cu$_2$(32edtaxanH$_{-4}$)]$^{4-}$. The pendant carboxylate groups, which cap the CuN$_4$ units, are not shown because they obscure the coordination sphere of copper. The structure is drawn by using the program HyperChem, only for visualizing the coordination sphere of copper.

replaced by nitrogen atoms.[16] In basic solutions, therefore, the amide nitrogen is deprotonated and the resulting negatively charged nitrogen is coordinated to copper (Figure 4), as reported for a Cu^{2+} complex with 2,9-dioxo-1,4,7,10-tetraaza-4,7-cyclotridecanediacetate, abbreviated as (13edtapn)$^{2-}$.[4d] A quasi-axial EPR spectrum was observed for the Cu$_2$(32edtaxan) complex in a 50% methanol glass matrix. The EPR parameters were approximately: $g_1 = 2.33$, $g_2 = 2.07$, $g_3 = 2.04$, and $A_1 = 145$ G in an acidic matrix (pH = 5.4); $g_1 = 2.25$, $g_2 = 2.04$, $g_3 = 2.02$, and $A_1 = 165$ G in a basic matrix (pH = 12.0). The g values of Cu^{2+} complexes with an elongated D_{4h} ligand field are given by[17]

$$g_1 = 2.0023 + 8\lambda_{LS}/\Delta E(\mathrm{d}_{x^2-y^2} - \mathrm{d}_{xy}) \tag{1}$$

$$g_{2,3} = 2.0023 + 2\lambda_{LS}/\Delta E(\mathrm{d}_{x^2-y^2} - \mathrm{d}_{yz,zx}) \tag{2}$$

where λ_{LS} is the spin−orbit coupling constant. An increase in the strength and/or the elongation of a D_{4h} ligand field lead to an increase of the energy differences, $\Delta E(\mathrm{d}_{x^2-y^2} - \mathrm{d}_{xy})$ and $\Delta E(\mathrm{d}_{x^2-y^2} - \mathrm{d}_{yz,zx})$, and consequently the g values are closer to 2.0023. The smaller g values observed for the basic matrix show that the ligand field around a Cu^{2+} ion is stronger in the basic matrix. This is consistent with the d−d transition spectrum and is indirect evidence for the coordination of the amide nitrogen in basic solutions. With the objective of obtaining additional support for the coordination of amide nitrogen, an electron spin echo envelope modulation (ESEEM) spectrum was recorded. An ESEEM spectrum associated with nitrogen is observed only when a copper nucleus has a weak $I{\cdot}S$ (nitrogen nuclear spin−copper electron spin) coupling whose energy is of the same order of magnitude as the Zeeman energy of the nucleus and the nuclear quadrupole energy.[18] An ESEEM spectrum, therefore, can be observed only when the oxygen atom of an amide group is coordinated to copper:[4d] When the amide nitrogen is directly coordinated to copper, the interaction between the amide nitrogen and the copper is too strong for the appearance of an ESEEM spectrum; in the other extreme case that neither amide oxygen nor nitrogen is coordinated to copper, interaction between the amide nitrogen and the copper is too weak to yield an ESEEM spectrum. Since the chemical species formed in a solution is frozen in a glass matrix, ESEEM signals give information about the structure of the species in solution. A Fourier-transformed ESEEM spectrum observed for the glass matrix at pH = 12.0 showed only a signal associated with protons, and no signal was detected in the nitrogen-related spectral region, thereby supporting the conclusion that the coordination of amide nitrogen occurred in basic solutions. It is reasonable to assume that the Cu^{2+} chelate in acidic solutions has an octahedral structure resembling that of [Zn$_2$(32edtaxan)]^0. For the acidic matrix at pH = 5.4, however, no nitrogen-related ESEEM signal was observed (only a proton-related signal was present), in contrast to [Cu(13edtapn)]^0 for which a set of nitrogen-related ESEEM signals have been observed at frequencies below 5 MHz in addition to a proton-related signal.[4d] Usually, an amide oxygen atom is a weakly coordinating donor, and can be readily replaced by other donor atoms under certain conditions. [Cu$_2$(32edtaxan)]^0 is expected to have a structure resembling that of the corresponding Zn^{2+} complex in the solid state; in aqueous media, however, the amide oxygen atoms that may be coordinated to copper in the solid state are replaced by water oxygen atoms.

