Preparation and Spectral Properties of Nickel(II) and Chloroiron(III) Complexes with a Macrocyclic N_4-Ligand: 5,14-Dihydro-7,16-diethyldibenzo [b, i] [1,4, 8,11] tetraazacyclotetradecine

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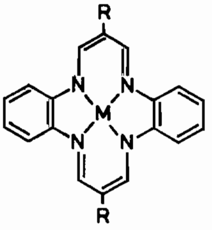
Received October 11, 1984

Our earlier studies on the structural aspects of the transition-metal complexes of tetraaza[14]-annulenes have been roughly divided into two main facts [1, 2]. Firstly, metal ions, which are in the divalent state of favorable stability, form the metal complexes of a 1:1 molar ratio of ligand to metal without any other additional ligand. These metal complexes trend to the square-planar configurations. Secondly, the central metals, which have the sparingly stable trivalent state compared to the divalent, yield complexes with some other additional ligand. Their metal complexes become pentacoordinated by having an anion in the axial position as the fifth ligand. While considerable effort has been expended on the investigation of iron–porphyrin complexes [3], examples of synthetic unsaturated N_4-macrocyclic ligands complexed to iron are rare. Goedken *et al.* [4–6] merely reported the synthesis and X-ray diffraction study of the iron(III) complex with 5,14-dihydro-6,8,15,17-tetramethyldibenzo[b,i] [1,4,8,11] tetraazacyclotetradecine and the nickel(II) complex with 5,14-dihydrodibenzo[b,i] [1,4,8, 11] tetraazacyclotetradecine without the research of spectral properties.

In the present work we employed two metal complexes of the unsaturated N_4-macrocyclic ligand; (7,16-diethyldibenzo[b,i] [1,4,8,11] tetraazacyclotetradecinato)nickel(II) and chloro(7,16-diethyldibenzo[b,i] [1,4,8,11] tetraazacyclotetradecinato)iron(III). We elucidated the correlation between the valence state of iron and nickel in complexes and the structural aspect. The electronic spectra for the nickel(II) and chloroiron(III) complexes, the detailed NMR study for the nickel(II) complex, and the magnetic susceptibility and ESR datum for the chloroiron(III) complex are also provided. In addition, we report the solvent effect in the 580–630 nm range for the chloroiron(III) complex because of the lack of systematic work of the solvent effect on the charge-transfer (CT) transition for iron complexes.



R = CH_2CH_3
M = Cl-Fe(III), Ni(II)

Experimental

Preparation of the Macrocyclic Ligand

5,14-Dihydro-7,16-diethyldibenzo[b,i][1,4,8,11]-tetraazacyclotetradecine (1)

Prepared after Breitmaier *et al.* [7] from 1,2-diaminobenzene (9.1 g) and 2-ethyl-3-ethoxyacrolein (10.3 g) [8–11] in N,N-dimethylformamide (40 ml). The crystalline solid was washed with methanol (10 ml) and recrystallized from chloroform as glittering dark-red needles; yield 3.5 g (25%), m.p. 232.0–233.5 °C (lit., [7] m.p. 200 °C). IR (KBr disk)†: 3180 (N–H str.), 1651 (C=N str.), 1596 (C=C str. (conjugated ring)) and 1554 cm^{-1} (macrocyclic skeletal str.). *Anal.* Found: C, 76.84; H, 7.05; N, 16.15%; M^+, 344††. Calcd. for $C_{22}H_{24}N_4$: C, 76.71; H, 7.02; N, 16.27%; M, 344.46.

