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The characterization and spectroscopic properties of nickel(II) and copper(II) complexes of 2,3,11,12-bis(1′,4′,7′,10′,13′-pentaoxatridecamethylene)-5,14-dihydro-7,16-diethyldibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecine – a ligand with both tetraazamacrocyclic and crown ether functionalities

Kazunori Sakata* and **Takamichi Annoura**

Department of Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Tobata-ku, Kitakyushu 804 (Japan)

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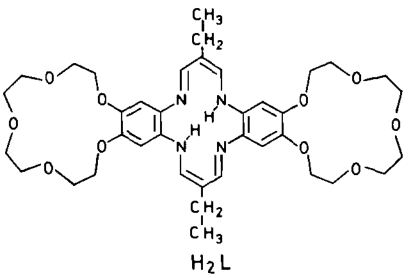
Abstract

Tetraaza[14]annulene appended with two crown ethers, benzo-15-crown-5, at 2,3- and 11,12-positions and its metal complexes (Ni(II) and Cu(II)) have been synthesized and characterized. Tetraaza[14]annulene and its complexes describe two crown ether cavities which are able to recognize cations. The capability of these macrocyclic compounds to complex cations (Na^+, K^+ and NH_4^+) is studied with the aid of electronic and ESR spectra. The cations (K^+ and NH_4^+), which need two crown ether cavities for complexation, accelerate dimerization of the macrocyclic compounds. The copper(II) complex was shown by ESR to dimerize in the presence of added K^+ ions.

Introduction

Aggregation of tetrapyrrol pigments in particular is one of the properties of significance in biological systems. Although dimerization of crown porphyrins [1] and crown phthalocyanines [2] has been intensively investigated, examples of synthetic macrocyclic tetraaza[14]annulene with two crown ether voids are rare. Kruse and Breitmaier reported the syntheses of nickel(II) and cobalt(II) complexes with 2,3,11,12-bis(1′,4′,7′,10′,13′-pentaoxatridecamethylene)-5,14-dihydro-7,16-diisopropyl[*b*,*i*][1,4,8,11]tetraazacyclotetradecine, but did not report any spectral properties [3].

We report here the preparations of tetraaza[14]annulene functionalized at the 2,3- and 11,12-positions with two crown ether voids, that is, 2,3,11,12-bis(1′,4′,7′,10′,13′-pentaoxatridecamethylene)-5,14-dihydro-7,16-diethyldibenzo[*b*,*i*][1,4,8,11]-tetraazacyclotetradecine (H_2L) and of its nickel(II) (Ni-L) and copper(II) (Cu-L) complexes. We also report the spectral (mass, vibrational, electronic, NMR and ESR) properties of the present crown tetraaza[14]annulene and those of its nickel(II) and copper(II) complexes, together with the cation- or solvent-induced dimerization of the ligand and its complexes. Various cations are employed for the complexation study. The dimerization was followed by electronic and ESR spectral methods.



H_2L

Experimental

Physical measurements

EI mass spectra of H_2L and its nickel(II) complex and the FD mass spectrum of its copper(II) complex were obtained using a JEOL JMS-DX 300 gas chromatograph–mass spectrometer at an ionization potential of 20 eV. Infrared spectra in the 400–4000 cm^{-1} region were taken on a Hitachi 260-30 spectrophotometer at room temperature, where a KBr disk technique was employed. Ultraviolet and visible spectra covering the 14 000–37 000 cm^{-1} range were

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*Author to whom correspondence should be addressed.

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recorded on a Shimadzu UV-200S double beam spectrophotometer for chloroform and chloroform–methanol (4:1 vol./vol.) solutions at room temperature. A JEOL JNM-FX 60 spectrometer operating in the Fourier transform mode was used to obtain ^{1}H and ^{13}C NMR spectra in chloroform-d and dimethyl sulfoxide-d$_6$ at room temperature. Chemical shifts are reported in ppm relative to tetramethylsilane as an internal reference standard. ESR spectra were obtained on a JEOL JES-MX-1 X-band spectrometer equipped with a 100 kHz field modulation unit. The spectra of the copper(II) complex were measured in dichloromethane at room temperature and in chloroform–methanol (4:1 vol./vol.) at 77 K, the sample concentration being maintained at *c.* 10^{-3} mol dm^{-3}. Manganese ion diffused into magnesium oxide was utilized to acquire the standard reference signals for all measurements. Melting points were determined on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. Elemental analyses were performed with a Yanaco CHN Corder MT-3.

