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Preparation and Spectroscopic Properties of Cobalt(III), Nickel(II), Copper(II) and Zinc(II) Complexes with a Novel Saturated Macrocyclic Ligand: 1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22-Docosahydrodibenzo-[b,i][1,4,8,11]tetraazacyclotetradecine

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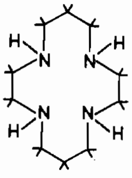
Abstract

1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19, 20,21,22-Docosahydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine was prepared by hydrogenation of the benzo-analogue. Five isomers are feasible as a result of this hydrogenation but only two have been isolated: isomer **A** (melting point 158.5–161.0 °C) and isomer **B** (melting point 194.5–196.0 °C). The ^{13}C NMR study was initiated to clear up the conformational differences between isomers. The cobalt(III), nickel(II), copper(II) and zinc(II) complexes of isomers **A** and **B** were prepared and investigated by near-ultraviolet, visible, infrared, NMR and ESR measurements. The ligand-field band in the 15 000–30 000 cm^{-1} region for the cobalt(III), nickel(II) and copper(II) complexes provided information on their geometry around the central metal atom. That is to say, the cobalt(III) complexes are subjected to the octahedral ligand-field with axial elongation. The copper(II) complexes and the nickel(II) complex of isomer **A** are subjected to the square-planar ligand-field in these complexes. The ligand-field bands for the nickel(II) complex of isomer **B** display the square-planar-distorted octahedral equilibrium in the coordinating solvent. ESR measurements for the copper(II) complexes also presented the spin Hamiltonian parameters in accord with the square-planar coordination. A strong band appearing at *ca.* 3200 cm^{-1} was assigned to the N–H stretching mode and this band was slightly shifted to lower frequency upon metal coordination. The vibrational spectra and the conductance data provided evidences for the formation of the complexes with perchlorate ion as the counter ion. ^{13}C NMR suggest that the complexes of isomer **A** are the *cis–syn–cis* form and the complexes of isomer **B** are the *cis–anti–cis* form.

Introduction

Among the saturated N_4-macrocycles, the 1,4,8,11-tetraazacyclotetradecine (**1**) has been sufficiently studied as a ligand toward divalent and trivalent metal ions [1]. However, the substituted 1,4,8,11-tetraazacyclotetradecine except for the *N*-alkylated [2] and the carbonylated [3] analogue has been hardly investigated as a ligand of metal complexes. We have studied oxovanadium(IV), manganese(III), iron(III), cobalt(II), nickel(II), copper(II) and palladium(II) complexes of unsaturated N_4-macrocycles from the standpoint of their spectral properties [4].



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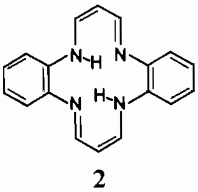
In the present work we have hydrogenated one of the unsaturated N_4-macrocycles, 5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine (**2**), and obtained all saturated N_4-macrocycle, 1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22-doco-



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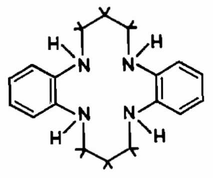

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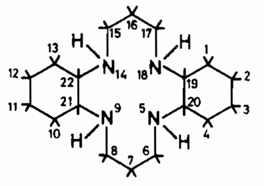

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sahydrodibenzo[b,i] [1,4,8,11] tetraazacyclotetradecine (**4**), which is a mixture of isomers. Though all five isomers are theoretically possible, only two kinds of isomers are isolated by column chromatography on alumina and repeated recrystallization from petroleum ether. These isomeric structures are investigated primarily by means of ^{13}C NMR spectroscopy. If two cyclohexyl groups are formally substituted for four hydrogen atoms at 2-, 3-, 9- and 10-positions of **1**, **4** is obtained. Different from **1**, **4** would exhibit the steric effect in the formation of complexes owing to the bulkiness of cyclohexyl groups and the stereochemical difference of two kinds of **4** would also affect the coordination structure of the complexes to a great extent. Therefore, we prepared the cobalt(III), nickel(II), .copper(II) and zinc(II) complexes of two isomers. We report the results of electronic spectra of the cobalt(III), nickel(II) and copper(II) with ligand-field interpretations as well as vibrational spectra of the complexes. The detailed NMR studies for the cobalt(III), nickel(II) and zinc(II) complexes and the ESR data for the copper(II) complexes are also provided.

Experimental

Physical Measurements

Conductivity measurements were made on acetonitrile and water solutions of the complexes thermostated to 25.0 ± 0.1 °C with a Coolnics Thermo-Bath (model CTE-310). Conductivities were measured with a TOA Electronics LTD, CM-20E. Infrared spectra in the range of the 400–4000 cm^{-1} were measured with a Hitachi 260-10 spectrophotometer at room temperature by a KBr disk method. EI mass spectra (at 70 eV) for metal free isomer (**4-P**, **4-N**) and their nickel(II), copper(II) and zinc(II) complexes and FAB mass spectra (in a matrix of neat glycerin) for their cobalt(III) complexes were obtained on a JEOL JMS-DX 300 gas chromatograph-mass spectrometer. Argon was used as the fast-atom beam. Electronic absorption spectra covering the 11 000–34 000 cm^{-1} region were recorded on a Shimadzu UV-200S double beam spectrophotometer for *N,N*-dimethylformamide solutions at room temperature. ESR spectra were performed on a JEOL JES-ME-1 X-band spectrometer equipped with a 100 kHz field modulation unit. The copper(II) complexes were measured in *N,N*-dimethylformamide at room temperature and at 77 K, concentrations being maintained in the $\sim 10^{-3}$ mol dm^{-3}. The manganese ion diffused into magnesium oxide was used to obtain standard reference signals for measurements. Proton (60 MHz) and carbon-13 (15 MHz) NMR measurements were carried out with a JEOL JNM-FX 60 spectrometer operating in the Fourier transform mode. The NMR spectra were run in chloroform-d, dimethyl sulfoxide-d_6, or trifluoroacetic acid-d and chemical shifts are reported in ppm relative to tetramethylsilane as an internal reference standard.

