

## Preparation and Characterization of Cobalt(II), Nickel(II) and Copper(II) Complexes with Water-soluble Macrocyclic N<sub>4</sub>-Ligands: 6,15-Diethyl-4,13-dihydro-1,10-dimethyl-(*E*)-dipyridinio [b,i] [1,4,8,11] tetraazacyclotetradecine iodide or methyl sulfate

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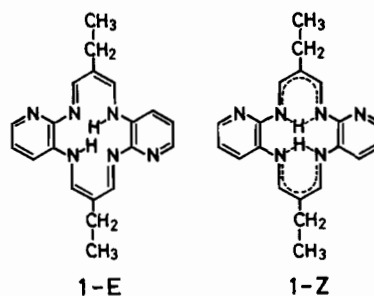
### Abstract

The mixture of 6,15-diethyl-4,13-dihydro-(*E*)-dipyrido[b,i] [1,4,8,11] tetraazacyclotetradecine (2-*E*) and 6,15-diethyl-4,13-dihydro-(*Z*)-dipyrido[b,i] [1,4,8,11] tetraazacyclotetradecine (2-*Z*) was prepared by cyclization of 3,4-diaminopyridine and 2-ethyl-3-ethoxyacrolein. Two kinds of isomers were separated by repeated recrystallization from chloroform. Methylation of pyridine comprised in 2-*E* using iodomethane or dimethyl sulfate afforded the corresponding dimethylated product (2-*E*-I or 2-*E*-S), which is soluble in water. The cobalt(II), nickel(II) and copper(II) complexes of 2-*E*-I and 2-*E*-S were prepared. The absorption bands appearing in the energy range greater than 18 000 cm<sup>-1</sup> were attributed to the  $\pi \rightarrow \pi^*$  transitions within a ligand molecule and CT transitions from metal to ligand. Since the  $d \rightarrow d^*$  bands for nickel(II) and copper(II) complexes were obscured by the  $\pi \rightarrow \pi^*$  and CT bands, no significant absorption bands were found in the region more than 18 000 cm<sup>-1</sup>. One of the  $d \rightarrow d^*$  bands for the cobalt(II) complex was observed at around 13 000 cm<sup>-1</sup>. These complexes assume the square-planar structures. A strong IR band due to the C=N stretching mode of the macrocycle moiety was observed at *ca.* 1640 cm<sup>-1</sup> and shifted slightly toward lower energy upon metal-coordination. *cis* (2-*Z*) and *trans* (2-*E*) isomers in the present macrocycle can be judged by the amine proton signals of NMR spectra. All proton signals except for amine protons show downfield shifts due to the deshielding effect of the positive charge provided by methylation of pyridine contained in the metal-free macrocycle. Upon formation of the nickel(II) complex all proton signals, except the aromatic protons adjacent to the

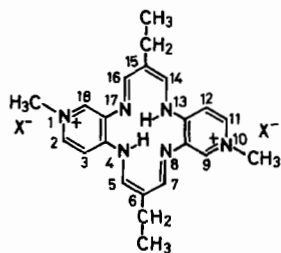
nitrogen atom of a pyridine ring, also show a downfield shift, which is attributed to the deshielding effect based on the positive charge given by nickel(II). The intensity change of the electronic spectrum at 425 nm is available for the determination of copper(II) concentrations in the aqueous solution using the water-soluble macrocycles (2-*E*-I and 2-*E*-S) and a good linear correlation is observed up to  $8 \times 10^{-6}$  mol dm<sup>-3</sup>.

### Introduction

In our previous work, the mixture of the two novel macrocycles containing pyridine rings, that is 7,16-diethyl-5,14-dihydro-(*E*)-dipyrido[b,i] [1,4,8,11] tetraazacyclotetradecine (1-*E*) and 7,16-diethyl-5,14-dihydro-(*Z*)-dipyrido[b,i] [1,4,8,11] tetraazacyclotetradecine (1-*Z*) was synthesized and separated by silica gel chromatography. The cobalt(II) complexes of each isomer were prepared and investigated by means of various spectroscopic methods [1]. In the presence of pyridine and O<sub>2</sub> in toluene-benzene (3:2 *v/v*) solutions at 77 K, the Co(1-*Z*) complex assumes the N<sub>5</sub>-penta-coordinated low-spin configuration, but the Co(1-*E*) complex becomes the monomeric oxygen adduct.



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2-E-I : X = I

2-E-S : X = SO<sub>4</sub>CH<sub>3</sub>

In the present work we synthesized two novel water-soluble macrocycles possessing pyridine rings, namely 6,15-diethyl-4,13-dihydro-1,10-dimethyl-(*E*)-dipyridinio[b,i][1,4,8,11]tetraazacyclotetradecine iodide (2-E-I) and methyl sulfate (2-E-S). We prepared the cobalt(II), nickel(II) and copper(II) complexes of 2-E-I and 2-E-S. We characterized the spectral properties of the present macrocycles and their cobalt(II), nickel(II) and copper(II) complexes by virtue of mass, electronic, vibrational and NMR spectroscopy as well as by conductivity measurements. Though the chemistry of water-soluble porphyrin and its metal complex has been studied [2], this is the first example of well characterized cobalt(II), nickel(II) and copper(II) complexes formed with water-soluble macrocyclic N<sub>4</sub>-ligands. We also describe the determination of copper(II) concentrations in the aqueous solution utilizing the present macrocycle.