Synthesis of the macrocycle

1,11-Dichloro-3,6,9-trioxaundecane (1)

This was prepared after the method of Pedersen [4] from bis[2-(2-hydroxyethoxy)ethyl]ether (110.5 g), pyridine (105.3 g) and thionyl chloride (151.6 g) in benzene (500 ml). The crude product was distilled at about 130 °C (4 torr) to give a light yellow liquid; yield 104.2 g (80%). ^{1}H NMR (chloroform-d, TMS): δ 3.68 ppm (16H, m, $\mathrm{Cl{-}C\mathit{H}_2{-}C\mathit{H}_2{-}O{-}C\mathit{H}_2{-}C\mathit{H}_2{-}O{-}C\mathit{H}_2{-}C\mathit{H}_2{-}O{-}C\mathit{H}_2{-}C\mathit{H}_2{-}Cl}$).

2,3-Benzo-1,4,7,10,13-pentaoxacyclopentadeca-2-ene (2)

This was prepared from **1** (60.97 g), catechol (31.11 g) and sodium hydroxide (25.0 g) dissolved in water (130 ml) and 1-butanol (500 ml) after Pedersen [4]. The crude product was extracted with n-heptane and gave white flakes; yield 37.96 g (50%), melting point (m.p.) 73.0–78.0 °C. An analytically pure compound was obtained by recrystallizing from n-heptane. UV ($\mathrm{CH_3OH}$): 224(ϵ 6220) and 276(ϵ 2420) nm. IR (KBr disk): 2900, 2860 (C–H str.), 1255, 1125 (C–O–C str.) and 745 (out of plane C–H ben.) cm^{-1}. EIMS: *m/z* (relative intensity) 269(5.7), 268(35.8, M^{+}), 136(100) (molecular weight 268.31). ^{1}H NMR (chloroform-d, TMS): δ 3.76 (8H, s, $\mathrm{-O(CH_2)_2{-}O(C\mathit{H}_2)_2O(C\mathit{H}_2)_2O(CH_2)_2O{-}}$), 3.96 (4H, m, $\mathrm{-O{-}CH_2{-}C\mathit{H}_2{-}O{-}(CH_2)_2O{-}(CH_2)_2O{-}C\mathit{H}_2{-}CH_2{-}O{-}}$), 4.07 (4H, m, $\mathrm{-O{-}C\mathit{H}_2{-}CH_2O(CH_2)_2{-}O(CH_2)_2{-}OCH_2{-}C\mathit{H}_2{-}O{-}}$) and 6.89 (4H, s, aromatic) ppm. *Anal.* Found: C, 62.88; H, 7.81. Calc. for $\mathrm{C_{14}H_{20}O_5}$: C, 62.67; H, 7.51%.

2,3-(3′,4′-Dinitrobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene (3)