Preparation of Macrocycles

5,14-Dihydrodibenzo[b,i] [1,4,8,11] tetraazacyclotetradecine (2)

The synthetic procedure for **2** has been described previously [4a].

5,6,7,8,9,14,15,16,17,18-Decahydrodibenzo[b,i]-[1,4,8,11] tetraazacyclotetradecine (3)

Prepared after Hiller *et al.* [5] from **2** (5.0 g) and Raney nickel W1 (5.0 g) in a solvent of 2-methoxyethanol (200 ml) at a hydrogen pressure of about 50 kg/cm^2. The crystalline solid was washed with methanol (20 ml) and recrystallized from ethanol as colorless needles; yield 3.8 g (74%), melting point 196.5–198.0 °C (lit., [5], yield 34%, melting point 180–181 °C). UV (CH_3CN): 33 200 (ϵ 1.08 × 10^4), 39 900 (ϵ 1.84 × 10^4) and 45 500 cm^{-1} (ϵ 6.53 × 10^4). IR (KBr disk): 3260 (N–H str.) and 1600 (C=C str. (benzene ring)). NMR (chloroform-d, TMS): δ 1.99 (4H, m, J = 7.0 Hz, 7- and 16-CH_2-), 3.19 (8H, t, J = 7.0 Hz, 6-, 8-, 15- and 17-CH_2-), 4.98 (4H, s, 5-, 9-, 14- and 18-N-*H*) and 6.55 ppm (8H, m, aromatic). *Anal.* Found: C, 72.98; H, 8.27; N, 18.78; M^+, 296. Calc. for $C_{18}H_{24}N_4$: C, 72.94; H, 8.16; N, 18.90%; M, 296.42.

1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19, 20,21,22-Docosahydrodibenzo[b,i] [1,4,8,11] tetraazacyclotetradecine (4)

A 300 ml autoclave was charged with a mixture of **3** (2.00 g), ethanol (200 ml), acetic acid (0.4 ml) and 5% rhodium on alumina (2.00 g, Nippon Engelhards Ltd). The mixture was hydrogenated at 110 °C and a hydrogen pressure of about 50 kg/cm^2 for 6 h. The reaction mixture was cooled to room temperature and was filtered to remove the catalyst. The filtrate was evaporated to dryness *in vacuo.* The dichloromethane solution of this residue was applied to the top of a chromatographic column of activated neutral alumina (W-200, super I, Woelm Pharma GmbH & Co.) and eluted with dichloromethane (400 ml). The solvent was removed from the combined eluates under reduced pressure to leave the mixture of isomers of **4**. This mixture was recrystallized from petroleum ether to give colorless plates (**4-P**); yield 0.29 g (14%), melting point 194.5–196.0 °C. NMR (chloroform-d, TMS): δ1.42 (24H, m, 1-, 2-, 3-, 4-, 7-, 10-, 11-, 12-, 13- and 16-C*H*$_2$- and 5-, 9-, 14- and 18-N-*H*) and 2.63 ppm (12H, m, 6-, 8-, 15- and 17-C*H*$_2$- and 19-, 20-, 21- and 22-*H*). *Anal.* Found: C, 70.03, H, 12.27; N, 18.25; M^+, 308. Calc. for $C_{18}H_{36}N_4$: C, 70.08; H, 11.76; N, 18.16%; *M*, 308.51.

The filtrate of recrystallization was concentrated *in vacuo* to obtain colorless crystalline solid. Repeated recrystallization from petroleum ether gave colorless needles (**4-N**); yield 0.25 g (12%), melting point 158.5–161.0 °C. NMR (chloroform-d, TMS): δ1.42 (24H, m, 1-, 2-, 3-, 4-, 7-, 10-, 11-, 12-, 13- and 16-C*H*$_2$- and 5-, 9-, 14- and 18-N-*H*) and 2.63 ppm (12H, m, 6-, 8-, 15- and 17-C*H*$_2$- and 19-, 20-, 21- and 22-*H*). *Anal.* Found: C, 69.30; H, 11.86; N, 17.82; M^+, 308. Calc. for $C_{18}H_{36}N_4$: C, 70.08; H, 11.76; N, 18.16%; *M*, 308.51.