## Experimental

### Physical Measurements

Conductivity measurements were made on water solutions of the compounds kept at 25.0 ± 0.1 °C with a Coolnics Thermo-Bath (model CTE-310). Conductivities were measured with a TOA Electronics LTD, CM-20E. EI mass spectra (at 20 eV) for metal-free macrocycles (2-E and 2-Z) and FAB mass spectra (in a matrix of neat glycerin) for water-soluble metal-free macrocycles (2-E-I and 2-E-S) and their nickel(II), copper(II) and cobalt(II) complexes were carried out with a JEOL JMS-DX 300 gas chromatograph-mass spectrometer. Argon was employed as the fast-atom beam. Electronic spectra covering the 12 500–40 000 cm<sup>-1</sup> range were taken on a Shimadzu UV-200S double beam spectrophotometer for methanol and water solutions at room temperature. Infrared spectra in the region of the 400–4000 cm<sup>-1</sup> were performed on a Hitachi 260-10 spectrophotometer at room temperature by a KBr disk technique. Proton NMR measurements were recorded on a JEOL JNM-FX 60 spectrometer operating in the Fourier transfer mode. The NMR spectra were run in chloroform-d

or dimethyl sulfoxide-d<sub>6</sub> and chemical shifts are reported in ppm relative to tetramethylsilane as an internal reference standard.

### Preparation of Macrocycles and their Complexes

6,15-Diethyl-4,13-dihydro-(*E*)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecine (2-E) and 6,15-diethyl-4,13-dihydro-(*Z*)-dipyrido[b,i][1,4,8,11]-tetraazacyclotetradecine (2-Z)

3,4-Diaminopyridine (3.0 g) was dissolved in 11 ml of *N,N*-dimethylformamide at ca. 100 °C. The mixture to which was added 2-ethyl-3-ethoxyacrolein (4.0 g) [3–6] was heated under reflux with stirring for 7 h. After the reaction mixture was allowed to stand overnight at room temperature, the precipitated crystalline solid was recovered by filtration and washed a few times with methanol to give dark red needles (the mixture of 2-E and 2-Z); yield 0.45 g (10%).

This mixture was recrystallized from chloroform as dark red needles (2-E); melting point >300 °C. The mass spectrum showed M<sup>+</sup> at *m/z* 346 and peaks for [M – CH<sub>3</sub>]<sup>+</sup> and [M – C<sub>2</sub>H<sub>5</sub>]<sup>+</sup> at *m/z* 331 and 317, respectively. IR (KBr disk): 3150 (N–H str.), 1650 (C=N str.), 1589 (C=C str. (conjugated ring)) and 1557 cm<sup>-1</sup> (macrocyclic skeletal str.).

The filtrate of recrystallization was concentrated under reduced pressure to acquire a dark red crystalline precipitate. Repeated recrystallization from chloroform gave dark red needles (2-Z); melting point >300 °C. The mass spectrum showed M<sup>+</sup> at *m/z* 346 and peaks for [M – CH<sub>3</sub>]<sup>+</sup> and [M – C<sub>2</sub>H<sub>5</sub>]<sup>+</sup> at *m/z* 331 and 317, respectively. IR (KBr disk): 3145 (N–H str.), 1648 (C=N str.), 1590 (C=C str. (conjugated ring)) and 1560 cm<sup>-1</sup> (macrocyclic skeletal str.).

6,15-Diethyl-4,13-dihydro-1,10-dimethyl-(*E*)-dipyridinio[b,i][1,4,8,11]tetraazacyclotetradecine iodide (2-E-I)

Iodomethane (7.0 g) and 2-E (0.10 g) were dissolved in 700 ml of chloroform and the mixture was stirred at room temperature for 2 days. The deposited crystalline product was filtered off and recrystallized from methanol to give reddish brown needles; yield 0.14 g (77%), melting point >300 °C. The mass spectrum showed [M – 2I]<sup>+</sup> at *m/z* 376 and a peak for [M – 2I – CH<sub>3</sub>]<sup>+</sup> at *m/z* 361. IR (KBr disk): 3120 (N–H str.), 1640 (C=N str. and C=C str. (conjugated ring)) and 1561 cm<sup>-1</sup> (macrocyclic skeletal str.).

6,15-Diethyl-4,13-dihydro-1,10-dimethyl-(*E*)-dipyridinio[b,i][1,4,8,11]tetraazacyclotetradecine methyl sulfate (2-E-S)

A mixture of 2-E (0.10 g), dimethyl sulfate (0.60 g) and chloroform (700 ml) was heated under reflux

with stirring for 2 days. The crystalline product was separated and recrystallized from methanol as reddish brown needles; yield 0.11 g (64%), melting point 250.5–252.3 °C (dec). The mass spectrum showed  $[M - 2SO_4CH_3]^+$  at  $m/z$  376 and a peak for  $[M - 2SO_4CH_3 - CH_3]^+$  at  $m/z$  361. IR (KBr disk): 3140 (N–H str.), 1642 (C=N str. and C=C str. (conjugated ring)), 1567 (macrocyclic skeletal str.), 1222 (S=O str.), 1020 and 750  $cm^{-1}$  (S–O–C str.).

