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Macrocycles, 7,16-diethyl-5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (**2B**), 7,16-diethyl-5,6,7,8,9,14,15,16,17,18-decahydro-(*E*)-dipyrido[*b,i*][1,4,8,11]tetraazacyclotetradecine (**2E**) and 7,16-diethyl-5,6,7,8,9,14,15,16,17,18-decahydro-(*Z*)-dipyrido[*b,i*][1,4,8,11]tetraazacyclotetradecine (**2Z**), have been synthesized by hydrogenation of 7,16-diethyl-5,14-dihydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine and 7,16-diethyl-5,14-dihydro-(*E*)- or -(*Z*)-dipyrido[*b,i*][1,4,8,11]tetraazacyclotetradecine. In each case, two isomers were produced with differing orientations of the ethyl groups relative to the macrocyclic plane. The isomers were separated by repeated recrystallization. Carbon-13 nmr spectra for the metal-free ligands were used to distinguish between the two isomers. The nickel(II), copper(II) and zinc(II) complexes of the two isomers of **2B** were prepared and their spectroscopic data were determined. The ligand-field bands in the 15000-30000  $\text{cm}^{-1}$  region for the nickel(II) and copper(II) complexes are consistent with square-planar configurations. A strong band appearing at *ca.* 3200  $\text{cm}^{-1}$  in the infrared spectra was assigned to the N-H stretching mode which shifted to lower frequency upon metal coordination.

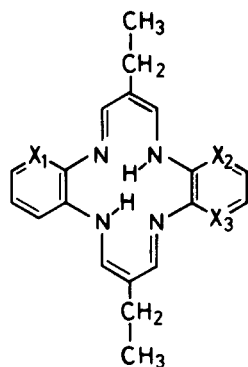
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### Introduction.

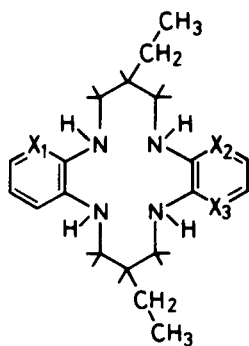
Saturated tetradentate  $\text{N}_4$  macrocycles like 1,4,8,11-tetraazacyclotetradecine (cyclam) and its derivatives have been widely investigated. Compared with an unsubstituted cyclam, the introduction of benzo groups such as in dibenzocyclam [1,2] or of *N*-alkyl groups such as in 1,4,8,11-tetramethylcyclam [3-5] considerably reduces the flexibility of the 14-membered ring system. Cyclams with a pendant pyridine or benzene group at the 5- or 6-position of the macrocyclic skeleton often yield penta coordinated complexes in which the pendant group is coordinated in an axial site [6-11]. Macrocycles with two pendant groups may in principle exist in either the *anti* or the *syn* form, depending upon the orientation of the groups with respect to the macrocyclic plane. Some examples of the separation

of such complexes are reported in the literature [12,13], but it is rare to find reports describing the separation of the free macrocycles.

In the present work, we have synthesized and isolated the 7,16-diethyl-5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (**2B**), 7,16-diethyl-5,6,7,8,9,14,15,16,17,18-decahydro-(*E*)-dipyrido[*b,i*][1,4,8,11]tetraazacyclotetradecine (**2E**) and 7,16-diethyl-5,6,7,8,9,14,15,16,17,18-decahydro-(*Z*)-dipyrido[*b,i*][1,4,8,11]tetraazacyclotetradecine (**2Z**). Subsequently, we have also prepared the nickel(II), copper(II) and zinc(II) complexes of the two isomers of **2B**. The spectral properties of the macrocycles and of their nickel(II), copper(II) and zinc(II) complexes have also been investigated.

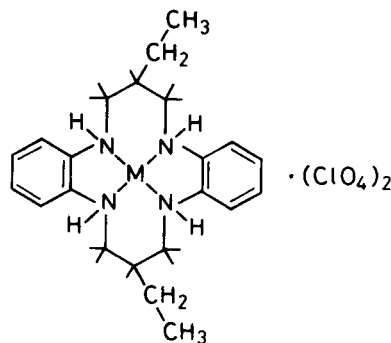


1-B :  $\text{X}_1=\text{X}_2=\text{X}_3=\text{CH}$   
1-E :  $\text{X}_1=\text{X}_3=\text{N}$ ,  $\text{X}_2=\text{CH}$   
1-Z :  $\text{X}_1=\text{X}_2=\text{N}$ ,  $\text{X}_3=\text{CH}$



2-B :  $\text{X}_1=\text{X}_2=\text{X}_3=\text{CH}$   
2-E :  $\text{X}_1=\text{X}_3=\text{N}$ ,  $\text{X}_2=\text{CH}$   
2-Z :  $\text{X}_1=\text{X}_2=\text{N}$ ,  $\text{X}_3=\text{CH}$

Formula 1



M = Ni(II), Cu(II), Zn(II)

Formula 2

### Results and Discussion.

Preparation and Properties of the Macrocycles and their Complexes.

