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Preparation and Characterization of Cobalt(II) Complexes with Novel Macrocyclic N_4-Ligands: 5,14-Dihydro-7,16-diethyl-(E)-dipyrido[b,i] [1,4,8,11]-tetraazacyclotetradecine and 5,14-Dihydro-7,16-diethyl-(Z)-dipyrido[b,i] [1,4,8,11] tetraazacyclotetradecine

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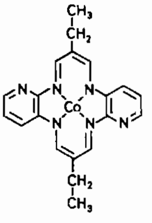
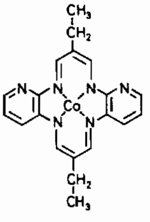
Though substantial effort has been expended on the study of tetraaza[14]annulene complexes containing benzene rings [1], examples of tetraaza-[14]annulene complexes containing pyridine rings are rare. Woehrle and Mueller reported only the synthesis of the copper(II) complex with 5,14-dihydrodipyrido [b, i] [1,4,8,11]tetraazacyclotetradecine without the separation of *cis-trans* isomers generated from relative positions of N-atoms to heteroatoms of other pyridine rings [2]. Scheibelein *et al.* also presented the synthesis of the cobalt(II), nickel(II) and copper(II) complexes with 5,14-dihydro-7,16-diphenylazo-, 5,14-dihydro-7,16-dinitro- and 5,14-dihydro-7,16-dicyanodipyrido[b, i] [1,4,8,11] tetraazacyclotetradecine out of the separation of *cis-trans* isomers and the detailed investigation of spectral properties [3].

In the present work, we synthesized two novel tetraaza[14]annulenes having pyridine rings; 5,14-dihydro-7,16,-diethyl-(E)-dipyrido[b,i] [1,4,8,11]-tetraazacyclotetradecine (**1-E**) and 5,14-dihydro-7,16-diethyl-(Z)-dipyrido[b,i] [1,4,8,11] tetraazacyclotetradecine (**1-Z**). Subsequently, we prepared the cobalt(II) complexes (Co(**1**-E), Co(**1**-Z)) of **1-E** and **1-Z**. We characterized the spectral properties of the present tetraaza[14]annulenes and their cobalt(II) complexes by means of electronic, NMR and ESR spectroscopy.



Co(**1**-E)



Co(**1**-Z)

Experimental

Physical Measurements

Mass spectral measurements were carried out with a JEOL JMS-DX 300 gas chromatograph-mass spectrometer at 70 eV. Infrared spectra in the range of the 400–4000 cm^{-1} were measured with a Hitachi 260-10 spectrophotometer at room temperature using a KBr disk technique. Ultraviolet and visible spectra covering the 15 000–40 000 cm^{-1} region were recorded on Shimadzu UV 200S double beam spectrophotometer for chloroform solutions at room temperature. Proton NMR measurements were performed on a JEOL JNM-FX 60 spectrometer operating in the Fourier transform mode. The NMR spectra were run in chloroform-d and chemical shifts are reported in ppm relative to tetramethylsilane as an internal reference standard. ESR spectra were taken on a JEOL JES-ME-1 X-band spectrometer equipped with a 100 kHz field modulation unit. All samples were measured in toluene–benzene (3:2 v/v) at 77 K, concentrations being maintained in the 10^{-2} mol dm^{-3} range. The manganese ion diffused into magnesium oxide was used to obtain the standard reference signals for measurements.