*(6,15-Diethyl-1,10-dimethyl-(E)-dipyridinio[b,i]-[1,4,8,11]tetraazacyclotetradecinato)nickel(II) iodide (Ni(2-E-I))*

Nickel(II) acetate tetrahydrate (0.046 g) and 2-E-I (0.100 g) were dissolved in a mixed solvent composed of *N,N*-dimethylformamide (50 ml) and ethanol (10 ml). The mixture was heated at 110 °C with stirring for 4 h and concentrated to one fourth of its original volume *in vacuo*. To the reaction mixture was added ethyl ether (50 ml). The precipitates were recovered and recrystallized from methanol to give reddish brown needles; yield 0.068 g (62%), melting point >300 °C. The mass spectrum showed  $[M - 2I]^+$  at  $m/z$  432 and peaks for  $[M - 2I - CH_3]^+$ ,  $[M - 2I - C_2H_5]^+$ ,  $[M - 2I - C_2H_5 - CH_3]^+$  and  $[M - 2I - 2C_2H_5]^+$  at  $m/z$  417, 403, 388 and 374, respectively. IR (KBr disk): 1637 (C=N str.), 1612 (C=C str. (conjugated ring)) and 1472  $cm^{-1}$  (macrocyclic skeletal str.).

*(6,15-Diethyl-1,10-dimethyl-(E)-dipyridinio[b,i]-[1,4,8,11]tetraazacyclotetradecinato)nickel(II) methyl sulfate (Ni(2-E-S))*

This complex was prepared from 2-E-S (0.100 g) and nickel(II) acetate tetrahydrate (0.048 g) in a mixed solvent composed of *N,N*-dimethylformamide (35 ml) and ethanol (15 ml) following the above procedure, and recrystallized from methanol to give reddish brown needles; yield 0.060 g (55%), melting point >300 °C. The mass spectrum showed  $[M - 2SO_4CH_3]^+$  at  $m/z$  432 and peaks for  $[M - 2SO_4CH_3 - CH_3]^+$ ,  $[M - 2SO_4CH_3 - C_2H_5]^+$ ,  $[M - 2SO_4CH_3 - C_2H_5 - CH_3]^+$  and  $[M - 2SO_4CH_3 - 2C_2H_5]^+$  at  $m/z$  417, 403, 388 and 374, respectively. IR (KBr disk): 1633 (C=N str.), 1610 (C=C str. (conjugated ring)), 1467 (macrocyclic skeletal str.), 1220 (S=O str.), 1010 and 750  $cm^{-1}$  (S–O–C str.).

*(6,15-Diethyl-1,10-dimethyl-(E)-dipyridinio[b,i]-[1,4,8,11]tetraazacyclotetradecinato)copper(II) iodide (Cu(2-E-I))*

Copper(II) acetate monohydrate (0.035 g) and 2-E-I (0.100 g) were dissolved in a blended solvent composed of *N,N*-dimethylformamide (50 ml) and ethanol (10 ml). The mixture was heated at 110 °C with stirring for 4 h and concentrated to *ca.* 15 ml under reduced pressure. To the reaction mixture

was added ethyl ether (50 ml). The precipitates were filtered off and recrystallized from methanol as bluish violet needles; yield 0.053 g (48%), melting point >300 °C. The mass spectrum showed  $[M - 2I]^+$  at  $m/z$  437 and a peak for  $[M - 2I - CH_3]^+$  at  $m/z$  422. IR (KBr disk): 1628 (C=N str.), 1600 (C=C str. (conjugated ring)) and 1460  $cm^{-1}$  (macrocyclic skeletal str.).

*(6,15-Diethyl-1,10-dimethyl-(E)-dipyridinio[b,i]-[1,4,8,11]tetraazacyclotetradecinato)copper(II) methyl sulfate (Cu(2-E-S))*

This was prepared from 2-E-S (0.100 g) and copper(II) acetate monohydrate (0.040 g) in a blended solvent composed of *N,N*-dimethylformamide (35 ml) and ethanol (15 ml) following the above procedure, and recrystallized from methanol to give bluish violet needles; yield 0.067 g (61%), melting point >300 °C. The mass spectrum showed  $[M - 2SO_4CH_3]^+$  at  $m/z$  437 and a peak for  $[M - 2SO_4CH_3 - CH_3]^+$  at  $m/z$  422. IR (KBr disk): 1628 (C=N str.), 1601 (C=C str. (conjugated ring)), 1465 (macrocyclic skeletal str.), 1218 (S=O str.), 1020 and 750  $cm^{-1}$  (S–O–C str.).