5,6,7,8,9,14,15,16,17,18-Decahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine was prepared from 5,14-dihydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine and Raney nickel **W1** in 2-methoxyethanol under hydrogen pressure [1]. Macrocycle **2B** could be prepared from 5,14-dihydro-7,16-diethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (**1B**) according to the above procedure, but the hydrogenation reactions of 5,14-dihydro-7,16-diethyl-(*E*)-dipyrido[*b,i*][1,4,8,11]tetraazacyclotetradecine (**1E**) and 5,14-dihydro-7,16-diethyl-(*Z*)-dipyrido[*b,i*][1,4,8,11]tetraazacyclotetradecine (**1Z**) were unsuccessful by that procedure. Macrocycles **2E** and **2Z** were obtained from **1E** and **1Z** using Raney nickel **W2** instead of Raney nickel **W1**. The hydrogenation of macrocycles **1E** and **1Z** was more difficult than macrocycle **1B** due to the presence of pyrido groups instead of benzo groups. The hydrogenation of **1B**, **1E** and **1Z** yielded two isomers in each case. The two isomeric forms of compound **2B**, *i.e.* **2Ba** and **2Bb** were separated by repeated recrystallization from 2-methoxyethanol/ethanol. Benzene was used for the separation of **2Ea** and **2Eb**. Carbon tetrachloride was used for **2Za** and **2Zb**.

The reaction of macrocycles **2Ba** and **2Bb** with nickel(II), copper(II) or zinc(II) diperchlorate gave the corresponding diperchlorate complexes [ML] (M = Ni, Cu or

Zn; L = **2Ba** or **2Bb**) in good yields. Analytical data for the macrocycles and their metal complexes are summarized in Table I. Nickel(II) and zinc(II) complexes were soluble in polar solvents, and unstable in solution when allowed to stand for a time exposed to the air. Solid samples of the above compounds could be stored opened to the air without undergoing oxidative reactions. In dilute solutions, on the other hand, the color of freshly prepared methanol solutions of nickel(II) complexes changed from pale yellow to deep green and, eventually to reddish orange. The complete oxidation occurred in 2 days at room temperature. This change may be attributable to oxidation of the macrocyclic skeleton of nickel(II) complexes. The details of this reaction will be described in future articles. The zinc(II) complexes were also susceptible to air oxidation in solution. Moreover, the zinc(II) complexes were dissociated when in the presence of water, either in alcoholic solution or in the solid state, and hence macrocycles **2Ba** and **2Bb** were recovered unchanged. The metal complexes of macrocycles **2Ea**, **2Eb**, **2Za** and **2Zb** could not be prepared. Even stable copper(II) complexes could not be formed by standard procedures in the case of macrocycles **2Ea**, **2Eb**, **2Za** and **2Zb**, but were formed for macrocycles **2Ba** and **2Bb**.

Molar Conductivity.

The molar conductivities for the nickel(II) and zinc(II) complexes which were susceptible to air oxidation were measured while argon was continuously bubbled through the solutions. Those for the copper(II) complexes were measured in air. The molar conductivity for the complexes are listed in Table II. The diperchlorate salts of [ML] (M = Ni, Cu or Zn; L = **2Ba** or **2Bb**) are 1:2 electrolytes in acetonitrile and hence are tetra coordinated in this solvent with ionized perchlorate anions.

Table I

Analytical Data and Melting Points for New Macrocycles and their Metal(II) Complexes

Compound	Empirical Formula	Elemental Analyses			mp (°C)
		Calcd./ (Found) (%)			
		C	H	N	
<b>2Ba</b>	C <sub>22</sub> H <sub>32</sub> N <sub>4</sub>	74.96 (74.82)	9.15 (9.09)	15.89 (15.78)	180.0-183.0
<b>2Bb</b>	C <sub>22</sub> H <sub>32</sub> N <sub>4</sub>	74.96 (75.12)	9.15 (9.26)	15.89 (16.08)	177.0-177.5
<b>2Ea</b>	C <sub>20</sub> H <sub>30</sub> N <sub>6</sub>	67.76 (67.73)	8.53 (8.65)	23.71 (23.46)	210.0-211.5
<b>2Eb</b>	C <sub>20</sub> H <sub>30</sub> N <sub>6</sub>	67.76 (67.86)	8.53 (8.71)	23.71 (23.96)	164.0-166.0
<b>2Za</b>	C <sub>20</sub> H <sub>30</sub> N <sub>6</sub>	67.76 (67.89)	8.53 (8.62)	23.71 (23.64)	225.0-227.0
<b>2Zb</b>	C <sub>20</sub> H <sub>30</sub> N <sub>6</sub>	67.76 (67.33)	8.53 (8.49)	23.71 (23.50)	187.0-189.0
Ni( <b>2Ba</b> )	C <sub>22</sub> H <sub>32</sub> N <sub>4</sub> NiCl <sub>2</sub> O <sub>8</sub>	43.31 (43.37)	5.29 (5.34)	9.18 (8.88)	>300
Ni( <b>2Bb</b> )	C <sub>22</sub> H <sub>32</sub> N <sub>4</sub> NiCl <sub>2</sub> O <sub>8</sub>	43.31 (43.36)	5.29 (5.36)	9.18 (8.81)	>300
Cu( <b>2Ba</b> )	C <sub>22</sub> H <sub>32</sub> N <sub>4</sub> CuCl <sub>2</sub> O <sub>8</sub>	42.97 (43.07)	5.25 (5.30)	9.11 (9.10)	285-292 dec
Cu( <b>2Bb</b> )	C <sub>22</sub> H <sub>32</sub> N <sub>4</sub> CuCl <sub>2</sub> O <sub>8</sub>	42.97 (43.15)	5.25 (5.27)	9.11 (9.15)	290-292 dec
Zn( <b>2Ba</b> )	C <sub>22</sub> H <sub>32</sub> N <sub>4</sub> ZnCl <sub>2</sub> O <sub>8</sub>	42.84 (42.36)	5.23 (5.29)	9.08 (8.62)	289-295 dec
Zn( <b>2Bb</b> )	C <sub>22</sub> H <sub>32</sub> N <sub>4</sub> ZnCl <sub>2</sub> O <sub>8</sub>	42.84 (42.60)	5.23 (5.50)	9.08 (8.53)	296-299 dec