Synthesis of Macrocyclic Ligands

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

A mixture of 2,3-diaminopyridine (2.8 g) [4], 2-ethyl-3-ethoxyacrolein (4.0 g) [5] and N,N-dimethylformamide (6 ml was heated under reflux for 6 h with stirring. Upon cooling the reaction mixture with ice-water, the crystalline solid was recovered by filtration and washed several times with methanol to give dark red needles; yield 1.2 g (27%). The dichloromethane solution of this material (0.41 g) was applied to the top of a chromatographic column of silica gel (60–80 mesh, Kanto Chemical Co., Inc.) and eluted with dichloromethane. The solid material, which was recovered by evaporating the initial effluent to dryness *in vacuo*, was recrystallized from carbon tetrachloride to obtain the **1**-E as glittering red needles; yield 0.20 g, m.p. 252.0–253.0 °C (dec). IR (KBr disk): 3160 (N–H str.), 1639 (C=N str.), 1580 (C=C str. (conjugated ring)) and 1542 cm^{-1} (macrocyclic skeletal str.).

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Anal. Found: C, 69.27; H, 6.64; N, 23.93%; M$^+$, 346. Calcd. for $C_{20}H_{22}N_6$: C, 69.34; H, 6.40; N, 24.26%; M, 346.43. The second effluent was evaporated to dryness *in vacuo*. The solid residue was recrystallized from hexane to obtain the **1-Z** as glittering green plates; yield 0.20 g, m.p. 206.0–208.0 °C (dec). IR (KBr disk) 3135 (N–H str.), 1641 (C=N str.), 1590 (C=C str. (conjugated ring)) and 1538 cm^{-1} (macrocyclic skeletal str.). *Anal.* Found: C, 69.64; H, 6.50; N, 24.13%; M$^+$, 346. Calcd. for $C_{20}H_{22}N_6$: C, 69.34; H, 6.40; N, 24.26%; M, 346.43.

Preparation of Complexes

(7,16-Diethyl-(E)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (Co(1-E))

A mixture of **1-E** (0.18 g), cobalt(II) acetate tetrahydrate (0.16 g) and N,N-dimethylformamide (6 ml) was heated under reflux for 6 h while nitrogen gas was continuously bubbled through it. After the reaction mixture was cooled down with ice-water, the crystalline solid was recovered by filtration, washed with water and methanol and recrystallized from benzene to give glittering blue-violet needles; yield 0.16 g (80%), m.p. >300 °C. IR (KBr disk): 1580 (C=C str. (conjugated ring)), 1560 (C=N str.) and 1422 cm^{-1} (macrocyclic skeletal str.). *Anal.* Found: C, 59.86; H, 5.34; N, 20.79%; M$^+$, 403. Calcd. for $C_{20}H_{20}N_6Co$: C, 59.56; H, 5.00; N, 20.84%; M, 403.35.

(7,16-Diethyl-(Z)-dipyrido[b, i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (Co(1-Z))

The reaction of **1-Z** (0.18 g) and cobalt(II) acetate tetrahydrate (0.15 g), following the above procedure, gave glittering dark-brown needles; yield 0.14 g (70%), m.p. >300 °C. IR (KBr disk): 1579 (C=C str. (conjugated ring)), 1555 (C=N str.) and 1430 cm^{-1} (macrocyclic skeletal str.). *Anal.* Found: C, 59.63; H, 4.95; N, 20.67%; M$^+$, 403. Calcd. for $C_{20}H_{20}N_6Co$: C, 59.56; H, 5.00; N, 20.84%, M, 403.35.

Results and Discussion

The novel macrocyclic ligand, 5,14-dihydro-7,16-diethyldipyridido[b,i] [1,4,8,11] tetraazacyclotetradecine, produces *cis* (**1-Z**) and *trans* (**1-E**) isomers in relative positions of N-atoms to heteroatoms of other pyridine rings. The separation of *cis-trans* isomers is effected by chromatography of silica gel and the ratio of this product is approximately equivalent. **1-Z** is highly soluble in polar solvents, but **1-E** is very soluble in nonpolar solvents. It is quite interesting to note that the solubilities of these present ligands are substantially greater in various solvents than those of the tetraaza[14] annulenes having benzene rings.