Preparation of Complexes

Dichloro(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22-docosahydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine)cobalt(III) chloride

(a) A mixture of **4-P** (0.11 g) and methanol (5 ml) was added into cobalt(II) chloride hexahydrate (0.10 g) which was dissolved in methanol (5 ml) and was heated at 50 °C for 1 h while air was continuously bubbled through it. 6 M hydrochloric acid (0.4 ml) was added into the reaction mixture, which was heated at 50 °C for another 1 h with stirring. After addition of a few drops of hydrogen peroxide, the reaction mixture was allowed to stand at room temperature overnight. The crystalline product was recrystallized from water to give green plates {[Co(4-P)Cl$_2$]Cl•2H$_2$O}, yield 0.10 g (59%), melting point >300 °C. *Anal.* Found: C, 42.84; H, 7.65; N, 11.13. Calc. for $C_{18}H_{36}N_4Cl_3Co\cdot 2H_2O$: C, 42.76; H, 7.97; N, 11.08%.

(b) The reaction of **4-N** (0.11 g) and cobalt(II) chloride hexahydrate (0.10 g), following the above procedure, gave green plates {[Co(4-N)Cl$_2$]Cl•2H$_2$O}; yield 0.09 g (53%), melting point >300 °C. *Anal.* Found: C, 43.14; H, 7.63; N, 11.20. Calc. for $C_{18}H_{36}N_4Cl_3Co\cdot 2H_2O$: C, 42.76; H, 7.97; N, 11.08%.

1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22-Docosahydrodibenzo[b,i][1,4,8,11]-tetraazacyclotetradecine)nickel(II) diperchlorate

(a) A mixture of **4-P** (0.20 g) and ethanol (6 ml) was added into nickel(II) chloride hexahydrate (0.20 g) which was dissolved in ethanol (6 ml) and was heated at 50 °C for 2 h with stirring. Upon cooling the mixture with ice–water, the precipitates were separated and dissolved in hot water (25 ml). An aqueous solution (1 ml) of sodium perchlorate monohydrate (0.12 g) was added into the hot reaction mixture, which was subsequently kept at room temperature overnight. The recovered crystalline solid was recrystallized from water to give orange plates {[Ni(**4-P**)](ClO$_4$)$_2$}; yield 0.22 g (60%), melting point >300 °C. *Anal.* Found: C, 38.27; H, 6.49; N, 10.15. Calcd. for $C_{18}H_{36}N_4O_8Cl_2Ni$: C, 38.19; H, 6.41; N, 9.91%.

(b) The reaction of **4-N** (0.10 g) and nickel(II) chloride hexahydrate (0.08 g), following the above procedure, gave yellow plates {[Ni(**4-N**)](ClO$_4$)$_2$}; yield 0.11 g (58%), melting point >300 °C. *Anal.* Found: C, 37.81; H, 6.29; N, 9.84. Calc. for $C_{18}H_{36}N_4O_8Cl_2Ni$: C, 38.19; H, 6.41; N, 9.91%.

(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22-Docosahydrodibenzo[b,i][1,4,8,11]-tetraazacyclotetradecine)copper(II) diperchlorate

(a) A mixture of **4-P** (0.24 g) and methanol (8 ml) was added into copper(II) perchlorate (0.33 g) which was dissolved in methanol (5 ml) and was heated at 50 °C for 2 h with stirring. After being stored overnight in a refrigerator, the crystalline solid was recovered by filtration. Recrystallization from water gave red plates {[Cu(**4-P**)](ClO$_4$)$_2$}; yield 0.29 g, (67%), melting point >300 °C. *Anal.* Found: C, 37.92; H, 6.36; N, 9.71. Calc. for $C_{18}H_{36}N_4O_8Cl_2Cu$; C, 37.87; H, 6.36; N, 9.81%.

(b) The reaction of **4-N** (0.30 g) and copper(II) perchlorate hexahydrate (0.43 g), following the above procedure, gave red plates {[Cu(**4-N**)](ClO$_4$)$_2$}; yield 0.23 g (40%), melting point >300 °C. *Anal.* Found: C, 37.51; H, 6.41; N, 9.63. Calc. for $C_{18}H_{36}N_4O_8Cl_2Cu$; C, 37.87; H, 6.36; N, 9.81%.

(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22-Docosahydrodibenzo[b,i][1,4,8,11]-tetraazacyclotetradecine)zinc(II) diperchlorate

(a) A mixture of **4-P** (0.25 g) and ethanol (6 ml) was added into zinc(II) perchlorate hexahydrate (0.36 g) which was dissolved in ethanol (6 ml) and was heated at 50 °C for 2 h with stirring. Upon cooling the reaction mixture in a refrigerator overnight, the crystalline product was recrystallized from water as colorless needless {[Zn(**4-P**)](ClO$_4$)$_2$}; yield 0.17 g (38%), melting poing >300 °C. *Anal.* Found: C, 37.96; H, 6.31; N, 9.88. Calc. for $C_{18}H_{36}N_4O_8Cl_2Zn$; C, 37.74; H, 6.33; N, 9.78%.

TABLE I. Molar Conductances for the Complexes at 25 °C

Complex	Solvent	Λ_M[a] S (cm^2 mol^{-1})	Type of electrolyte[b]
[Co(4-P)Cl_2]Cl·$2H_2O$	H_2O	120(339)[c]	1:1(1:3)[c]
	CH_3CN	173	1:1
[Co(4-N)Cl_2]Cl·$2H_2O$	H_2O	112(316)[c]	1:1(1:3)[c]
	CH_3CN	174	1:1
[Ni(4-P)]$(ClO_4)_2$	H_2O	198	1:2
	CH_3CN	395	1:2
[Ni(4-N)]$(ClO_4)_2$	H_2O	197	1:2
	CH_3CN	350	1:2
[Cu(4-P)]$(ClO_4)_2$	H_2O	190	1:2
	CH_3CN	373	1:2
[Cu(4-N)]$(ClO_4)_2$	H_2O	203	1:2
	CH_3CN	354	1:2
[Zn(4-P)]$(ClO_4)_2$	H_2O	197	1:2
	CH_3CN	385	1:2
[Zn(4-N)]$(ClO_4)_2$·$2H_2O$	H_2O	189	1:2
	CH_3CN	384	1:2

[a] For *ca.* 10^{-3} mol dm^{-3} solutions. [b] Assignment of the type of electrolyte present in solution was made on the basis of the conductance data compiled by Geary [17]. [c] Data after being stored overnight at 25 °C.