*(6,15-Diethyl-1,10-dimethyl-(E)-dipyridinio[b,i]-[1,4,8,11]tetraazacyclotetradecinato)cobalt(II) methyl sulfate (Co(2-E-S))*

Cobalt(II) acetate tetrahydrate (0.048 g) and 2-E-S (0.100 g) were dissolved in a mixed solvent composed of *N,N*-dimethylformamide (35 ml) and ethanol (15 ml). The mixture was heated at 110 °C under nitrogen atmosphere with stirring for 4 h and concentrated to *ca.* 12 ml *in vacuo*. To the reaction mixture was added ethyl ether (50 ml). The precipitates were separated and recrystallized from ethanol as blackish brown needles; yield 0.072 g (66%), melting point >300 °C. The mass spectrum showed  $[M - 2SO_4CH_3]^+$  at  $m/z$  433 and peaks for  $[M - 2SO_4CH_3 - CH_3]^+$ ,  $[M - 2SO_4CH_3 - C_2H_5]^+$  and  $[M - 2SO_4CH_3 - C_2H_5 - CH_3]^+$  at  $m/z$  418, 404 and 389, respectively. IR (KBr disk): 1635 (C=C str.), 1605 (C=C str. (conjugated ring)), 1472 (macrocyclic skeletal str.), 1222 (S=O str.), 1020 and 770  $cm^{-1}$  (S–O–C str.).

## Results and Discussion

### Synthesis of Water-soluble Macrocycles

6,15-Diethyl-4,13-dihydrodipyrido[b,i][1,4,8,11]-tetraazacyclotetradecine was prepared by cyclization of 3,4-diaminopyridine and 2-ethyl-3-ethoxyacrolein, and makes *cis* (2-Z) and *trans* (2-E) isomers in relative sites of N-atoms to heteroatoms of alternate pyridine rings. Two kinds of isomers are separated by repeated recrystallization from chloroform. These isomeric structures were determined by means

TABLE I. Analytical Data for Macrocycles and their Complexes

Compound		Found (%)			Calc. (%)		
		C	H	N	C	H	N
C <sub>20</sub> H <sub>22</sub> N <sub>6</sub>	2-E	69.11	6.50	24.08	69.34	6.40	24.26
C <sub>20</sub> H <sub>22</sub> N <sub>6</sub>	2-Z	68.81	6.48	23.99	69.34	6.40	24.26
C <sub>22</sub> H <sub>28</sub> N <sub>6</sub> I <sub>2</sub>	2-E-I	42.02	4.65	13.29	41.92	4.48	13.33
Ni(C <sub>22</sub> H <sub>26</sub> N <sub>6</sub> )I <sub>2</sub>	Ni(2-E-I)	37.95	3.98	11.91	38.46	3.81	12.23
Cu(C <sub>22</sub> H <sub>26</sub> N <sub>6</sub> )I <sub>2</sub>	Cu(2-E-I)	38.38	3.81	12.08	38.19	3.79	12.15
C <sub>24</sub> H <sub>34</sub> N <sub>6</sub> O <sub>8</sub> S <sub>2</sub>	2-E-S	47.85	5.78	13.82	48.15	5.72	14.04
Ni(C <sub>22</sub> H <sub>26</sub> N <sub>6</sub> )(C <sub>2</sub> H <sub>6</sub> O <sub>8</sub> S <sub>2</sub> )	Ni(2-E-S)	43.94	5.06	12.70	43.99	4.92	12.82
Cu(C <sub>22</sub> H <sub>26</sub> N <sub>6</sub> )(C <sub>2</sub> H <sub>6</sub> O <sub>8</sub> S <sub>2</sub> )	Cu(2-E-S)	43.58	5.05	12.51	43.66	4.89	12.73
Co(C <sub>22</sub> H <sub>26</sub> N <sub>6</sub> )(C <sub>2</sub> H <sub>6</sub> O <sub>8</sub> S <sub>2</sub> )	Co(2-E-S)	43.77	4.94	12.47	43.97	4.92	12.86

of proton NMR spectroscopy (see Table III below). The ratio (2-E:2-Z = 3:2) of the isomers was determined by the integration of <sup>1</sup>H NMR spectroscopy. The two macrocycles, 2-E and 2-Z, gave mass spectra with a prominent parent peak at *m/z* 346.