The method of Smid *et al.* [5] was modified for the preparation of this compound. A mixture of **2** (10.41 g) and nitric acid (25 ml, 70%) was heated at 60 °C for 7 h with stirring. After the reaction mixture was allowed to stand overnight at room temperature, the crystalline solid obtained by the addition of methanol (30 ml) and water (40 ml) was recovered by filtration and washed five times with methanol (20 ml) to give light yellow crystals; yield 5.60 g (40%), m.p. 173.0–175.0 °C. An analytical sample was obtained by recrystallizing from ethanol to give yellow plates. UV ($\mathrm{CH_3OH}$): 220(ϵ 19 600), 242(ϵ 8130), 265(ϵ 4040), 305(ϵ 3350) 334(ϵ 3480) and 440(ϵ 140) nm. IR (KBr disk): 2900, 2865 (C–H str.), 1523 and 1295 (N–O str.) cm^{-1}. EIMS: *m/z* (relative intensity) 359(13.0), 358(72.9, M^{+}), 226(100) (molecular weight 358.30). ^{1}H NMR (chloroform-d, TMS): δ 3.74 (8H, s, $\mathrm{-O(CH_2)_2O{-}(C\mathit{H}_2)_2O(C\mathit{H}_2)_2O{-}(CH_2)_2O{-}}$), 4.00 (4H, m, $\mathrm{-O{-}CH_2{-}C\mathit{H}_2{-}O(CH_2)_2O(CH_2)_2O{-}C\mathit{H}_2{-}CH_2{-}O{-}}$), 4.19 (4H, m, $\mathrm{-O{-}C\mathit{H}_2{-}CH_2{-}(CH_2)_2{-}O(CH_2)_2O{-}CH_2{-}C\mathit{H}_2{-}O{-}}$) and 7.30 (2H, s, aromatic) ppm. ^{13}C NMR (chloroform-d, TMS): δ 68.69 ($\mathrm{-O(CH_2)_2O{-}CH_2{-}\mathit{C}H_2{-}O{-}\mathit{C}H_2{-}CH_2{-}O(CH_2)_2O{-}}$), 69.72 ($\mathrm{-O(CH_2)_2O{-}\mathit{C}H_2{-}CH_2{-}O{-}CH_2{-}\mathit{C}H_2{-}O{-}(CH_2)_2O{-}}$), 70.16 ($\mathrm{-O{-}CH_2{-}\mathit{C}H_2{-}O(CH_2)_2O(CH_2)_2O{-}\mathit{C}H_2{-}CH_2{-}O{-}}$), 71.14 ($\mathrm{-O{-}\mathit{C}H_2{-}CH_2O{-}(CH_2)_2{-}O(CH_2)_2O{-}CH_2{-}\mathit{C}H_2{-}O{-}}$), 108.54 (2′- and 5′-positions in aromatic), 136.75 (3′- and 4′-positions in aromatic) and 151.86 (1′- and 6′-positions in aromatic) ppm. *Anal.* Found: C, 47.15; H, 5.20; N, 7.67. Calc. for $\mathrm{C_{14}H_{18}N_2O_9}$: C, 46.93; H, 5.06; N, 7.82%.

2,3-(3′,4′-Diaminobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene (4)

A 300 ml autoclave was charged with a mixture of **3** (2.61 g), ethanol (50 ml), methanol (30 ml) and Raney nickel W2 (5 g). The mixture was hydrogenated at 60–80 °C and a hydrogen pressure of *c.* 60 kg/cm^2 for 6 h. The reaction mixture was cooled to room temperature and filtered to remove the catalyst. The filtrate was evaporated to dryness *in vacuo* under an argon atmosphere. The crystalline solid was washed three times with methanol (10 ml) under an argon atmosphere to give palely purplish crystals; yield 1.41 g (65%), m.p. 129.5–131.0 °C. UV ($\mathrm{CH_3OH}$): 212(ϵ 18 900), 230sh(ϵ 6020) and 308(ϵ 4100) nm. IR (KBr disk): 3350, 3240 (N–H str.), 2900, 2860 (C–H str.), 1605 (N–H ben.), 1250 and 1123 (C–O–C str.) cm^{-1}. FDMS: *m/z* (relative intensity) 299(12.5), 298 (100, M^{+}) (molecular weight 298.34). ^{1}H NMR (chloroform-d, TMS): δ 3.06 (4H, s, $-NH_2$), 3.74 (8H, s, $-O-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-O-$), 3.92 (8H, m, $-O-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-O-$) and 6.36 (2H, s, aromatic) ppm. *Anal.* Found: C, 56.51; H, 7.62; N, 9.43. Calc. for $C_{14}H_{22}N_2O_5$: C, 56.36; H, 7.43; N, 9.39%.