TABLE II. Characteristic IR Bands for the Cobalt(III), Nickel(II), Copper(II) and Zinc(II) Complexes of **4**[a]

Sample	IR bands (cm^{-1})[b]	Assignment
4-P	3290(s)	ν_{NH}
4-N	3260(s)	ν_{NH}
[Co(**4-P**)Cl_2]Cl·$2H_2O$	3400(s,br)	ν_{OH} (lattice water)
	3220(s)	ν_{NH}
	3175(s)	
	1620(m)	δ_{OH} (lattice water)
[Co(**4-N**)Cl_2]Cl·$2H_2O$	3400(s,br)	ν_{OH} (lattice water)
	3240(s)	ν_{NH}
	3180(s)	
	1620(m)	δ_{OH} (lattice water)
[Ni(**4-P**)]$(ClO_4)_2$	3200(s)	ν_{NH}
	1100(s,br)	$\nu_{ClO_4^-}$
	620(s)	$\delta_{ClO_4^-}$
[Ni(**4-N**)]$(ClO_4)_2$	3100(s)	ν_{NH}
	1100(s,br)	$\nu_{ClO_4^-}$
	625(s)	$\delta_{ClO_4^-}$
[Cu(**4-P**)]$(ClO_4)_2$	3240(s)	ν_{NH}
	1090(s,br)	$\nu_{ClO_4^-}$
	620(s)	$\delta_{ClO_4^-}$
[Cu(**4-N**)]$(ClO_4)_2$	3240(s)	ν_{NH}
	1090(s,br)	$\nu_{ClO_4^-}$
	625(s)	$\delta_{ClO_4^-}$
[Zn(**4-P**)]$(ClO_4)_2$	3260(s)	ν_{NH}
	1120(s,br)	$\nu_{ClO_4^-}$
	630(s)	$\delta_{ClO_4^-}$
[Zn(**4-N**)]$(ClO_4)_2$·$2H_2O$	3400(s,br)	ν_{OH} (lattice water)
	3230(s)	ν_{NH}
	3180(s)	
	1625(m)	δ_{OH} (lattice water)
	1100(s,br)	$\nu_{ClO_4^-}$
	618(s)	$\delta_{ClO_4^-}$

[a] Measured by the KBr disk method at room temperature. [b] Relative intensities: s, strong; m, medium, br, broad.

(b) The reaction of **4-N** (0.15 g) and zinc(II) perchlorate hexahydrate (0.22 g) following the above procedure, gave colorless needles {[Zn(**4-N**)]$(ClO_4)_2 \cdot 2H_2O$}; yield 0.10 g (38%), melting point 293–296 °C (dec.) *Anal.* Found: C, 35.50; H, 6.58; N, 9.18. Calc. for $C_{18}H_{36}N_4O_8Cl_2Zn \cdot 2H_2O$: C 35.51; H,6.62; N, 9.20%.

Results and Discussion

Molar Conductances

The molar conductances for the complexes are summarized in Table I. [ML]$(ClO_4)_2$ (M = Ni, Cu, or Zn; L = **4-P**, or **4-N**) are 1:2 electrolytes in water and acetonitrile solutions and are four-coordinated in these solvents. Hence, the perchlorate anion is ionized on dissolution in these solvents. {[$CoLCl_2$]Cl} are 1:1 electrolytes and are six-coordinated in acetonitrile solution, and, therefore, two chloride anions except an ionic chloride are not ionized on dissolution in this solvent. Since the coordinated chloride ions of the cobalt(III) complexes are hydrolyzed in water solution, aqueous solutions are 1:3 electrolytes as shown in Table I.

Vibrational Spectra

The characteristic IR bands, which are meaningful for the present discussion, are compiled in Table II. A strong absorption band observed in the 3200 cm^{-1} range can be attributed to a N–H stretching mode and shifts slightly to lower frequency upon metal-coordination. All these complexes, except for [Co(**4-P**)Cl_2]$Cl \cdot 2H_2O$ [Co(**4-N**)Cl_2]$Cl \cdot 2H_2O$ and [Zn(**4-N**)]$(ClO_4)_2 \cdot 2H_2O$, show the presence of only one sharp intense band near 3200 cm^{-1} arising from the secondary amine stretching vibration On the other hand, for [Co(**4-P**)Cl_2]$Cl \cdot 2H_2O$, [Co(**4-N**)Cl_2]$Cl \cdot 2H_2O$ and [Zn(**4-N**)]$(ClO_4)_2 \cdot 2H_2O$, the splitting of the amine stretching vibration in the vicinity of 3200 cm^{-1} is presumably a consequence of hydrogen bonding involved between the secondary amines and the water of crystallization in the crystal lattice.