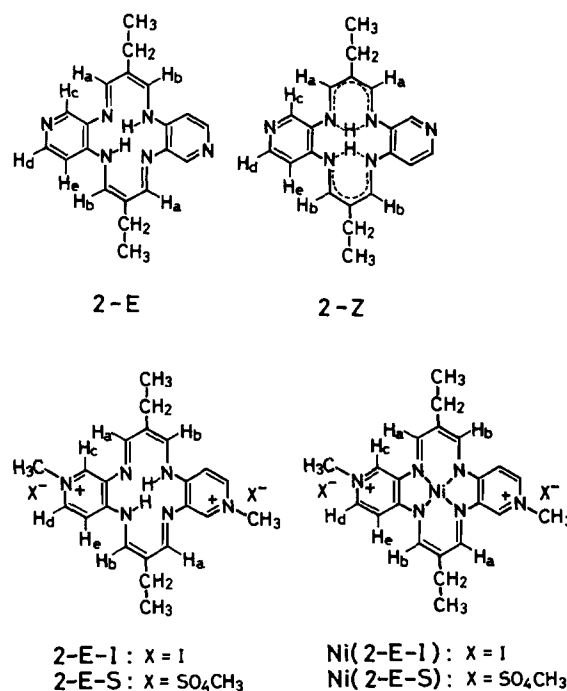
Methylation of pyridine comprised in the macrocycle (2-E) using iodomethane or dimethyl sulfate in chloroform afforded the corresponding dimethylated product (2-E-I or 2-E-S). 2-E-I and 2-E-S are soluble in polar solvents such as methanol and water. The analytical data for macrocycles and their complexes are compiled in Table I. Elemental analyses of crystalline samples of 2-E-I and 2-E-S were consistent with compounds for the formula dimethylated macrocycle. A peak at mass numbers 376 in the mass spectra of the dimethylated macrocycles, 2-E-I or 2-E-S, was observed to have the characteristic structure as that of [2-E]<sup>+</sup> shifted by 30 mass units to higher numbers. This peak was therefore assigned to arise from [(2-E-I) - 2I]<sup>+</sup> or [(2-E-S) - 2SO<sub>4</sub>CH<sub>3</sub>]<sup>+</sup>. The NMR spectrum of 2-E-I or 2-E-S showed a new methyl signal (N<sup>+</sup>-CH<sub>3</sub>) at around 4.05 ppm. This result supports the dimethylated macrocycles.

#### Molar Conductances

The molar conductances for the methylated macrocycles and their complexes are summarized in Table II. LX<sub>2</sub> (L = methylated macrocycle; X = I or SO<sub>4</sub>CH<sub>3</sub>) are 1:2 electrolytes in water solutions. Consequently methylation of this macrocycle leads to the corresponding dimethylated compound. MLX<sub>2</sub> (M = Ni, Cu, or Co) are also 1:2 electrolytes in water solutions. Accordingly, the iodate or methyl sulfate anion is ionized on dissolution in this solvent.

#### Mass Spectra

Mass spectra data for the macrocycles and their complexes are given in 'Experimental'. The EI mass spectra for macrocycles, 2-E or 2-Z, exhibit the presence of a molecular ion M<sup>+</sup> at *m/z* 346 which



is the bases peak in the mass spectrum. The masses of the major fragment at *m/z* 331 and 317 correspond to [M - CH<sub>3</sub>]<sup>+</sup> and [M - C<sub>2</sub>H<sub>5</sub>]<sup>+</sup>, respectively.

On the other hand, the dimethylated macrocycles, 2-E-I or 2-E-S, show a cluster of ions at *m/z* 376 corresponding to [M - 2I]<sup>+</sup> or [M - 2SO<sub>4</sub>CH<sub>3</sub>]<sup>+</sup> in the FAB mass spectrum attained in a glycerin matrix. When the nickel(II), copper(II) and cobalt(II) complexes of dimethylated macrocycles were analysed by the use of FAB and FD mass spectra, these complexes do not show molecular ions but a cluster of ions corresponding to [M - 2I]<sup>+</sup> or [M - 2SO<sub>4</sub>CH<sub>3</sub>]<sup>+</sup> and the major fragment ions corresponding to [M - 2I - CH<sub>3</sub>]<sup>+</sup>, [M - 2I - C<sub>2</sub>H<sub>5</sub>]<sup>+</sup>, [M - 2SO<sub>4</sub>CH<sub>3</sub> - CH<sub>3</sub>]<sup>+</sup> and [M - 2SO<sub>4</sub>CH<sub>3</sub> - C<sub>2</sub>H<sub>5</sub>]<sup>+</sup>.

TABLE II. Molar Conductances for Dimethylated Macrocycles and their Complexes

Compounds		$\Lambda_M^a$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	Type of electrolyte <sup>b</sup>
$C_{22}H_{28}N_6I_2$	2-E-I	287	1:2
$Ni(C_{22}H_{26}N_6)I_2$	Ni(2-E-I)	292	1:2
$Cu(C_{22}H_{26}N_6)I_2$	Cu(2-E-I)	284	1:2
$(C_{22}H_{28}N_6)(C_2H_6O_8S_2)$	2-E-S	324	1:2
$Ni(C_{22}H_{28}N_6)(C_2H_6O_8S_2)$	Ni(2-E-S)	262	1:2
$Cu(C_{22}H_{28}N_6)(C_2H_6O_8S_2)$	Cu(2-E-S)	260	1:2
$Co(C_{22}H_{28}N_6)(C_2H_6O_8S_2)$	Co(2-E-S)	295	1:2

<sup>a</sup>For ca.  $10^{-4}$  mol  $\text{dm}^{-3}$  solutions. <sup>b</sup>Assignments of the type of electrolyte present in solution were made on the basis of the conductance data compiled by Geary [7].