Visible and ultraviolet spectra covering the 15000–40000 cm^{-1} range are shown in Fig. 1 for Co(**1-E**) and Co(**1-Z**) complexes. The absorption bands appearing in the energy region greater than 16000 cm^{-1} are attributed to charge-transfer transitions from metal to ligand and $\pi \rightarrow \pi^*$ transitions within a ligand molecule, and not of $d \rightarrow d^*$ origin.

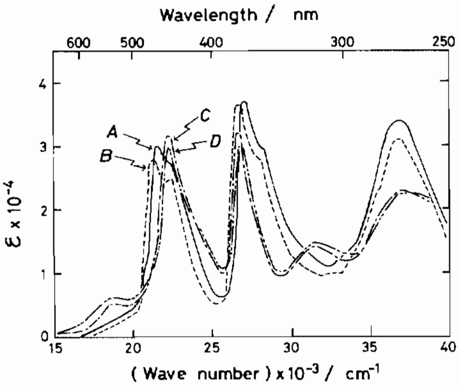


Fig. 1. Electronic absorption spectra of (7,16-diethyl-(E)- and -(Z)-dipyrido[b,i] [1,4,8,11] tetraazacyclotetradecinato)-cobalt(II) complexes in chloroform at room temperature. A, 1-E; B, 1-Z; C, Co(1-E); D, Co(1-Z).

TABLE I. Proton NMR Data for the Macrocyclic Ligands (1-E and 1-Z).[a]

Ligand	Ethyl		Aromatic			Methine		Amine
	$-CH_3$	$-CH_2-$	$-H_c$	$-H_d$	$-H_e$	$-H_a$	$-H_b$	$-NH$
1-E	1.07(t) (J = 7.0 Hz)	2.20(q) (J = 7.0 Hz)	7.83(dd) (J = 4.6 Hz) (J = 1.5 Hz)	6.63(dd) (J = 8.1 Hz) (J = 4.6 Hz)	7.29(dd) (J = 8.1 Hz) (J = 1.5 Hz)	8.13(d) (J = 2.7 Hz)	7.66(d) (J = 11.0 Hz) (J = 2.7 Hz)	13.86(d) (J = 11.0 Hz)
1-Z	1.13(t) (J = 7.0 Hz) 1.16(t) (J = 7.0 Hz)	2.18(q) (J = 7.0 Hz) 2.26(q) (J = 7.0 Hz)	7.87(dd) (J = 4.6 Hz) (J = 1.7 Hz)	6.78(dd) (J = 8.1 Hz) (J = 4.6 Hz)	7.25(dd) (J = 8.1 Hz) (J = 1.7 Hz)	8.38(d) (J = 5.6 Hz)	7.57(d) (J = 6.1 Hz)	13.61(t) (J = 6.1 Hz) 14.39(t) (J = 5.6 Hz)

[a] Chemical shifts in ppm for TMS. Measured in chloroform-d with TMS as an internal reference. Multiplicity of a proton signal is given in parentheses after δ-value: d = doublet; t = triplet; q = quartet; dd = doublet of doublets.

Two reasons for this conclusion are given below. The molar extinction coefficients of these bands ($\sim 10^4$ mol^{-1} dm^3 cm^{-1}) are larger than those normally assigned to d → d* transition [6]. Moreover, the general features of the spectra for Co(**1-E**) and Co(**1-Z**) complexes are analogous to those observed for tetraaza[14]annulene cobalt(II) complexes containing benzene rings, as reported previously [1(i)].