Table II  
Molar Conductances for the Complexes at 25° [a]

Complex	$\Lambda_M$ S(cm <sup>2</sup> mol <sup>-1</sup> )	Type of electrolyte [b]
Ni( <b>2Ba</b> )	352	1:2
Ni( <b>2Bb</b> )	368	1:2
Cu( <b>2Ba</b> )	348	1:2
Cu( <b>2Bb</b> )	347	1:2
Zn( <b>2Ba</b> )	326	1:2
Zn( <b>2Bb</b> )	333	1:2

[a] For *ca.* 10<sup>-4</sup> mol dm<sup>-3</sup> solutions. [b] Assignment of the type of electrolyte presented in solutions was made on the basis of the conductance data compiled by Geary [19].

Mass Spectra.

The EI mass spectra for metal-free macrocycles establish the presence of a molecular ion M<sup>+</sup> as described in the Experimental. The nickel(II), copper(II) and zinc(II)

complexes were analyzed using FAB mass spectra, but molecular ions were not observed. The nickel(II) complexes show a cluster of ions corresponding to  $[M\text{-ClO}_4\text{-H}]^+$  at  $m/e$  508 and  $[M\text{-2ClO}_4\text{-H}]^+$  at  $m/e$  409. The latter peak was the base peak in the mass spectrum. The copper(II) complexes also exhibited a cluster of ions corresponding to  $[M\text{-2ClO}_4\text{-Cu}]^+$  at  $m/e$  352,  $[M\text{-2ClO}_4\text{-H}]^+$  at  $m/e$  414 and  $[M\text{-ClO}_4\text{-H}]^+$  at  $m/e$  513. The peak at  $m/e$  352 was the base peak in the mass spectrum. The zinc(II) complexes exhibited peaks at  $m/e$  515, 451 and 416 corresponding to  $[M\text{-ClO}_4]^+$ ,  $[M\text{-ClO}_4\text{-O}_4]^+$  and  $[M\text{-2ClO}_4]^+$ . The peak at  $m/e$  451 is consistent with recombination of the chloride atom arising from Cl-O bond cleavage of perchlorate radicals. The mass spectrum made no distinction between **2Ba** and **2Bb** in these complexes.

#### Vibrational Spectra.

A strong absorption band observed in the  $3200\text{ cm}^{-1}$  range was attributed to a N-H stretching mode and shifted slightly to lower frequency upon metal coordination. A strong broad band at around  $1100\text{ cm}^{-1}$  was observed for the nickel(II), copper(II) and zinc(II) complexes and was attributable to the stretching vibrational mode of the perchlorate ion. The perchlorate group in the present metal complexes may be present not as a coordinated group but as a simple isolated ion, judging from the vibrational frequency [14].

#### Electronic Spectra.

Ligand-field spectra for the two nickel(II) complexes in acetonitrile are shown in Figure 1. The Ni(TMC) $^{2+}$  (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) complex of the *trans*-I type (*syn*) is penta coordinated, having one solvent in the axial coordination site, while that of the *trans*-III type (*anti*) is hexa coordinated through having two solvent molecules [15,16]. Ligand-field spectra for the two novel nickel(II) complexes were similar to each other and consisted of one broad band at about  $22000\text{ cm}^{-1}$ . This seems to indicate that the structures of  $[\text{Ni}(\mathbf{2Ba})(\text{ClO}_4)_2]$  and  $[\text{Ni}(\mathbf{2Bb})(\text{ClO}_4)_2]$  assume a square-planar configuration.