2,3,11,12-Bis(1',4',7',10',13'-pentaoxatrideca-methylene)-5,14-dihydro-7,16-diethyldibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecine (H_2L)

A mixture of **4** (1.50 g), 2-ethyl-3-ethoxyacrolein (0.68 g) [6] and ethanol (5.0 ml) was heated under reflux for 12 h with stirring. Upon cooling the mixture with ice-water, the crystalline solid was recovered by filtration and recrystallized from *N,N*-dimethylformamide to give red needles of green lustre; yield 0.52 g (30%), m.p. 251.0–252.0 °C (dec). EIMS: *m/z* (relative intensity) 726(8.9), 725(53.4), 724(100, M^+) (molecular weight 724.85). IR (KBr disk): 2920, 2860 (C–H str.), 1641 (C=N str.), 1603 (C=C str. (conjugated ring)) and 1545 (macrocyclic skeletal str.) cm^{-1}. *Anal.* Found: C, 62.56; H, 7.19; N, 7.65. Calc. for $C_{38}H_{52}N_4O_{10}$: C, 62.97; H, 7.23; N, 7.73%.

Preparation of the macrocyclic complexes

(2,3,11,12-Bis(1',4',7',10',13'-pentaoxatrideca-methylene)-7,16-diethyldibenzo[b,i][1,4,8,11]-tetraazacyclotetradecinato)nickel(II) (Ni–L)

(a) After nickel(II) acetate tetrahydrate (0.047 g) dissolved in *N,N*-dimethylformamide (4.0 ml) was added with stirring at 150 °C into a mixture of H_2L (0.040 g) and *N,N*-dimethylformamide (4.0 ml), the reaction mixture was heated under reflux for 15 min with stirring. Upon cooling the mixture with ice-water, the crystalline solid was recovered by filtration and washed three times with methanol (10 ml). Repeated recrystallization from *N,N*-dimethylformamide to which small amounts of activated carbon was added gave dark violet needles of indigo-blue lustre; yield 0.011 g (25%), m.p. >300 °C. EIMS: *m/z* (relative intensity) 782(45.2), 781(7.1), 780(100, M^+, ^{58}Ni) (molecular weight 781.52). IR (KBr disk): 2920, 2860 (C–H str.), 1635 (C=N str.), 1600 (C=C str. (conjugated ring)) and 1450 (macrocyclic skeletal str.) cm^{-1}. *Anal.* Found: C, 58.26; H, 6.45; N, 7.26. Calc. for $C_{38}H_{50}N_4O_{10}Ni$: C, 58.40; H, 6.45; N, 7.17%.

(b) 2-Ethyl-3-ethoxyacrolein (0.358 g) was added to a mixture of **4** (0.416 g), nickel(II) acetate tetrahydrate (0.350 g) and ethanol (20 ml) at 80 °C. The reaction mixture was heated under reflux for 10 h with stirring and cooled down with ice-water. After filtration, the crystalline solid was washed three times with methanol (20 ml) and then recrystallized twice from *N,N*-dimethylformamide as dark violet needles of indigo-blue lustre; yield 0.200 g (20%), m.p. >300 °C.

(2,3,11,12-Bis(1',4',7',10',13'-pentaoxatrideca-methylene)-7,16-diethyldibenzo[b,i][1,4,8,11]-tetraazacyclotetradecinato)copper(II) (Cu–L)

A mixture of H_2L (0.053 g), copper(II) acetate monohydrate (0.050 g) and *N,N*-dimethylformamide (5.0 ml) was heated at 80 °C for 5 min with stirring. After the reaction mixture was cooled down with ice-water, the crystalline product was separated, washed three times with methanol (10 ml) and recrystallized from *N,N*-dimethylformamide to give glittering reddish brown needles; yield 0.037 g (64%), m.p. >300 °C. FDMS: *m/z* (relative intensity) 787 (75.1), 786(56.0), 785(100, M^+, ^{63}Cu) (molecular weight 786.38). IR (KBr disk): 2920, 2860 (C–H str.), 1638 (C=N str.), 1590 (C=C str. (conjugated ring)) and 1470 (macrocyclic skeletal str.) cm^{-1}. *Anal.* Found: C, 57.85; H, 6.38; N, 7.10. Calc. for $C_{38}H_{50}N_4O_{10}Cu$: C, 58.04; H, 6.41; N, 7.12%.