A strong broad band at around 1100 cm^{-1} was observed for the nickel(II), copper(II) and zinc(II) complexes and attributable to the stretching vibrational mode of perchlorate ion [6]. The perchlorate group in the present metal complexes may be present not as a coordinated group but as a simple isolated ion as judged by the vibrational frequency [7]. This is buttressed by the conductance data (Table I). Another peak due to the perchlorate group was observed at about 620 cm^{-1}, which may be attributed to its bending vibration [7].

Mass Spectra

The FAB mass spectrum, obtained in a glycerin matrix, establish the presence of a molecular ion $(M + 1)^+$ at m/z 473, namely [Co(**4-P**)Cl_2]Cl and [Co(**4-N**)Cl_2]Cl cation, as shown in Fig. 1. The masses of the major fragment at m/z 366, 402 and 438 correspond to $[M - 3Cl - H]^+$, $[M - 2Cl]^+$ and $[M - Cl + H]^+$, respectively and the peak at m/z 438 is the base peak in the mass spectrum. These fragments are consistent with the loss of chloride radicals from the molecular ion. On the other hand, the nickel(II), copper(II) and zinc(II) complexes show a cluster of ions corresponding to $[M - ClO_4]^+$ and $[M - 2ClO_4 - 2H]^+$, and the latter is the base peak in the EI mass spectrum. Table III lists the molecular weights and the ions observed. Molecular ions were not also observed when the sample was analyzed using the FAB and the field desorption (FD) mass spectra. The mass spectrum makes no distinction between **4-P** and **4-N** in these complexes.

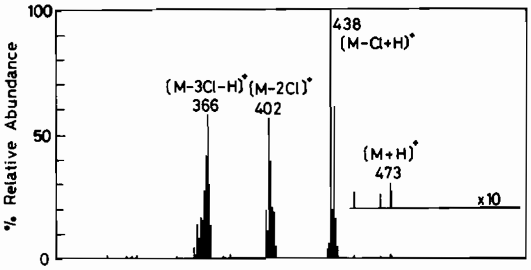

Fig. 1. Fast atom bombardment mass spectrum of [Co(4-N)-Cl_2]Cl in a glycerin matrix. The inset of the molecular ion region is magnified by a factor of 10.

TABLE III. Characteristic Ions Observed in EI Mass Spectra for the Nickel(II), Copper(II) and Zinc(II) Complexes

Sample	Molecular weight	Ions observed[a]
[Ni(4-P)$(ClO_4)_2$	364	$[M - 2ClO_4 - 2H]^+$
	465	$[M - ClO_4]^+$
[Ni(4-N)$(ClO_4)_2$	364	$[M - 2ClO_4 - 2H]^+$
	465	$[M - ClO_4]^+$
[Cu(4-P)]$(ClO_4)_2$	369	$[M - 2ClO_4 - 2H]^+$
	470	$[M - ClO_4]^+$
[Cu(4-N)]$(ClO_4)_2$	369	$[M - 2ClO_4 - 2H]^+$
	470	$[M - ClO_4]^+$
[Zn(4-P)]$(ClO_4)_2$	370	$[M - 2ClO_4 - 2H]^+$
	471	$[M - ClO_4]^+$
[Zn(4-N)]$(ClO_4)_2 \cdot 2H_2O$	370	$[M - 2ClO_4 - 2H]^+$
	471	$[M - ClO_4]^+$

[a] *M* is a molecular ion.

Electronic Spectra

The ligand-field spectra for the two cobalt(III) complexes in solution are similar to each other and consist of one broad band at *ca.* 15300 cm^{-1} and two shoulders of bands in the 21000–31000 cm^{-1} range as shown in Fig. 2. The *trans*-$[Co(NH_3)_4Cl_2]^+$

TABLE IV. Ligand-field Bands for Cobalt(III), Nickel(II) and Copper(II) Complexes and their Assignments[a]

Complex	Ligand-field band, cm^{-1} (ϵ)	Symmetry	Assignment
$[Co(4\text{-}P)Cl_2]Cl \cdot 2H_2O$	15250(37)	D_{4h}	$^1E_g \leftarrow {}^1A_{1g}$
	20900sh(31)		$^1A_{2g} \leftarrow {}^1A_{1g}$
	30100sh(975)		$^1B_{2g} \leftarrow {}^1A_{1g}$
$[Co(4\text{-}N)Cl_2]Cl \cdot 2H_2O$	15300(42)	D_{4h}	$^1E_g \leftarrow {}^1A_{1g}$
	21000sh(38)		$^1A_{2g} \leftarrow {}^1A_{1g}$
	30400sh(2150)		$^1B_{2g} \leftarrow {}^1A_{1g}$
$[Ni(4\text{-}P)](ClO_4)_2$	14750(2)	O_h	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$
	21700(33)	D_{4h}	$^1A_{2g} \leftarrow {}^1A_{1g}$
	29200(8)	O_h	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$
$[Ni(4\text{-}N)](ClO_4)_2$	22400(105)	D_{4h}	$^1A_{2g} \leftarrow {}^1A_{1g}$
$[Cu(4\text{-}P)](ClO_4)_2$	19200(127)	D_{4h}	$^2A_{1g}, {}^2B_{2g}, {}^2E_g \leftarrow {}^2B_{1g}$
$[Cu(4\text{-}N)](ClO_4)_2$	19750(144)	D_{4h}	$^2A_{1g}, {}^2B_{2g}, {}^2E_g \leftarrow {}^2B_{1g}$

[a] Measured in *N,N*-dimethylformamide at room temperature.