### Electronic Spectra

The electronic spectra covering the 15 000–40 000  $\text{cm}^{-1}$  region are shown in Fig. 1 for the metal-free macrocycle (2-E) and the metal-free dimethylated macrocycle methyl sulfate (2-E-S). The general feature of the spectrum for 2-E is analogous to those observed for macrocycles including benzene rings as reported previously [8, 9]. It is interesting to note that delocalization of the higher conjugated system remains nearly unaltered upon substitution of a benzene ring with a pyridine ring in the macrocycle. Moreover, the general feature of the spectrum for the dimethylated macrocycle (2-E-S) is similar to that of the unmethylated macrocycle (2-E) as shown in Fig. 1 and is hardly influenced by the distinction of counteranions such as iodate (2-E-I) and methyl sulfate (2-E-S) too.

Visible and ultraviolet spectra for 6,15-diethyl-1,10-dimethyl-(*E*)-dipyridinio[b,i][1,4,8,11]tetraaza-

cyclotetradecine methyl sulfate metal complexes are shown in Fig. 2 covering the 11 000–45 000  $\text{cm}^{-1}$  range. The absorption bands lying above 18 000  $\text{cm}^{-1}$  are reasonably attributed to the  $\pi \rightarrow \pi^*$  transitions within a ligand molecule and CT transitions from metal to ligand, because the molar extinction coefficients of these bands ( $\sim 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) are larger than those usually assigned to ligand-field transitions [10].

An extremely intense absorption band observed at about 27 000  $\text{cm}^{-1}$  shows a larger shift to lower energy upon metal-coordination. The spectral behavior is similar to that observed for Soret bands of metal porphyrins [11, 12]. The nickel(II) and copper(II) complexes do not indicate any significant absorption bands in the energy range less than 15 000  $\text{cm}^{-1}$ . This spectral action is consistent with the square-planar coordination of nickel(II) and copper(II) [10].

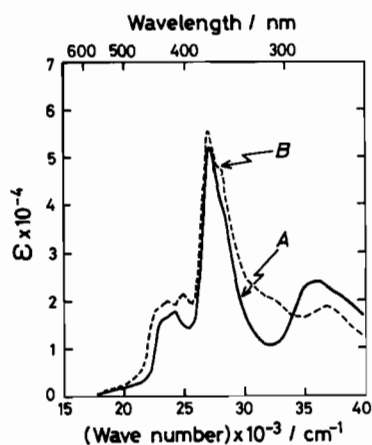


Fig. 1. Electronic absorption spectra of 6,15-diethyl-4,13-dihydro-(*E*)-dipyridino[b,i][1,4,8,11]tetraazacyclotetradecine (2-E) and 6,15-diethyl-4,13-dihydro-1,10-dimethyl-(*E*)-dipyridinio[b,i][1,4,8,11]tetraazacyclotetradecine (2-E-S) at room temperature. A, 2-E in chloroform, B, 2-E-S in methanol.

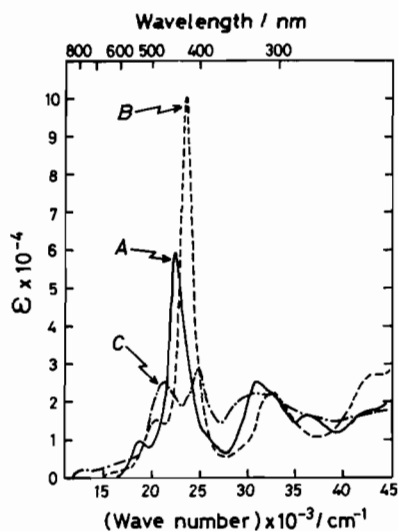


Fig. 2. Electronic absorption spectra of (6,15-diethyl-1,10-dimethyl-(*E*)-dipyridinio[b,i][1,4,8,11]tetraazacyclotetradecinato)metal complexes methyl sulfate in methanol at room temperature. A, Ni(2-E-S); B, Cu(2-E-S); C, Co(2-E-S).

TABLE III. Proton NMR Data for Macrocycles and their Nickel(II) Complexes<sup>a</sup>