The ^{1}H NMR spectra for macrocyclic ligands (**1-E** and **1-Z**) are shown in Fig. 2 and their assignments are listed in Table I. The H_f-amine proton shown by **1-E** couples with the H_b-methine proton, and the H_f-signal is split into a doublet, as shown in Fig. 2,A. The H_g-amine proton (α-position to the pyridinic nitrogen) shown by **1-Z** is considered to provide a proton signal in a lower field relative to the H_f-amine proton (β-position to the pyridinic nitrogen). The H_g-amine proton couples with both H_a-methine protons, and the H_f-amine proton also couples with both H_b-methine protons, each signal being split into a triplet, as seen in Fig. 2,B. The signal for these amine protons was found to vanish upon replacement of the amine proton by deuterium (D). The H_a-methine proton for **1-E** couples with H_b-methine proton, the H_a-signal being split into a doublet. The H_b-methine proton couples with both H_a-methine proton and H_f-amine proton; the H_b-signal is split into a doublet of doublets, which was observed as a quartet. On the other hand, the H_a-methine proton for **1-Z** couples with H_g-amine proton, and the H_b-methine proton couples with H_f-amine proton, each signal being split into a doublet. Upon substitution of the amine proton with D in metal-free macrocycles, both these methine proton signals turned out to be singlets. As the drop in symmetry is produced by the substitution of benzene rings for pyridine rings in the tetraaza[14] annulene skeleton, NMR spectra are moderately complicated. Further, the methine and aromatic proton signals are observed in a lower field, compared to those of benzene rings, upon the electron-withdrawing effect of pyridinic nitrogens. The methyl protons and the methylene protons of the 7- and 16-ethyl groups for **1-E** couple with one another, and the proton signals for the former and for the latter are split into a triplet and a quartet, respectively. The methyl and methylene proton signals of the 7- and 16-ethyl groups for **1-Z** are observed as a quintet and a sextet, in each case. These peaks are analyzed as the overlap of two quartets and the stagger of two triplets, respectively, for the quintet and sextet signals. This is primarily due to the fact that the ethyl groups from the adjacent pyridinic nitrogens are placed in different spaces.

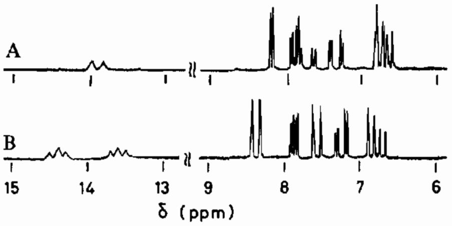
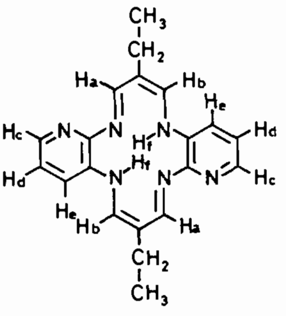
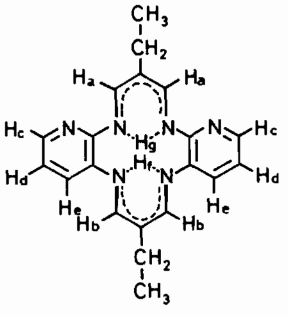


Fig. 2. NMR spectra of 5,14-dihydro-7,16-diethyl-(E)- and -(Z)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecine for the 6–15 ppm range in chloroform-d at room temperature; TMS as an internal reference. A, 1-E; B, 1-Z.



1-E



1-Z

The ESR spectrum of Co (**1-Z**) in the presence of pyridine and O_2 in the toluene–benzene solutions at 77 K is shown in Fig. 3,B. Since a triplet nitrogen superhyperfine coupling, due to axial coordination of a pyridine molecule, is observed on the parallel cobalt hyperfine lines, it may be concluded that the unpaired electron of cobalt(II) is undoubtedly in the

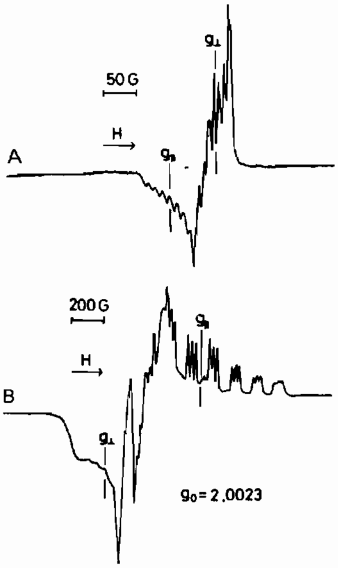


Fig. 3. ESR spectra of (7,16-diethyl-(E)- and -(Z)-dipyrido-[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) complexes in toluene–benzene (3:2 v/v) containing pyridine and O_2 at 77 K. A, Co(1-E); B, Co(1-Z).