Preparation of the Complexes

(7,16-Diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)nickel(II) (Ni(II)–1)

A mixture of **1** (0.52 g), nickel(II) acetate tetrahydrate (0.42 g) and N,N-dimethylformamide (10 ml) was heated under reflux for 2 h. After the reaction mixture was cooled down with ice-water, the precipitated crystalline solid was recrystallized from N,N-dimethylformamide as glittering dark-violet needles; yield 0.54 g (89%), m.p. >300 °C. IR (KBr disk)†: 1609 (C=N str.), 1596 (C=C str. (conjugated ring)) and 1462 cm^{-1} (macrocyclic skeletal str.). *Anal.* Found: C, 65.77; H, 5.57; N, 13.90%; M^+, 400††. Calcd. for $C_{22}H_{22}N_4Ni$: C, 65.87; H, 5.53; N, 13.97%; M, 401.14.

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†Infrared spectra covering the 650–4000 cm^{-1} range were measured with a Hitachi 260 spectrophotometer at room temperature by a KBr disk technique.

††Mass spectra were recorded on a JEOL JMS-DX 300 gas chromatograph-mass spectrometer.

0020-1693/85/$3.30

TABLE I. Magnetic Susceptibility Results for Macrocyclic Complexes.

Complex[a]	Electronic configuration	Coordination number	Temp. (K)	μ_{eff}[b]	$[4S(S+1)]^{1/2}$	No. of unpaired electrons	Ref.
Ni(II)–1	8	4	298.5	dia.	0	0	This work
Fe(III)–1–Cl	5	5	298.5	3.85	3.87	3	This work
Fe(III)ProtoIX–Cl	5	5	77–300	5.89	5.92	5	13
Fe(III)TPP–$(Im)_2$	5	6	4.2–50	2.36	1.94	1	14
Fe(III)OEP–ClO_4	5	5	84	4.1	3.87	3	15
Fe(III)(Ph_2[14]N_4)Br	5	5	17–295	3.91	3.87	3	16

[a] 1, 5,14-Dihydro-7,16-diethyldibenzo[b,i] [1,4,8,11] tetraazacyclotetradecine; ProtoIX, 13,17-dicarboxyethyl-3,8-divinyl-2,7,12,18-tetramethylporphine; TPP, 5,10,15,20-tetraphenylporphine; Im, imidazole; OEP, 2,3,7,8,12,13,17,18-octaethylporphine; Ph_2-[14]N_4, 6,13-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene. [b] dia., diamagnetism.

Chloro(7,16-diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)iron(III) (Fe(III)–1–Cl)

An acetonitrile solution (40 ml) of hydrated iron(II) chloride (0.89 g) was added into an acetonitrile suspension (50 ml) of **1** (1.0 g). The reaction mixture was refluxed for 2.5 h while nitrogen gas was continuously bubbled through it. After the mixture was cooled down with ice–water in an atmosphere of nitrogen, the crystalline solid was recovered by filtration and washed with methanol (10 ml) to give glittering dark green prisms; yield 0.75 g (59%), m.p. >300 °C. IR (KBr disk)[†]: 1596 (C=C str. (conjugated ring)), 1586 (C=N str.) and 1438 cm^{-1} (macrocyclic skeletal str.). *Anal.* Found: C, 60.92; H, 5.13; N, 13.04%; M^+, 433[††]. Calcd. for $C_{22}H_{22}N_4ClFe$: C, 60.92; H, 5.11; N, 12.92%; M, 433.74.

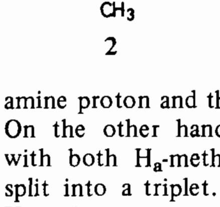
Physical Measurements

Magnetic susceptibility measurements of solid powdered samples were carried out by the Faraday method. Calibrations were made with use of sodium chloride and Mohr's salt, while diamagnetic corrections were performed by using Pascal's constants. A JEOL JNM-FX 60 spectrometer was used to obtain NMR spectra in chloroform-d_1 (Aldrich Chemical Co. 99.8%D) at room temperature and chemical shifts were reported in ppm from internal TMS. Ultraviolet and visible spectra covering the 12500–45000 cm^{-1} region were recorded on a Shimadzu UV-200S double beam spectrophotometer at room temperature. ESR spectrum was obtained with a JEOL JES-ME-1 X-band spectrometer equipped with a 100-kHz field modulation unit. The chloroiron(III) complex was measured in N,N-dimethylformamide at 77 °K, concentrations being maintained in the ~10^{-2} mol dm^{-3}. The manganese ion diffused into magnesium oxide was used to obtain standard reference signals for a measurement. Solvents for spectroscopic measurements were prepared by standard procedures [12].