Results and discussion

Synthesis of crown tetraaza[14]annulene and its metal complexes

Since substitution reactions on the aromatic rings of tetraaza[14]annulenes have never been reported, tetraaza[14]annulene (H_2L) containing crown ether voids can be obtained by starting with reactants which already have these groups. The complexes have been prepared either from 2-alkyl-3-ethoxyacrolein, 3,4-diaminobenzocrown ether and the metal ion employing a metal template reaction or from H_2L and the metal ion. The first route in refluxing ethanol is favourable for acquiring the nickel(II) complex, but it is inadequate for the synthesis of the metal-free ligand and the copper(II) complex. The second route is the usual method for the preparation of the complexes.

The ligand H_2L was synthesized by cyclization of 2,3-(3',4'-diaminobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene and 2-ethyl-3-ethoxyacrolein in refluxing ethanol for 12 h. The reaction of H_2L with the metal salt in boiling *N,N*-dimethylformamide gave the corresponding metal complex. For the purpose of introducing the alkali metal salts to vacant crown cavities, H_2L and its complexes were dissolved in chloroform–methanol (4:1 vol./vol.) and a solution of alkali metal or ammonium salt was added in excess. K^+ and NH_4^+ ions formed complexes with the crown ether group in a 1:2 (cation:ether) stoichiometry, while Na^+ formed a 1:1 complex. The analytical data for H_2L, Ni–L and Cu–L are given in 'Experimental'. Elemental analyses of crystalline samples of H_2L, Ni–L and Cu–L were consistent with compounds of these compositions.

Mass spectra

Mass spectral data for H_2L, Ni–L and Cu–L are reported in 'Experimental'. The EI mass spectrum of H_2L indicates the presence of a molecular ion M^+ at m/z 724 that is the base peak in the mass spectrum. When the nickel(II) and copper(II) complexes of H_2L were analysed using EI and FD mass spectra, these complexes also exhibited molecular ions at m/z 780 and at 785, respectively, which are base peaks.

Vibrational spectra

The characteristic IR bands are collected in 'Experimental'. The metal-free ligand (H_2L) shows a very weak band at *c.* 3200 cm^{-1} which is due to a N–H stretching mode. This band is absent in spectra of the metal complexes. A strong band depending upon the C=N stretching mode of H_2L appears at 1641 cm^{-1}. This band is the most sensitive to metal coordination in the 400–4000 cm^{-1} range and shifts slightly to lower energy on complex formation. There is little change in the absorption bands which are associated with the crown ether groups (ν(C–H) 2920, 2860; ν(C–O–C) 1280, 1120 cm^{-1}) after adduct formation with alkali metal salts.

Electronic spectra

The ultraviolet and visible spectra for crown tetraaza[14]annulene (H_2L) and its metal complexes are shown in Fig. 1, covering the 14 000–37 000 cm^{-1} region. The absorption bands appearing above 18 000 cm^{-1} are attributed to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and to metal to ligand charge transfer transitions. These absorptions are not of $d \rightarrow d^*$ origin, since the molar extinction coefficients of these bands are larger than those usually assigned to $d \rightarrow d^*$ transitions [7, 8]. The general features of the spectra for H_2L, Ni–L and Cu–L are very similar to those reported previously [6, 9] of the corresponding tetraaza[14]annulene ligands which do not contain any crown ether groups, and of metal(II) complexes of these latter ligands. This seems to indicate that the electronic spectra are scarcely affected by the electronic effect of the crown ether groups.