Ligand-field spectra for the two copper(II) complexes in acetonitrile were similar to each other and were composed of only one broad band in a region lying below  $25000\text{ cm}^{-1}$  as shown in Figure 2. The general features and peak positions of the ligand-field spectra are not diagnostic of copper complexes adopting square-planar geometries but the spectra are not inconsistent with other complexes having this geometry.

#### Nmr Spectra.

The  $^1\text{H}$  nmr data and their assignments for the macrocycles and their zinc(II) complexes are listed in Table III. The spectra of **2Ba** and its zinc(II) complex

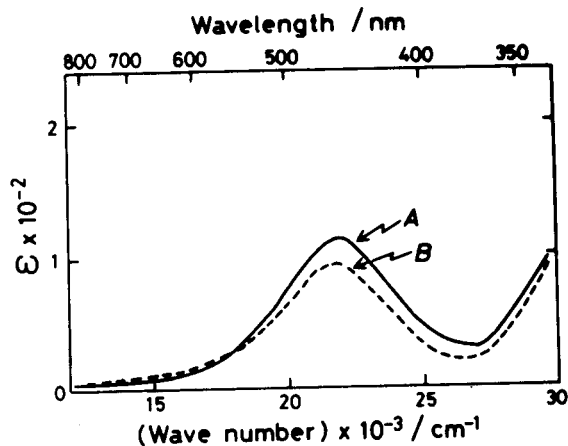


Figure 1. Ligand-field spectra for nickel(II) complexes in acetonitrile at room temperature. A, Ni(**2Ba**); B, Ni(**2Bb**).

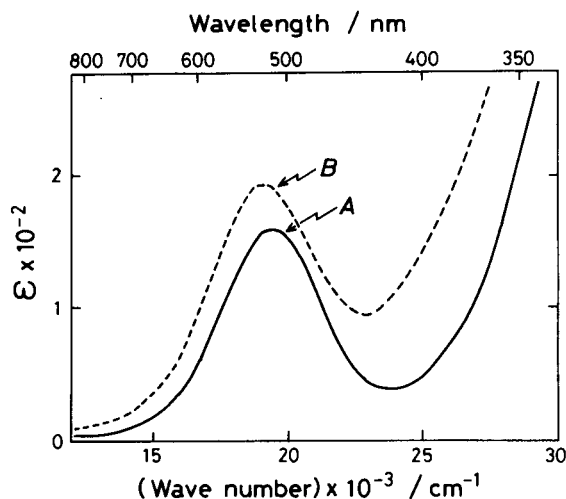
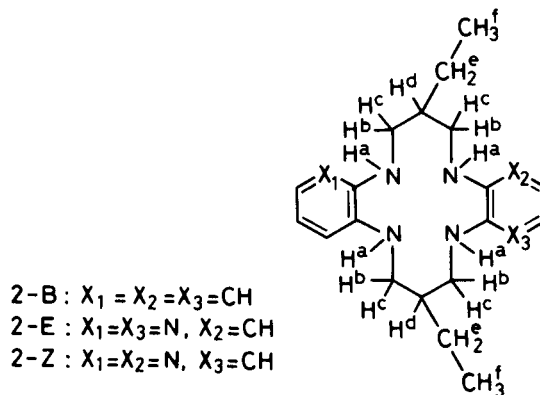


Figure 2. Ligand-field spectra for copper(II) complexes in acetonitrile at room temperature. A, Cu(**2Ba**); B, Cu(**2Bb**).

(Zn(**2Ba**)) are shown in Figure 3. The H $^a$ -amine protons for **2Ba** and **2Bb** provide one broad signal. On the other



Formula 3

Table III  
Proton NMR Data for the Macrocycles and their Zinc(II) Complexes [a]