Results and Discussion

The results of magnetic susceptibility measurements are listed in Table I, together with those for Fe(III)ProtoIX–Cl, Fe(III)TPP$(Im)_2$, Fe(III)OEP–ClO_4 and Fe(III)(Ph_2[14]N_4)Br [13–16]. It became obvious that the Fe(III)–1–Cl complex, as well as the Fe(III)OEP–ClO_4 and Fe(III)(Ph_2[14]N_4)Br, holds an intermediate-spin state ($S = 3/2$). It is interesting to note that the present iron(III) complex is in an intermediate-spin ground state, as opposed to the high-spin state of the corresponding manganese(III) complexes [2]. The effective magnetic moment for the Fe(III)–1–Cl complex suggests that the nuclear iron has an oxidation state of +3, which is compatible with the spin-only value and that observed for Fe(III)(Ph_2[14]N_4)Br. Examples of an intermediate-spin ground state are normally much less than those of a high-spin and a low-spin state in the iron(III) complexes.

NMR data for a macrocyclic ligand (**1**) and the nickel(II) chelate are summarized in Table II. The H_a-methine proton shown by **2** couples with the H_b-amine proton and the H_a-signal is split into a doublet. On the other hand, the H_b-amine proton couples with both H_a-methine proton, the H_b-signal being split into a triplet. The signal (13.57 ppm) for the H_b-amine proton was found to disappear upon



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[†,††] For footnotes see previous page.

TABLE II. Proton NMR Data for the Macrocycle and the Nickel(II) Complex.[a]

Sample	Methyl 7,16-CH_3-CH_2-	Methylene 7,16-CH_3-CH_2-	Aromatic	Methine -CH=N-(=CH-NH-)	Amine -N-H
1	1.13(t, J = 7.3 Hz)	2.25(q, J = 7.3 Hz)	6.7–7.2(m)	7.65(d, J = 5.9 Hz)	13.57(t, J = 5.9 Hz)
Ni(II)–1	1.19(t, J = 7.4 Hz)	2.42(q, J = 7.4 Hz)	6.7–7.4(m)	7.62(s)	

[a] Chemical shifts in ppm from internal TMS. Measured in chloroform-d_1. S = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

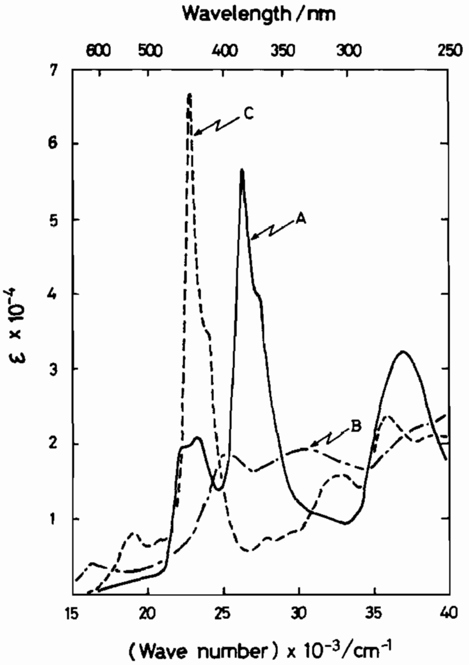

Fig. 1. Electronic absorption spectra of 5,14-dihydro-7,16-diethyldibenzo[b,i] [1,4,8,11] tetraazacyclotetradecine chelates in 1,2-dichloroethane at room temperature. A, Ligand; B, chloroiron(III); C, nickel(II).