^1H NMR spectra

^1H NMR data and their assignments for the crown tetraaza[14]annulene and its nickel(II) complex are listed in Table 1. The methylene protons of the crown ether groups couple with each other and the signal is split into a multiplet. Upon the formation of the nickel(II) complex the amine proton signal is extinguished, the aromatic proton signal is shifted downfield and the methine proton signal is shifted slightly upfield. The magnitude of these shifts is comparable to that reported for the tetraaza[14]annulene nickel(II) complex [6].

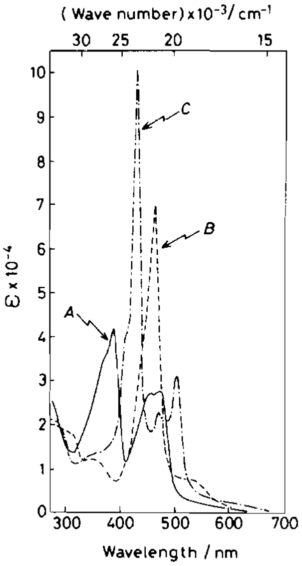

Fig. 1. Electronic absorption spectra for 2,3,11,12-bis-(1′,4′,7′,10′,13′-pentaoxatridecamethylene)-5,14-dihydro-7,16-diethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (H_2L) metal complexes at room temperature in chloroform. A, H_2L; B, Ni–L; C, Cu–L.

ESR spectra

The spin Hamiltonian parameters with those for a reference complex are compiled in Table 2. The general features of these spectra are analogous to those observed for the square-planar copper(II) complex derived from tetraaza[14]annulenes which do not contain any crown ether groups [9].

Aggregation

The ^1H NMR spectra of the free-base crown tetraaza[14]annulene (H_2L) in various solvents are shown in Fig. 2. The spectrum of H_2L in dimethyl sulfoxide-d_6 (Fig. 2(A)) is obvious and clearly resolved. We attribute this spectrum to monomeric tetraaza[14]annulene [6]. In chloroform-d, the spectrum changes and broad NMR signals appear (Fig. 2(B)). The porphyrin compounds show similar solvent-dependent NMR spectra which arise from self-aggregation of the porphyrins [10, 11]. Accordingly this spectral change can be ascribed to the presence of dimeric tetraaza[14]annulene species. It is very interesting that the tetraaza[14]annulene with crown ether groups is liable to aggregate itself and that the tetraaza[14] annulene with no crown ether group

TABLE 1. Proton NMR data for crown tetraaza[14]annulene and its nickel(II) complex[a]

Compound	Ethyl		Crown $-O-CH_2-$	Aromatic	Methine $-N=CH-$	Amine $-N-H$
	$-CH_3$	$-CH_2-$				
H_2L	1.10 (t, $J=7.2$ Hz)	2.20 (q, $J=7.2$ Hz)	3.62 (m)	6.79 (s)	7.57 (d, $J=5.6$ Hz)	13.71 (t, $J=5.6$ Hz)
Ni-L	1.15 (t, $J=7.4$ Hz)	2.32 (q, $J=7.4$ Hz)	3.63 (m)	7.11 (s)	7.51 (s)	

[a] Chemical shifts are given in ppm from TMS. Measured in dimethyl sulfoxide-d_6. Multiplicity of a proton signal is given in parentheses after δ value; s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet.

TABLE 2. Spin Hamiltonian parameters for tetraaza[14]annulene copper(II) complexes[a]

Ligand	Medium	$\bar{g}$	$\lvert g_0-g_\parallel\rvert$	$\lvert g_0-g_\perp\rvert$	$\bar{A}^{Cu}\times10^4$ (cm^{-1})	$A_\parallel{}^{Cu}\times10^4$ (cm^{-1})	$A_\perp{}^{N}\times10^4$ (cm^{-1})	Reference
L^{2-}	$CHCl_3$[b]	2.047			98.1			this work
L^{2-}	*N,N*-dimethylformamide[c]		0.127	$\begin{cases}0.034\\0.007\end{cases}$		218.5	7.4	this work
T^{2-} [d]	xylene–benzene (2:1 vol./vol.)	2.089			96.4			9
T^{2-}	ligand (H_2T)		0.128	$\begin{cases}0.033\\0.010\end{cases}$		218.0	7.3	9