Compound [b]	Aromatic			-NH <sup>a</sup>	N-CH <sub>2</sub> <sup>b,c</sup>	-CH <sup>d</sup>	-CH <sub>2</sub> <sup>e</sup>	-CH <sub>3</sub> <sup>f</sup>	Reference
<b>2Ba</b> [c]	6.5-6.9 (m)			4.38 (br, s)	2.7-3.6 (m)	2.1 (m)	1.48 (m)	1.09 (t) (J = 7.0 Hz)	
<b>2Bb</b> [c]	6.5-6.9 (m)			4.20 (br, s)	2.7-3.6 (m)	2.1 (m)	1.47 (m)	1.09 (t) (J = 7.0 Hz)	
<b>2Ea</b> [c]	7.73 (dd) (J = 5.0 Hz) (J = 1.6 Hz)	6.84 (dd) (J = 7.5 Hz) (J = 1.6 Hz)	6.54 (dd) (J = 7.5 Hz) (J = 5.0 Hz)	6.25 (br, s) 3.13 (br, s)	2.8-4.1 (m)	2.0 (m)	1.47 (m)	1.04 (t) (J = 6.3 Hz)	
<b>2Eb</b> [c]	7.72 (dd) (J = 4.7 Hz) (J = 1.8 Hz)	6.80 (dd) (J = 7.6 Hz) (J = 1.8 Hz)	6.56 (dd) (J = 7.6 Hz) (J = 4.7 Hz)	6.04 (br, s) 3.26 (br, s)	2.8-4.0 (m)	2.0 (m)	1.44 (m)	1.05 (t) (J = 6.1 Hz)	
<b>2Za</b> [c]	7.72 (dd) (J = 4.6 Hz) (J = 2.1 Hz)	6.81 (dd) (J = 7.6 Hz) (J = 2.1 Hz)	6.62 (dd) (J = 7.6 Hz) (J = 4.6 Hz)	4.59 (br, s) 4.27 (br, s)	2.8-4.0 (m)	2.0 (m)	1.52 (m)	1.08 (t) (J = 6.3 Hz) 1.06 (t) (J = 6.3 Hz)	
<b>2Zb</b> [c]	7.74 (dd) (J = 4.5 Hz) (J = 2.1 Hz)	6.79 (dd) (J = 7.5 Hz) (J = 2.1 Hz)	6.62 (dd) (J = 7.5 Hz) (J = 4.5 Hz)	5.01 (br, s) 4.41 (br, s)	2.7-4.0 (m)	2.0 (m)	1.52 (m)	1.09 (t) (J = 6.3 Hz) 1.07 (t) (J = 6.3 Hz)	
dibenzocyclam [c]	6.55 (m)			4.98 (s)	3.19 (t) (J = 7.0 Hz)	1.99 (m)			[1]
<b>Zn(2Ba)</b> [d]	7.3-7.8 (m)			[e]	2.8-3.7 (m)	2.2 (m)	1.48 (m)	1.10 (t) (J = 6.0 Hz)	
<b>Zn(2Bb)</b> [d]	7.3-7.8 (m)			[e]	2.8-3.7 (m)	2.2 (m)	1.49 (m)	1.09 (t)	

[a] Chemical shifts in ppm from TMS. Multiplicity of a proton signal is given in parentheses after  $\delta$ -value: s = singlet, t = triplet, m = multiplet, dd = doublet of doublets, br = broad. [b] Dibenzocyclam: 5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine. [c] Measured in chloroform-d. [d] Measured in methanol-d<sub>4</sub>. [e] This signal was found to vanish upon substitution with deuterium of methanol-d<sub>4</sub>.

Table IV  
Carbon-13 NMR Data for the Macrocycles [a]

Compound	C(1)	C(2)	C(3), C(4)	C(5)	C(6)	C(7), C(8)	C(9), C(10)	C(11)	C(12)
<b>2Ba</b> [b]		117.57	109.45		137.40	50.93 50.07	- 38.01	25.66 25.15	12.23
<b>2Bb</b> [b]		117.57	109.45		137.40	50.93	37.95	25.66	12.23
<b>2Ea</b> [c]	138.66	112.77	117.80	130.66	151.28	50.13 47.78	39.32	24.86	11.95
<b>2Eb</b> [c]	138.14	113.22	116.94	130.94	151.00	50.24 48.70	37.84	25.09	11.89
<b>2Za</b> [b]	135.12	112.25	113.57	131.57	148.89	49.84 47.27	38.81 37.66	25.09	11.95
<b>2Zb</b> [b]	135.17	112.25	113.28	131.51	148.95	49.95 48.01	38.24 36.92	25.15	12.00

[a] Chemical shifts in ppm from internal TMS. [b] Measured in hexamethylphosphoric triamide-d<sub>18</sub>. [c] Measured in chloroform-d.

hand, the H<sup>a</sup>-amine protons in **2Ea**, **2Eb**, **2Za** and **2Zb** provide two broad signals. The signal for the proton at the  $\alpha$ -position to the pyridine nitrogen is anticipated to be observed at a lower field compared to that of the proton at the  $\beta$ -position because of the electron-withdrawing effect of pyridine nitrogen. The signal for the H<sup>a</sup>-amine protons was found to disappear upon replacement of the amine

proton by deuterium in the metal-free macrocycles. The macrocycles may form metal complexes with five- and six-membered rings, where the nitrogen donor is separated by two or three carbon atoms. Since the six-membered chelate ring adopts a chair conformation, the H<sup>b</sup>- and H<sup>c</sup>-methylene protons are magnetically nonequivalent, the one is positioned axial and the other equatorial. These protons