The d−d absorption band and the EPR spectrum of the Cu$_2$(32edtaxan) complex indicate that the mode of coordination changes with pH: In acidic solutions, amide groups are protonated and a neutral [Cu$_2$(32edtaxan)]^0 complex is formed with an octahedral coordination geometry; in basic solutions, deprotonated amide nitrogens are coordinated to the central metal ion and a [Cu$_2$(32edtaxanH$_{-4}$)$^{8-}$]$^{4-}$ chelate is formed (Figure 4). The EPR signals observed for the basic matrix were broader than the corresponding signals for the acidic matrix: The full width at half-maximum (fwhm) of the hyperfine signal observed at the lowest magnetic field was 60 G for the basic matrix and 30 G for the acidic matrix. The broader signal for the basic media can be explained by a dipolar interaction between two copper atoms with a shorter interatomic distance. The unpaired electron of a Cu^{2+} ion in a binuclear chelate molecule produces a dipolar field, the characteristic value of which is μ/r^3, at the position of the other Cu^{2+} ion (r is the Cu−Cu distance).[19] This dipolar field results in a line broadening which depends on orientation of Cu^{2+}−Cu^{2+} spin pair in the g-tensor frame and may vary from 0 to $2\mu/r^3$ depending on the field position. An approximate Cu^{2+}−Cu^{2+} distance can be obtained by using the maximum value of the dipolar field, when dipolar interaction is the major controlling factor for line broadening. For a Cu−Cu distance of 11 Å identical to the Zn−Zn distance of [Zn$_2$(32edtaxan)]^0 in the solid, the value of $2\mu/r^3$ is only 12 G. When amide groups do not participate in coordination to copper, two Cu^{2+} ions are expected to be more distant, and the dipolar effect is less significant; the larger fwhm value observed for the acidic matrix indicates the presence of an additional effect such as an unresolved hyperfine structure. The fwhm value observed for the basic matrix is larger by 30 G than that for the acidic matrix. When this difference is attributed to a dipolar interaction between two Cu^{2+} ions in [Cu$_2$(32edtaxanH$_{-4}$)$^{8-}$]$^{4-}$, the Cu−Cu distance can be calculated as $r \approx 8.2$ Å on the basis of $2\mu/r^3$. For a structure shown in Figure 4, the Cu−Cu distance is approximately 9 Å, which is shorter than the metal−metal distance in [Zn$_2$(32edtaxan)]^0 and close to the distance predicted from the dipolar broadening. Although these calculations give only approximate Cu−Cu distances, the observation of the EPR line broadening supports the conclusion that the coordination of amide nitrogens in basic

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media results in the proximity of two Cu^{2+} ions in a metal chelate molecule.

The structural changes in the Cu^{2+} chelate are responsible for the spectral changes in the $\pi-\pi^*$ transition band of the coordinated ligand. The amide nitrogen is, however, isolated by a $-CH_2-$ group from the π-conjugated system. Therefore, the coordination of copper to amide nitrogens does not lead to a significant change in the electronic structure of the π-system *via* a direct effect such as an electron back-donation. On the other hand, the coordination of amide nitrogens to copper brings the two phenyl groups closer. The proximity of the two π-systems results in the spectral change of the $\pi-\pi^*$ band upon coordination of copper.

The fluorescence of the ligand was markedly weakened by the coordination of copper, contrary to the coordination of zinc (Table 3). The amide nitrogen that coordinates copper is isolated by a $-CH_2-$ group from the electronic system of the fluorophore. A long-range effect such as a photo-induced electron transfer[3a,b] is, however, operative between the fluorophores and the coordinating sites and results in the quenching of the fluorescence. The fluorescence from Cu(32edtaxan) and Cu_2(32edtaxan) was too weak for reliable measurements of the pH dependence.

Absorption and Emission Spectra of Ni−(32edtaxan)H_4. The 261 nm absorption band was not significantly changed by the coordination of Ni^{2+} ions, in contrast to the coordination of copper. Three d−d bands were observed at 285, 595, and 985 nm at pH = 10.2. This electronic spectrum is characteristic of an octahedral Ni^{2+} complex.[16] The Ni^{2+} complex of the dioxotetraazamacrocycle, (13edtapn)H_2, has an octahedral coordination geometry in acidic solutions, but at high pH where amide nitrogens can be deprotonated, a planar coordination geometry with four nitrogen atoms is formed around the central metal ion.[4d] In contrast, an octahedral coordination in $[Ni_2(32edtaxan)]^0$ is maintained without deprotonation of amide nitrogens even in basic solutions. The 290 nm fluorescence band was quenched by the coordination of Ni^{2+} ions. The extent of quenching in acidic solutions was of the same order of magnitude as that for copper, and the quenching in basic solutions occurred to a lesser extent (Table 3).

Conclusion

The fluorescence of the cyclophane is enhanced by the coordination of Zn^{2+} ions, whereas it is quenched by the coordination of Cu^{2+} and Ni^{2+} ions. This difference is explained by the electronic structures of the central metal ions. The open-shell structures of Cu^{2+} and Ni^{2+} ions favor a photo-induced electron transfer that quenches the fluorescence.[3] For Zn^{2+}, a photo-induced effect is not significant and the increase in the rigidity of the cyclophane upon coordination of Zn^{2+} results in a higher fluorescence quantum yield.[12]

Another marked spectral change is the enhancement of the molar absorptivity of the $\pi-\pi^*$ transition upon coordination of copper. This change is explained by the contraction of the cyclophane ring. In [*m.n*]paracyclophanes and [*n.n*](2,7)-pyrenophanes with short bridging groups, the aromatic rings are distorted and no longer planar, and this distortion may be responsible for their novel spectral properties.[15,20,21] Such a distortion of a phenyl ring does not occur in $[Cu_2(32edtaxanH_{-4})]^{4-}$, because the energy of a metal−ligand bond is usually much smaller than that of a π bond. On the other hand, coordination of Cu^{2+} results in the contraction of the cyclophane ring. This allosterism *via* ring contraction is a possible reason for the increase in the molar absorptivity. Interestingly, the spectral change is pronounced for the Cu^{2+} chelate but not significant for the Ni^{2+} and Zn^{2+} chelates.

Supporting Information Available: Tables of positional parameters, thermal parameters, bond lengths and angles, selected interatomic contacts, torsional angles, and least-squares planes and an ORTEP diagram of the unit cell for $[Zn_2(32edtaxan)]\cdot 7.5H_2O$, fluorescence spectra of cyclophane, and UV−vis, EPR, and ESEEM spectra of Cu−(32edtaxan) complexes (23 pages). Ordering information is given on any current masthead page.

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