Compound	Ethyl	Methyl		Aromatic		Methine		Amine
	-CH <sub>3</sub>	-CH <sub>2</sub> -	N <sup>+</sup> -CH <sub>3</sub>	H <sub>e</sub>	H <sub>d</sub>	H <sub>c</sub>	H <sub>b</sub>	N-H
2-E <sup>b</sup>	1.17(t) (J = 7.3 Hz)	2.30(q) (J = 7.3 Hz)		6.83(d) (J = 5.6 Hz)	8.13(d) (J = 5.6 Hz)	8.29(s)	6.99(dd) (J = 2.4, 11.2 Hz)	13.46(d) (J = 11.2 Hz)
2-Z <sup>b</sup>	1.16(t) (J = 7.3 Hz)	2.27(q) (J = 7.3 Hz)		6.87(d) (J = 5.4 Hz)	8.07(d) (J = 5.4 Hz)	8.27(s)	6.79(d) (J = 5.4 Hz)	13.47(t), 13.70(t) (J = 5.4 Hz)(J = 5.9 Hz)
2-E-I <sup>c</sup>	1.20(t) (J = 7.0 Hz)	2.47(q) (J = 7.0 Hz)	4.07(s)	7.84(d) (J = 5.5 Hz)	8.60(d) (J = 5.5 Hz)	8.89(s)	7.70(dd) (J = 2.4, 11.1 Hz)	13.44(d) (J = 11.1 Hz)
2-E-S <sup>c</sup>	1.18(t) (J = 7.3 Hz)	2.42(q) (J = 7.3 Hz)	4.05(s)	7.80(d) (J = 5.5 Hz)	8.46(d) (J = 5.5 Hz)	8.86(s)	7.70(dd) (J = 2.4, 11.2 Hz)	13.41(d) (J = 11.2 Hz)
Ni(2-E-I) <sup>c</sup>	1.24(t) (J = 7.8 Hz)	2.49(q) (J = 7.8 Hz)	4.15(s)	8.05(s)	8.19(s)	8.34(s)	8.27(d) (J = 2.4 Hz)	
Ni(2-E-S) <sup>c</sup>	1.23(t) (J = 7.5 Hz)	2.48(q) (J = 7.5 Hz)	4.13(s)	8.06(s)	8.17(s)	8.36(s)	8.26(d) (J = 2.5 Hz)	

<sup>a</sup>Chemical shifts are given in ppm for TMS as an internal reference. Multiplicity of a proton signal is given in parentheses after  $\delta$ -value; s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets. <sup>b</sup>Measured in chloroform-d. <sup>c</sup>Measured in dimethyl sulfoxide-d<sub>6</sub>.

The cobalt(II) complex shows a distinct absorption band at around 13 000 cm<sup>-1</sup>. The molar extinction coefficient of this band is comparable with that associated with d → d\* transitions. This spectral behavior is in agreement with the square-planar coordination of cobalt(II) [10].

#### Vibrational Spectra

The characteristic IR bands are listed in 'Experimental'. The macrocycle (2-E) shows a weak band at 3150 cm<sup>-1</sup> which is correlated with a N-H stretching mode and shifts sparingly to lower frequency on methylation of pyridine contained within the macrocycle. This vibration mode is extinguished upon complex formation.

A strong band due to the C=N stretching mode of the macrocycle moiety turns up at ca. 1640 cm<sup>-1</sup>. This band shows a slight shift to lower frequency and decreases its intensity upon metal-coordination. The formation of a square-planar complex seems to cause the reduction of IR activity.

A strong absorption band at about 1220 cm<sup>-1</sup> was observed for all the dimethylated macrocycle and all its metal complex methyl sulfate salts and attributable to the S=O stretching mode [13, 14]. Another peak due to the methyl sulfate group was observed at around 1020 and 750 cm<sup>-1</sup> which may be attributed to the S-O-C stretching mode [12]. Since no shift of these bands was detected upon metal-coordination, the methyl sulfate group in these metal complexes is present not as a coordinated group but as a mere isolated ion [15]. This result is buttressed by the molar conductances.

#### NMR Spectra

NMR data and their assignments for macrocycles and their nickel(II) complexes are collected in Table III. The amine proton shown by 2-E couples with the H<sub>b</sub>-methine proton and the amine signal is split into a doublet. On the other hand, the amine protons shown by 2-Z couple with both H<sub>a</sub>-methine or both H<sub>b</sub>-methine protons and the two amine signals are split into a triplet, respectively. Accordingly, NMR spectra can easily distinguish between *cis* (2-Z) and *trans* (2-E) isomers.

The H<sub>a</sub>-methine proton for 2-E couples with the H<sub>b</sub>-methine proton, the H<sub>a</sub>-signal being split into a doublet. The H<sub>b</sub>-methine proton couples with both H<sub>a</sub>-methine and amine protons, the H<sub>b</sub>-signal being split into a doublet of doublets, which is observed as a quartet. On the other hand, the H<sub>a</sub>-methine proton for 2-Z couples with the amine proton and the H<sub>b</sub>-methine proton also couples with the amine proton, each signal being split into a doublet.

The H<sub>e</sub>-aromatic proton for 2-E, or 2-Z does not couple with any protons, the H<sub>c</sub>-aromatic signal being a singlet. The H<sub>d</sub>- and H<sub>e</sub>-aromatic protons couple

with each other, the  $H_d$ - and  $H_e$ -signals being split into a doublet, respectively.

All proton signals except amine protons lead to downfield shifts upon methylation of pyridine embraced in the metal-free macrocycle. These downfield shifts are attributed to the deshielding effect due to the positive charge provided by the methylation. The new proton signal for the methyl group on the basis of methylation is freshly observed as a singlet at about 4.05 ppm.