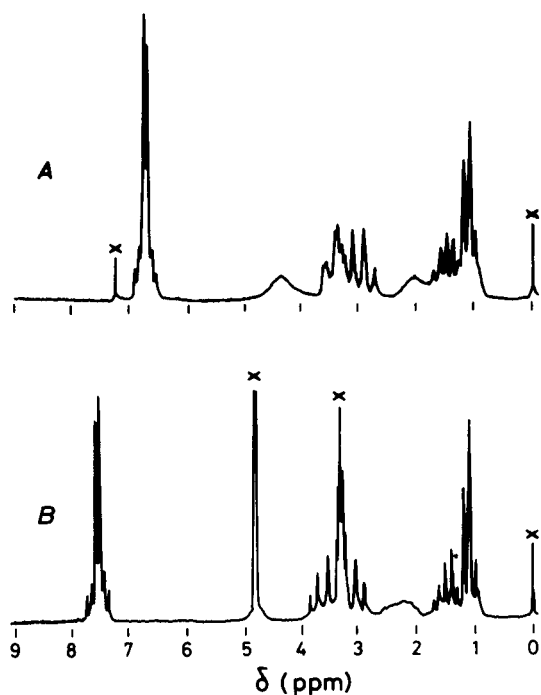


Figure 3. Proton nmr spectra of 7,16-diethyl-5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (**2Ba**) and its zinc(II) complex at room temperature. *A*, **2Ba** in chloroform-*d*; *B*, Zn(**2Ba**) in methanol-*d*<sub>4</sub>.

couple with the geminal and vicinal ( $H^d$ ) protons, and show multiplets in the 2.7-3.6 ppm range. Due to the complex splitting pattern in this region, the exact assignment of the protons is difficult. On the other hand, the methylene proton ( $N-CH_2$ ) signals of 5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine are observed as a triplet at 3.19 ppm, and are magnetically equivalent [1]. Accordingly, this seems to indicate that the fluctuation of six-membered chelate rings about the macrocyclic plane is suppressed by the 7- and 16-ethyl groups. The  $H^c$ -

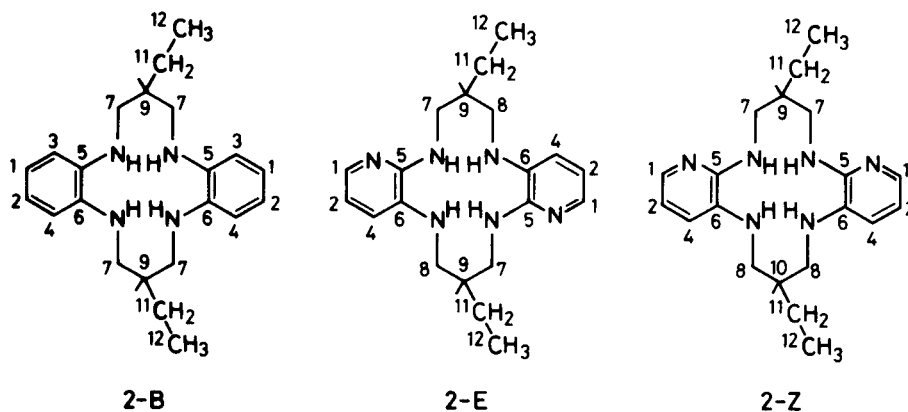
methyl proton signals for **2Za** and **2Zb** are observed as sextets, or more specifically, the overlapping of two triplets.

The  $^{13}C$  nmr data and their assignments for the macrocyclic ligands are compiled in Table IV. The  $^{13}C$  nmr was used to distinguish clearly between the two isomers which were separated by recrystallization. For the isomers **2Ba** and **2Bb**, the C7- and C9-carbon signals for **2Ba** were observed as split signals, while those for **2Bb** were observed as singlets at room temperature. The  $^{13}C$  nmr spectrum of **2Ba** recorded at 100° is similar to that taken at room temperature. Compound **2Ba** possesses a higher melting point and poorer solubility in polar solvents than **2Bb**. These facts may indicate that isomer **2Ba** is in the *anti* conformation and isomer **2Bb** is in the *syn* form. In the spectra for **2E** and **2Z**, the C7- and C8-carbon signals were observed as split signals illustrating the relative positions of the amine nitrogens to the heteroatoms in the pyridine rings. The lower-field signal for C7 and C8 showed a downfield shift (0.11 ppm) when comparing **2Ea** (or **2Za**) with **2Eb** (or **2Zb**), while the other signal was shifted downfield by 0.74-0.92 ppm. These facts show that the ring structure of **2Ea** and **2Za** are similar to that of **2Ba**, while the ring structures of **2Eb** and **2Zb** are similar to that of **2Bb**. However, the distinction between these spectroscopically similar pairs should be better able to be resolved by X-ray crystallography.

## EXPERIMENTAL

Unless otherwise noted all materials were reagent grade and were used without further purification.