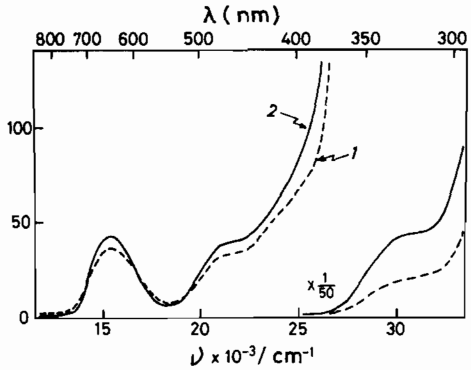

Fig. 2. Ligand-field spectra for cobalt(III) complexes in *N,N*-dimethylformamide at room temperature. (1) $[Co(4\text{-}P)Cl_2]Cl$. (2) $[Co(4\text{-}N)Cl_2]Cl$.

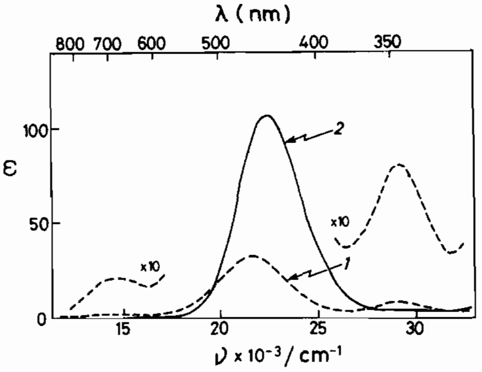

Fig. 3. Ligand-field spectra for nickel(II) complexes in *N,N*-dimethylformamide at room temperature. (1) $[Ni(4\text{-}P)](ClO_4)_2$; (2) $[Ni(4\text{-}N)](ClO_4)_2$.

complex has been shown to assume the effective D_{4h} symmetry with axial elongation and its spectrum analyzed quantitatively by the aid of the secular equations of Tanabe and Sugano [8, 9]. Similar interpretation would be applied to the present cobalt(III) complexes, since structural requirement of the present macrocyclic ligands forces cobalt(III) to occupy a square-planar ligand-field. The present ligand-field bands are as seen in Table IV.

The two nickel(II) complexes differ from one another in the ligand-field spectra. $[Ni(4\text{-}N)](ClO_4)_2$ complex demonstrates only one broad strong ligand-field band at 22400 cm^{-1} in a region lying below 34000 cm^{-1} as shown in Fig. 3. Similar ligand-field spectra have been observed for $Ni(DMG)_2$* [10], $Ni(cyclam)^{2+}$** [11], etc. This result seems to indicate that the structure of $[Ni(4\text{-}N)](ClO_4)_2$ complex assumes the square-planar configuration. Under assumption that the ground state becomes A_{1g} due to the D_{4h} field, the transition energies can be represented as given in Table IV. On the other hand, the ligand-field spectrum covering the 11000–34000 cm^{-1} range in *N,N*-dimethylformamide (DMF) is shown in Fig. 3 for $[Ni(4\text{-}P)](ClO_4)_2$ complex. Three optical bands can be identified in the spectrum which is indicative of the square-planar-distorted octahedral equilibrium as follows (eqn. (1)).

$$[Ni(4\text{-}P)](ClO_4)_2 + 2DMF \rightleftharpoons [Ni(4\text{-}P)(DMF)_2](ClO_4)_2 \qquad (1)$$

Their assignments are as shown in Table IV. Thus, the transition energies at 14750 and 29200 cm^{-1} arise from the tetragonal complex, while the transition energy at 21700 cm^{-1} results from the square-planar species [8]. It is the decrease of the concentration of the square-planar species that causes the decrease of the intensity of its absorption band observed at 21700 cm^{-1}. Hence, the absorption coefficient at around 22000 cm^{-1} for $[Ni(4\text{-}P)](ClO_4)_2$ is smaller in magnitude than that observed for $[Ni(4\text{-}N)](ClO_4)_2$.

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*DMG, dimethylglyoxime.

**cyclam, 1,4,8,11-tetraazacyclotetradecane.

It is quite interesting to note that $[Ni(4\text{-}P)](ClO_4)_2$ indicates the square-planar distorted octahedral equilibrium in contrast to the square-planar of $[Ni(4\text{-}N)](ClO_4)_2$.

Ligand-field spectra for the two copper(II) complexes in DMF solution are similar to each other and are composed of only one broad band in a region lying below 34 000 cm^{-1} as shown in Fig. 4. The general features and peak positions of the ligand-field spectra are analogous to those for $Cu(daco)_2^{2+}$*, $Cu(dach)_2^{2+}$**, etc. [12] which are square-planars. Consequently, under assumption that the ground state becomes B_{1g} due to the square-planar field, the present ligand-field bands are tentatively assigned as given in Table IV.