[a] Maximum possible errors: g, ±0.0005; $\bar{A}^{Cu}$, $A_\parallel{}^{Cu}$, $\pm0.5\times10^{-4}$ cm^{-1}; $A_\perp{}^{N}$, $\pm0.05\times10^{-4}$ cm^{-1}. [b] Measured at room temperature. [c] Measured at 77 K. [d] H_2T = 5,14-dihydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine.

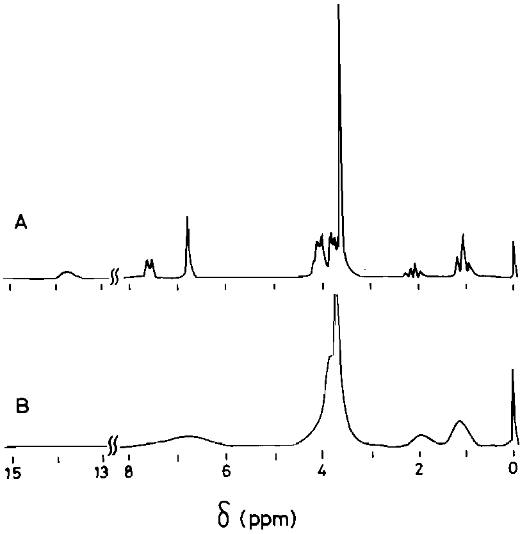

Fig. 2. ^1H NMR spectra of crown tetraaza[14]annulene at room temperature; TMS as an internal reference: A, in dimethyl sulfoxide-d_6; B, in chloroform-d.

does not self aggregate. This seems to indicate that the driving force of tetraaza[14]annulene aggregation rests on the substituent groups.

Cation complexation

The stoichiometry of complexation of various alkali metal salts with crown tetraaza[14]annulene (H_2L) and its metal(II) complexes (Ni–L and Cu–L) was studied through UV–Vis and ESR measurements in chloroform–methanol (4:1 vol./vol.). The crown tetraaza[14]annulene and its complexes were dissolved in chloroform–methanol and the alkali metal salts which were dissolved in methanol were added in small portions. Addition of Na^+ to the crown tetraaza[14]annulene and its metallo derivatives in chloroform–methanol solvent mixture does not produce any appreciable changes in the visible absorption spectra of the macrocycles. However, outstanding changes are determined when K^+ and $NH_4{}^+$ ions are added to H_2L, Ni–L and Cu–L. Figure 3 shows an example of the results. It can be seen that increasing addition of K^+ and $NH_4{}^+$ ions brings about (i) reduction in intensity of the 450–510 nm range, (ii) broadening and (iii) blue shift (~15 nm) of the intense band in the 375–430 nm region. These remarkable spectral changes are explained by the specific complexation behavior of the macrocycle and its complexes. It is known that K^+ and $NH_4{}^+$ ions form complexes with 2,3-benzo-1,4,7,10,13-pentaoxacyclopentadeca-2-ene (benzo-15-crown-5) in 1:2 (cation:crown ether) stoichiometry while Na^+ and Mg^{2+} ions form only 1:1 complexes [12]. Assuming that the appended crown ethers indicate similar complexation behavior, two modes of cation encapsulation

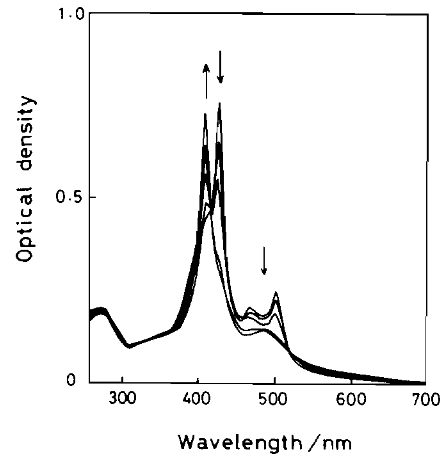

Fig. 3. The electronic absorption spectra of Cu–L containing various concentrations of CH_3COOK in chloroform–methanol (4:1 vol./vol.) at room temperature. Arrows indicate the direction of the spectroscopic change.