Conductivity measurements were performed with acetonitrile solutions of the complexes kept at  $25.0 \pm 0.1^\circ$  with a Coolnics Thermo-Bath (model CTE-310). Conductivities were measured using a TOA Electronics LTD, CM-20E. The EI mass spectra (at 70 eV) for the metal-free macrocycles and FAB mass spectra (in a



Formula 4

matrix of glycerin) for the nickel(II), copper(II) and zinc(II) complexes were obtained on a JEOL JMS-DX 300 gas chromatograph-mass spectrometer. Agron was used as the fast atom beam. Infrared spectra in the range of the 400-4000  $\text{cm}^{-1}$  were carried out on a Hitachi 260-30 spectrophotometer at room temperature with potassium bromide disks. Ultraviolet and visible spectra covering the 12500-50000  $\text{cm}^{-1}$  region were taken on a Shimadzu UV 200S double beam spectrophotometer at room temperature. Proton and  $^{13}\text{C}$  nmr measurements were recorded on a JEOL JNM-FX 60 spectrometer. The nmr spectra were run in deuteriochloroform, deuteriomethanol, or deuteriohexamethyl phosphoric triamide and chemical shifts are given in ppm relative to tetramethylsilane as an internal reference standard.

#### Preparation of Macrocycles.

5,14-Dihydro-7,16-diethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (**1B**), 5,14-dihydro-7,16-diethyl-(*E*)-dipyrido[*b,i*][1,4,8,11]-tetraazacyclotetradecine (**1E**) and 5,14-dihydro-7,16-diethyl-(*Z*)-dipyrido[*b,i*][1,4,8,11]tetraazacyclotetradecine (**1Z**).

The synthetic procedures for **1B**, **1E** and **1Z** have been reported previously [17,18].

7,16-Diethyl-5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (**2B**).

A mixture of **1B** (5.00 g), 2-methoxyethanol (200 ml) and Raney nickel W1 (3.5 g) was loaded into a 300 ml autoclave. The mixture was hydrogenated at 80° at a hydrogen pressure of ca. 100  $\text{kg}/\text{cm}^2$  for 6 hours. Hot ethanol (200 ml) was added to the hot reaction mixture, which was filtered to remove the catalyst and cooled down at room temperature. The crystalline solid was recovered by filtration, washed three times with ethanol (10 ml) and recrystallized from 2-methoxyethanol/ethanol (1:1) to give colorless needles (**2Ba**). The yield was 1.52 g (30%); ir:  $\nu$  N-H 3275,  $\nu$  C=C 1604, 1524, 1484, 1460,  $\delta$  C-H 734  $\text{cm}^{-1}$ ;  $\lambda$  max (acetonitrile): 302, 250, 223 nm; ms: *m/e* (relative intensity) 353 (2.5), 352 (11.3), 119 (100).

The filtrate was concentrated *in vacuo* under nitrogen atmosphere to obtain a crystalline solid. Recrystallization from chloroform/methanol (3:2) gave 1.86 g (36%) of fine colorless needles (**2Bb**); ir:  $\nu$  N-H 3260,  $\nu$  C=C 1606, 1516, 1460,  $\delta$  C-H 736  $\text{cm}^{-1}$ ;  $\lambda$  max (acetonitrile): 302, 250, 223 nm; ms: *m/e* (relative intensity) 354 (3.3), 353 (26.2), 352 (100), 119 (67.8).

7,16-Diethyl-5,6,7,8,9,14,15,16,17,18-decahydro-(*E*)-dipyrido[*b,i*][1,4,8,11]tetraazacyclotetradecine (**2E**).

A 300 ml autoclave was charged with a mixture of **1E** (2.00 g), 2-methoxyethanol (100 ml), ethanol (100 ml) and Raney nickel W2 (2.0 g). The mixture was hydrogenated at 140° at a hydrogen pressure of about 100  $\text{kg}/\text{cm}^2$  for 4 hours. After being allowed to stand at room temperature, the catalyst was removed by filtration. The filtrate was concentrated *in vacuo* under nitrogen atmosphere, washed three times with diethyl ether (100 ml) and recrystallized from benzene to give colorless needles (**2Ea**). The yield was 0.82 g (40%); ir:  $\nu$  N-H 3295,  $\nu$  C=C 1604, 1516, 1464, 1428,  $\delta$  C-H 762  $\text{cm}^{-1}$ ;  $\lambda$  max (acetonitrile): 312, 251 nm; ms: *m/e* (relative intensity) 355 (13.3), 354 (36.9), 120 (100).

The washings referred to above and the mother liquor from **2Ea** were concentrated *in vacuo* under nitrogen atmosphere and the residue was recrystallized from hexane to obtain 0.25 g (12%) of fine colorless plates (**2Eb**); ir:  $\nu$  N-H 3320,  $\nu$  C=C 1604, 1510, 1462, 1424,  $\delta$  C-H 766  $\text{cm}^{-1}$ ;  $\lambda$  max (acetonitrile): 312, 251 nm; ms:

*m/e* (relative intensity) 355 (36.2), 354 (100), 120 (78.4).

7,16-Diethyl-5,6,7,8,9,14,15,16,17,18-decahydro-(*Z*)-dipyrido[*b,i*][1,4,8,11]tetraazacyclotetradecine (**2Z**).