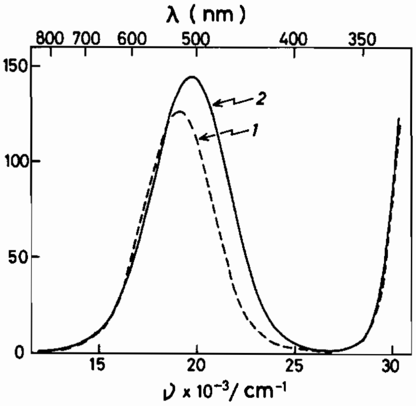

Fig. 4. Ligand-field spectra for copper(II) complexes in N,N-dimethylformamide at room temperature. (1) $[Cu(4\text{-}P)](ClO_4)_2$; (2) $[Cu(4\text{-}N)](ClO_4)_2$.

Ligand **4-N** exerts remarkably stronger in-plane interactions towards copper(II) and nickel(II) ions than ligand **4-P**, as judged from the energy of the ligand field absorption bands (Ni(II) complex: **4-N**, 22 400; **4-P**, 21 700 cm^{-1}. Cu(II) complex: **4-N**, 19 750; **4-P**, 19 200 cm^{-1}). Consequently, the complex of **4-N** is a stronger square-planar ligand field than that of **4-P**. This result seems to indicate that $[Ni(4\text{-}N)](ClO_4)_2$ is difficult to coordinate DMF molecules at the axial positions. The *cis–syn–cis* form explains the stronger binding of the metal to nitrogen donor atoms to decrease the distortion against more symmetrical *cis–anti–cis* and *trans–anti–trans* forms as shown in Fig. 6. It has been tentatively suggested that the complex of **4-N** is a *cis–syn–cis* form and that of **4-P** is *cis–anti–cis* from or *trans–anti–trans* form.

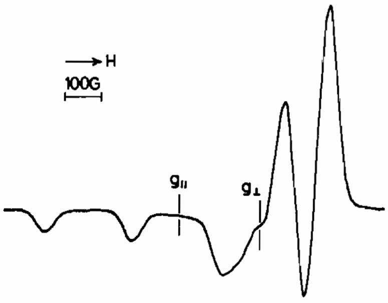

Fig. 5. ESR spectrum of $Cu(4\text{-}P)(ClO_4)_2$ complex in *N,N*-dimethylformamide at 77 K.

ESR

The ESR spectrum for the copper(II) complex of **4-P** in *N,N*-dimethylformamide at 77 K is shown in Fig. 5. The general feature of the spectrum is consistent with the square-planar coordination. The hyperfine lines due to the copper nucleus ($I = 3/2$) can be observed on the $g_{\parallel}$ positions while such hyperfine splittings are not obvious on the $g_{\perp}$ positions. Superhyperfine lines due to the nitrogen nuclei ($I = 1$) disappear on the $g_{\parallel}$ and $g_{\perp}$ positions. The solution spectra also show only four hyperfine lines due to the copper atom. The spin Hamiltonian parameters obtained in this work are almost comparable with the data for the porphyrin and tetraazacyclotetradecane complexes taken from the literature [3c, 13], as shown in Table V. Accordingly, the present

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*daco, 1,5-diazacyclooctane.

**dach, 1,4-diazacycloheptane.

TABLE V. Spin Hamiltonian Parameters for Copper(II) Complexes of Macrocycles[a]

Ligand	Medium	Temperature	$\bar{g}$	$g_{\parallel}$	$g_{\perp}$	$\bar{A}$ ($\times 10^4$ cm^{-1})	$A_{\parallel}$ ($\times 10^4$ cm^{-1})	Reference
4-P	$(CH_3)_2NCHO$	room temperature	2.094			92.2		
4-P	$(CH_3)_2NCHO$	77 K		2.193	2.066		208.1	
4-N	$(CH_3)_2NCHO$	room temperature	2.097			92.3		
4-N	$(CH_3)_2NCHO$	77 K		2.183	2.061		204.8	
H_2TPP[b]	$CHCl_3$	room temperature	2.1073			97.7		13
H_2TPP[b]	$CHCl_3$	77 K		2.187	2.067		218	13
TACM[b]	H_2O	77 K		2.18	2.07		210	3(c)

[a] Maximum possible errors: g, ±0.005; $\bar{A}$, $A_{\parallel}$, $\pm 0.5 \times 10^{-4}$ cm^{-1}. [b] H_2TPP, 5,10,15,20-tetraphenylporphine; TACM, 1,4,8,11-tetraazacyclotetradecane-2-one.

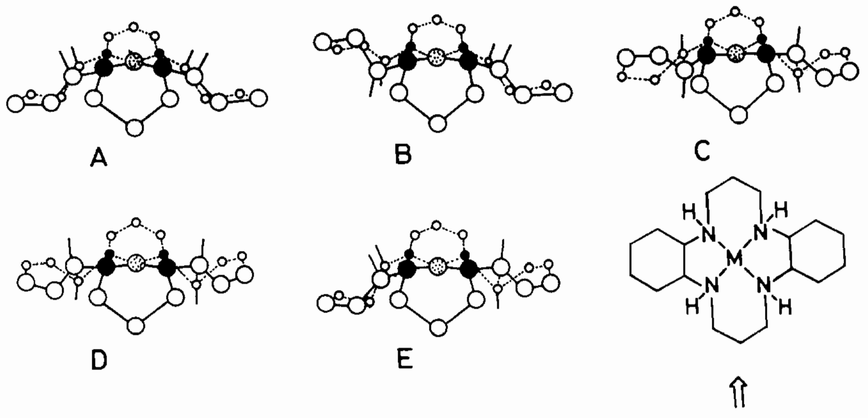
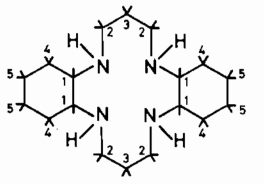


Fig. 6. The five theoretical isomers available for macrocyclic complexes (from the direction of an arrow). ⊚, Metal; ●, nitrogen; ○ carbon. A, *cis–syn–cis*; B, *cis–anti–cis*; C, *trans–anti–trans*; D, *trans–syn–trans*; E, *trans–anti–cis*.