The amine proton signal is found to vanish upon the formation of the nickel(II) complex (Ni(2-E-I) or Ni(2-E-S)). The  $H_b$ -methine proton signal also moves from a doublet of doublets to a doublet, coupling with no amine proton. The  $H_d$ - and  $H_e$ -aromatic proton signals vary from a doublet to a singlet upon nickel(II)-coordination too, but no explanation for this variation can be offered at the present time. The signals for  $H_a$ - and  $H_b$ -methine protons and the  $H_e$ -aromatic proton are shifted downfield on complex formation. This downfield shift is associated with the deshielding effect owing to the positive charge given by nickel(II). On the other hand, the signals for  $H_c$ - and  $H_d$ -aromatic protons show the upfield shift. It is interesting to note that the  $H_c$ - and  $H_d$ -aromatic proton signals are shifted upfield in contrast to the downfield shift of the  $H_e$ -aromatic proton signal. The metal complexes have resonance hybrids shown by 3 and 4. The limiting structure (4) decreases the influence of the positive charge furnished by methylation of pyridine in the macrocycle to  $H_c$ - and  $H_d$ -aromatic protons. Judging from the upfield shift for  $H_c$ - and  $H_d$ -aromatic proton signals, the limiting structure (4) may be doing a great deal for the nickel(II) complex. Having an electronic spectrum similar to the nickel(II) complex, the copper(II) complex probably has the limiting structure (4) too.

#### Analytical Applications

The electronic spectrum of 2-E-I dissolved in water underwent an outstanding variation upon addition of copper(II) chloride and pyridine as shown in Fig. 3. Since the spectral feature is almost identical with that for the copper(II) complex (Cu(2-E-I)) as shown in Fig. 2, 2-E-I becomes a copper(II) com-

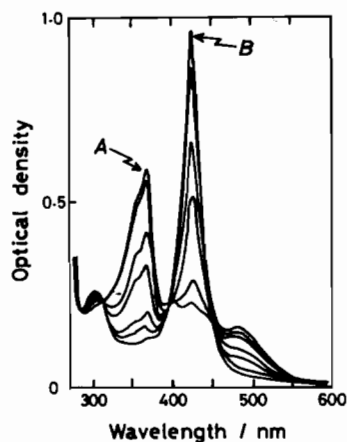
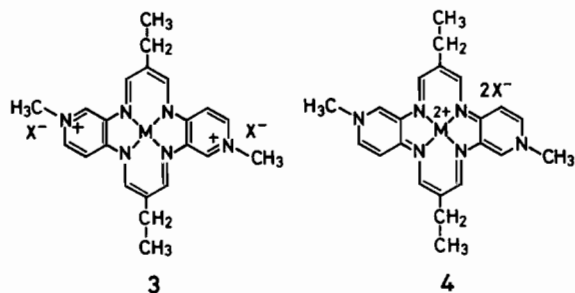


Fig. 3. Repeat scans of the visible spectrum for the reaction of 2-E-I in water with copper(II) ion ( $[2-E-I]:[Cu^{2+}] = 1:1$ ; read from A to B).

plex. The observation of isosbestic points at 310, 393 and 454 nm is an evidence for the 1:1 complex formation. The determination of copper(II) concentrations was obtained from the intensity change at 425 nm ( $\epsilon = 8.26 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) by adopting the following relation.

$$A_x(\text{Cu}) = A_x - A_0(1 - x) \quad (1)$$

$$x = [Cu^{2+}]/[2-E-I] \quad (0 < x \leq 1)$$

$$[Cu^{2+}] = A_x(\text{Cu})/82600 \quad (2)$$

In this equation,  $[Cu^{2+}]$  and  $[2-E-I]$  stand for the concentrations of copper(II) ion and dimethylated macrocycle iodide (2-E-I), respectively,  $A_x$  represents the absorbance on the basis of  $\{[Cu^{2+}]/[2-E-I]\}$ ,  $A_0$  is the absorbance for 2-E-I alone, and  $A_x(\text{Cu})$  is the absorbance for the formation of the copper(II) complex.

Employing the electronic spectra of 2-E-I ( $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ) in water at various concentrations

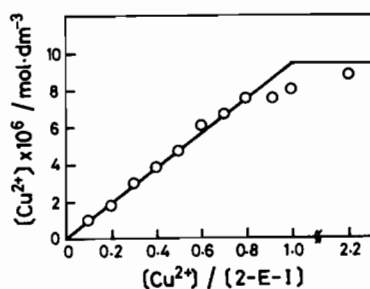


Fig. 4. Correlation between  $[Cu^{2+}]/[2-E-I]$  and  $[Cu^{2+}]$  on the basis of eqn. (2) in water:  $[2-E-I] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[Cu^{2+}] = (0 \sim 2.2 \times 10) \text{ mol dm}^{-3}$ ;  $[\text{pyridine}] = 3.3 \times 10 \text{ mol dm}^{-3}$ .

of copper(II) ion  $\{0 \sim 2.2 \times 10\} \text{ mol dm}^{-3}$  upon addition of pyridine  $(3.3 \times 10 \text{ mol dm}^{-3})$ , a good linear correlation based on eqn. (2) is observed up to  $8 \times 10^{-6} \text{ mol dm}^{-3}$ , as shown in Fig. 4. The result for the determination of copper(II) using 2-E-S is also in good agreement with that obtained for 2-E-I. Accordingly, this water soluble macrocycle (2-E-I or 2-E-S) makes the intensity change at 425 nm easily accessible for the determination of copper(II) concentrations in aqueous solution.

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