Macrocycle **2Z** was prepared from **1Z** (1.00 g), ethanol (200 ml) and Raney nickel W2 (3.5 g), following the above (**2E**) procedure. The filtrate was concentrated *in vacuo* under nitrogen atmosphere. The residue was washed three times with carbon tetrachloride (100 ml) and recrystallized from acetonitrile to give 0.25 g (24%) of colorless plates (**2Za**); ir:  $\nu$  N-H 3335, 3185,  $\nu$  C=C 1604, 1580, 1512, 1442, 1424,  $\delta$  C-H 766  $\text{cm}^{-1}$ ;  $\lambda$  max (acetonitrile): 312, 251 nm; ms: *m/e* (relative intensity) 356 (3.2), 355 (25.1), 354 (100).

The washing were concentrated *in vacuo* under nitrogen atmosphere. The residue was recrystallized from carbon tetrachloride to obtain 0.14 g (14%) of colorless plates (**2Zb**); ir:  $\nu$  N-H 3335, 3280,  $\nu$  C=C 1602, 1580, 1504, 1462, 1418,  $\delta$  C-H 766  $\text{cm}^{-1}$ ;  $\lambda$  max (acetonitrile): 312, 251 nm; ms: *m/e* (relative intensity) 356 (3.2), 355 (25.3), 354 (100).

(7,16-Diethyl-5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine)nickel(II) Dipерchlorate.

(A) A mixture of **2Ba** (0.18 g), nickel(II) perchlorate hexahydrate (0.23 g) and methanol (20 ml) was heated at 60° for 4 hours with stirring under nitrogen atmosphere. Upon cooling the reaction mixture with an ice-water bath, the crystalline solid was recovered by filtration and washed several times with methanol (10 ml) to give 0.25 g (80%) of fine pale yellow crystals [Ni(**2Ba**)]; ir:  $\nu$  N-H 3190,  $\nu$  C=C 1620, 1500, 1458,  $\delta$  C-H 766  $\text{cm}^{-1}$ ;  $\lambda$  max (acetonitrile): 455, 335 (sh), 303, 249 nm.

(B) A methanol (20 ml) solution of **2Bb** (0.18 g) was treated with nickel(II) perchlorate hexahydrate (0.22 g) as described above to yield 0.25 g (80%) of fine pale yellow crystals [Ni(**2Bb**)]; ir:  $\nu$  N-H 3200,  $\nu$  C=C 1622, 1504, 1462,  $\delta$  C-H 764  $\text{cm}^{-1}$ ;  $\lambda$  max (acetonitrile): 458, 335(sh), 303, 249 nm.

(7,16-Diethyl-5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine)copper(II) Dipерchlorate.

(A) This was prepared from **2Ba** (0.18 g), copper(II) perchlorate hexahydrate (0.22 g) and methanol (20 ml), following the above [Ni(**2Ba**)] procedure, and recrystallized from methanol to give 0.22 g (70%) of reddish violet plates [Cu(**2Ba**)]; ir:  $\nu$  N-H 3210,  $\nu$  C=C 1600, 1498, 1458,  $\delta$  C-H 764  $\text{cm}^{-1}$ ;  $\lambda$  max (acetonitrile): 515, 376 (sh), 299, 248 nm.

(B) Compound **2Bb** (0.18 g) in methanol (20 ml) reacted with copper(II) perchlorate hexahydrate (0.22 g) as described above to yield 0.22 g (70%) of reddish violet plates [Cu(**2Bb**)]; ir:  $\nu$  N-H 3210,  $\nu$  C=C 1595, 1500, 1463,  $\delta$  C-H 764  $\text{cm}^{-1}$ ;  $\lambda$  max (acetonitrile): 522, 376 (sh), 299, 248 nm.

(7,16-Diethyl-5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine)zinc(II) Dipерchlorate.

(A) A mixture of **2Ba** (0.18 g), zinc(II) perchlorate hexahydrate (0.22 g) and 1-propanol (20 ml) was heated at 60° for 4 hours with stirring under argon atmosphere. The reaction mixture was concentrated to about 1 ml *in vacuo*. Upon cooling the mixture with an ice-water bath, the crystalline solid was recovered by filtration and washed three times with cold 1-propanol (1 ml) to give 0.14 g (44%) of colorless plates [Zn(**2Ba**)]; ir:  $\nu$  N-H 3240,  $\nu$  C=C 1604, 1494, 1466,  $\delta$  C-H 760  $\text{cm}^{-1}$ ;  $\lambda$  max (acetonitrile): 302, 272 (sh), 254 nm.

(B) This was prepared from **2Bb** (0.21 g) zinc(II) perchlorate hexahydrate (0.17 g) and 1-propanol (20 ml), following the above procedure. The crystalline product was recovered by filtration and washed three times with diethyl ether (20 ml) to give 0.19 g (67%) of colorless plates [**Zn(2Bb)**]; ir:  $\nu$  N-H 3240,  $\nu$  C=C 1604, 1496, 1468,  $\delta$  C-H 762  $\text{cm}^{-1}$ ;  $\lambda$  max (acetonitrile): 301, 271 (sh), 261 nm.

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