TABLE VI. Carbon-13 NMR Data for the Macrocycles and their Metal Complexes[a,b]

Sample	C(1)	C(2)	C(3)	C(4)	C(5)
4-P[c]	56.87	43.20	30.21	28.26	22.54
4-N[c]	57.22	49.78	30.19	27.90	22.49
[Co(**4-P**)Cl_2]Cl·$2H_2O$[d]	65.59, 65.03	48.65, 47.82	30.43	26.35, 25.42	25.02, 20.93
[Co(**4-N**)Cl_2]Cl·$2H_2O$[d]	66.25, 64.88	48.01	30.31	26.21, 25.38	24.89, 20.63
[Ni(**4-P**)]$(ClO_4)_2$[d]	63.73, 63.43	48.01, 46.99	27.92	25.42, 25.18	24.25, 19.36
[Ni(**4-N**)]$(ClO_4)_2$[d]	65.42, 63.12	50.12	28.11	26.45, 25.13	22.25, 19.11
[Zn(**4-P**)]$(ClO_4)_2$[e]	56.26, 56.16	47.17, 45.44	27.22	23.83, 23.46	22.22, 17.45
[Zn(**4-N**)]$(ClO_4)_2$·$2H_2O$[e]	57.06	49.17	26.85	24.82	20.73

[a] Chemical shifts in ppm from internal TMS. [b] C(2)- and C(3)-signals for [Co(**4-N**)Cl_2]Cl·$2H_2O$ and [Ni(**4-N**)]$(ClO_4)_2$ are split into two peaks at −15 °C, respectively. [c] Measured in chloroform-d. [d] Measured in trifluoroacetic acid-d. [e] Measured in dimethyl sulfoxide-d_6.



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copper(II) complex assumes the square-planar configuration.

NMR

1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22-Docosahydrodibenzo[b,i] [1,4,8,11] tetraazacyclotetradecine (**4**) is made by hydrogenation of the benzo-analogue (**3**), so there is a possibility of *cis–trans* isomerism at the two bridge bonds. In the *trans*-isomer both nitrogen substituents are equatorial for complex formation, in the *cis*-isomer one substituent is axial and the other equatorial. In theory, five isomers, which are not interconvertible by conformational change, are feasible. These are shown diagramatically in Fig. 6.

Unambiguous assignments for these macrocyclic ligands (**4**) and their metal complexes are difficult to give only a few peaks of a multiplet at proton NMR spectra. Hence ^1H NMR cannot be used to distinguish clearly five isomers.

Carbon-13 NMR data for these macrocycles and their metal complexes are collected in Table VI. The number of carbon-13 NMR spectral lines, which are estimated in Fig. 6, is listed in Table VII. Isomers **D** and **E** are ruled out with ease by comparing Tables VI and VII. Being observed as singlet at room temperature, C(2)- and C(3)-signals for [Co(**4-N**)Cl_2]Cl·$2H_2O$ and [Ni(**4-N**)]$(ClO_4)_2$ are split into two lines at −15 °C, respectively. This seems to indicate that these complexes may adopt the *cis–syn–cis* form (**A**) as shown in Fig. 6 and also that in solution, even in the complexes, the six-membered chelate rings flip from one conformation to another at room temperature.

^{13}C NMR spectra for [Co(**4-P**)Cl_2]Cl·$2H_2O$ and [Ni(**4-P**)]$(ClO_4)_2$ suggest that both complexes are the *cis–anti–cis* form (**B**) or the *trans–anti–trans* form (**C**) as seen in Fig 6. As this ^{13}C NMR evidence on the conformation of isomers **B** or **C** is not conclusive, it is indistinguishable that these complexes are isomers **B** or **C**. By reference to the products based

TABLE VII. The Number of Estimated Carbon-13 NMR Spectral Lines for the Macrocyclic Complexes

Stereoisomer	C(1)	C(2)	C(3)	C(4)	C(5)
cis–syn–cis	2	2	2	2	2
cis-anti–cis	2	2	1	2	2
trans–anti–trans	2	2	1	2	2
trans–syn–trans	1	1	1	1	1
trans–anti–cis	4	4	2	4	4

upon the hydrogenation of the dibenzo-18-crown-6 [14–16], it is presumed that these complexes may probably by the *cis- anti–cis* form (**B**). ^{13}C NMR spectra for the zinc(II) complexes are too complicated to give satisfactory assignments

Also the magnitude of steric repulsion between cyclohexyl groups and DMF solvent molecules may affect coordinating at the axial sites of the nickel(II) complexes. Accordingly [Ni(**4-N**)]$(ClO_4)_2$ is the *cis–syn–cis* form and [Ni(**4-P**)]$(ClO_4)_2$ is the *cis–anti–cis* form or the *trans–anti–trans* form. The more definitive distinction between these spectroscopically similar pairs is expected to be resolved by X-ray crystallography.

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