TABLE II. Spin Hamiltonian Parameters for (7,16-Diethyl-(E)- and -(Z)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)-cobalt(II) Complexes Containing Pyridine and O_2 at 77 K.[a]

Complex	$g_\parallel$	$g_\perp$	$A_\parallel^{Co} \times 10^4$ (cm^{-1})	$A_\perp^{Co} \times 10^4$ (cm^{-1})	$A_\parallel^{N} \times 10^4$ (cm^{-1})
Co(**1**-E)	2.076	1.999	18.1	12.4	
Co(**1**-Z)	1.977	2.318	102.1	45.6	17.3

[a] Maximum possible errors: g, ±0.005; $A_\parallel^{Co}$, $\pm 0.5 \times 10^{-4}$ cm^{-1}; $A_\perp^{Co}$, $\pm 0.5 \times 10^{-4}$ cm^{-1}; $A_\parallel^{N}$, $\pm 0.05 \times 10^{-4}$ cm^{-1}.

d_{z^2} orbital. As summarized in Table II, the $g_\parallel$, $g_\perp$, $A_\parallel^{Co}$ and $A_\perp^{Co}$ values are similar in magnitude to those described by Hush and Woolsey for 1,19-diethoxycarbonyltetradehydrocorrinatocobalt(II) complexes [7, 8]. The formation of similar penta-coordinated cobalt(II) complexes of square pyramidal structure with axial coordination of pyridine has been reported for the 5,10,15,20-tetra(*p*-methoxyphenyl)porphinatocobalt(II) complex and the vitamine B_{12} and related complexes [9, 10]. On the other hand, the ESR spectrum of the dioxygen complex of Co(**1**-E) observed in toluene-benzene in the presence of pyridine and O_2 at 77 K is shown in Fig. 3,A. A set of eight hyperfine lines due to the cobalt nucleus ($I = 7/2$) was obtained on the parallel component of g-tensor at lower field and on the perpendicular component of g-tensor at higher field, respectively. The spin Hamiltonian parameters for Co(**1**-E) are comparable to those for Co(acacen)*-Py**-O_2, etc. [11]. The hyperfine splitting constant is much smaller in magnitude than those for the low-spin cobalt(II) complexes such as Schiff-base cobalt(II) [11] and present Co(**1**-Z) complexes. This indicates that the unpaired electron takes up much less time on the cobalt atom than one the π^*-level of O_2 molecule. The relation, $g_\parallel > g_\perp$, is maintained for Co(**1**-E) and the g values come close to 2.0. The ESR spectral pattern is compatible with the formation of monomeric dioxygen cobalt(II) complexes of a 1:1 molar ratio. An analogous spectral behavior has also been observed for Co(acacen)-Py-O_2 [12]. It is quite interesting to note that Co(**1**-E) is the dioxygen complex on the contrary to the N_5-penta-coordinated low-spin structure of Co(**1**-Z). The reason for the difference in coordination behavior of O_2 molecule is not clear at present.

In conclusion, the novel macrocycle, 5,14-dihydro-7.16-diethyldipyrido[b,i][1,4,8,11]tetraazacyclotetradecine, forms *cis* and *trans* isomers in relative positions of N-atoms to heteroatom of another pyridine ring. The separation of *cis-trans* isomers is obtained by a method of chromatography. Co(**1**-Z) complex assumes the N_5-penta-coordinated low-spin configuration and Co(**1**-E) complex has the monomeric oxygen adduct.

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*acacen, N,N′-bis(1-methyl-3-oxobutylene)ethylenediamine.

**Py, pyridine.

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