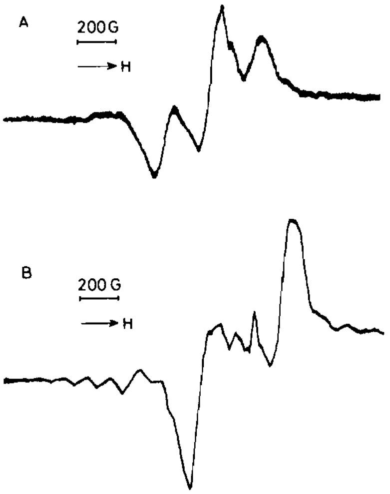

Fig. 4. ESR spectrum of crown tetraaza[14]annulene copper(II) complex in chloroform–methanol (4:1 vol./vol.) at 77 K: A, in the absence of any cations; B, in the presence of CH_3COOK.

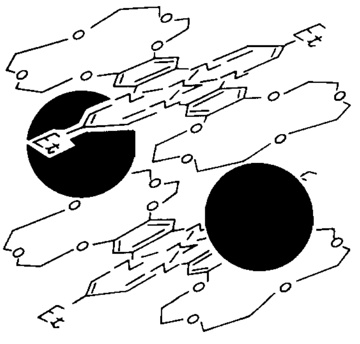

Fig. 5. A possible structure for the K^+-induced dimer of crown tetraaza[14]annulene metal(II) complex.

can be visualized. In case 1, H_2L, Ni–L and Cu–L can bind two cations, the cation being held in crown ether, leading to a stoichiometry of 1:2 (crown macrocycle:cation), while in case 2, two cations can be encapsulated by four crown ether cavities from two macrocycles, resulting in the formation of a 2:2 complex. The former case describes the introduction of Na^+ into crown ether cavities and the latter case implies dimerization of the macrocycle induced by the complexing behavior of the specific cations. The experimentally observed broadening, reduction in intensity of the 450–510 nm range and blue-shift of the intense band in the 375–430 nm region in the K^+ and $NH_4{}^+$ ion complexation investigations are similar to those observed for the formulation of a dimer in porphyrin systems [11, 13]. This seems to suggest that addition of K^+ and $NH_4{}^+$ causes dimerization of these compounds.

The selection of copper(II) in the tetraaza[14]annulene cavity provides an ESR probe to investigate the cation complexation of the appended crown ethers by these macrocyclic compounds. The ESR spectrum of addition of Na^+ ions to this copper(II) complex (Cu–L) is analogous to that observed for the copper(II) complex of cation-free tetraaza[14]annulene. This seems to indicate that the introduction of the Na^+ ion into crown ether cavities prevents any likely aggregation of the complex due to strong repulsion among the two complexes induced by two Na^+ ions on each complex. The dramatic change in the ESR spectrum of Cu–L is observed by the addition of K^+ ions and the spectrum is shown in Fig. 4. The four parallel lines of the copper(II) ($I=3/2$) are decomposed and the set is split into seven lines which are not appreciably resolved. In addition to this, two strong perpendicular transitions are observed in the $g \approx 2$ range. This is typical of a triplet state with axial symmetry. The hyperfine structure reveals the existence of two equivalent copper(II) nuclei. Strong support for the presence of an axial dimer arises from the appearance of a half-field spectrum with seven lines of equal spacing of 100 G. This spectrum is similar to that obtained for an axial dimer of porphyrin copper(II) complexes [1(d), 2(f)]. These indicate that sandwiching the two K^+ ions by four crown ether moieties, the K^+ ions are held by the crown ether cavities, so that this complex assumes an axial dimer type (Fig. 5).

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