nickel-coordination. The methine proton peak (7.65 ppm) observed for macrocycle (**1**) in the lowest field is shifted upon complex formation by 0.03 ppm up-field. This up-field shift is comparable to that observed for the meso-methine protons of nickel(II)–porphyrin [3(a)]. This may be attributable to decrease of the ring current by combination of the nickel. Upon substitution of the H_b-proton on the nitrogen with deuterium (D) in metal-free ligand, the H_a-signal at 7.65 ppm turned out to be a singlet. An analogous spectral change was observed upon nickel(II)-coordination. The proton signals for methyl, methylene and aromatic groups indicate down-field shift upon formation of the nickel complex, as shown in Table II. These down-field shifts can be attributable to the de-shielding effect provided by the positive charge on nickel(II).

The electronic spectra covering the 15000–40000 cm^{-1} range are shown in Fig. 1 for the metal chelates of 5,14-dihydro-7,16-diethyldibenzo-[b,i] [1,4,8,11] tetraazacyclotetradecine (**1**). The absorption bands appearing in the energy range greater than 16000 cm^{-1} are reasonably attributable to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and CT transitions from metal to ligand. The reason for this conclusion is given below. The molar extinction coefficients of these band ($10^3 \sim 10^4$ mol^{-1} dm^3 cm^{-1}) are larger than those commonly assigned to ligand-field transitions [17]. Furthermore, the general features of the spectra for the nickel(II) and chloroiron(III) complexes are similar to those observed for tetraaza[14]annulene complexes described previously [1, 2].

In marked contrast to the nickel(II) complex, the chloroiron(III) complex was observed to show a strong absorption band in a longer wavelength range (*e.g.*, λ_{max} 616 nm with $\epsilon = 4.15 \times 10^3$ in 1,2-dichloroethane). This band is attributed to the intramolecular CT transition for which the Fe–Cl bond is concerned. The reasons for this assignment are as follows. The transition energy is appreciably sensitive to the solvent nature; the λ_{max} value being extended from 581 nm in methanol to 629 nm in benzene. In addition, the behavior of the chloroiron(III) complex studied here is similar to those observed for isothiocyanatomanganese(III) complexes of tetraaza[14]annulenes described previously [2]. The transition energy (E_T, kcal mol^{-1}) is adequately correlated with a solvent polarity parameter (Z-value), as shown in Fig. 2. Consequently, the present absorption band can be reasonably assigned to the CT transition. Since no systematic work of the solvent effects on CT transitions for iron complexes has been carried out, the present finding is of great use for examining the nature of coordinate bonds.

No ESR signal was observed at 293 °K for a polycrystalline sample of the chloroiron(III) complex by the very fast electronic relaxation, but the ESR spectrum was observed in N,N-dimethylformamide (DMF) at 77 °K, as shown in Fig. 3. This suggests that a part of DMF used as the glass-forming solvent is coordinated to the iron atom at the axial site *trans*

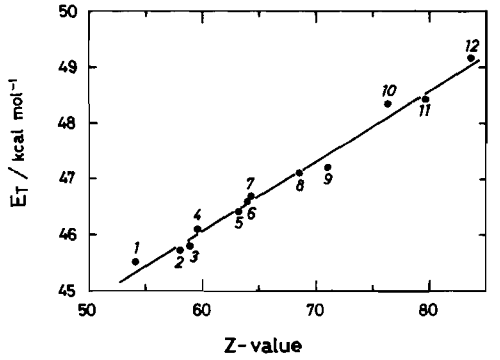

Fig. 2. Correlation between CT transition energy of chloroiron(III) complex and solvent polarity parameter (Z): 1, benzene; 2, chlorobenzene; 3, tetrahydrofuran; 4, ethyl acetate; 5, chloroform; 6, 1,2-dichloroethane; 7, dichloromethane; 8, N,N-dimethylformamide; 9, dimethyl sulfoxide; 10, 2-propanol; 11, ethanol; 12, methanol.

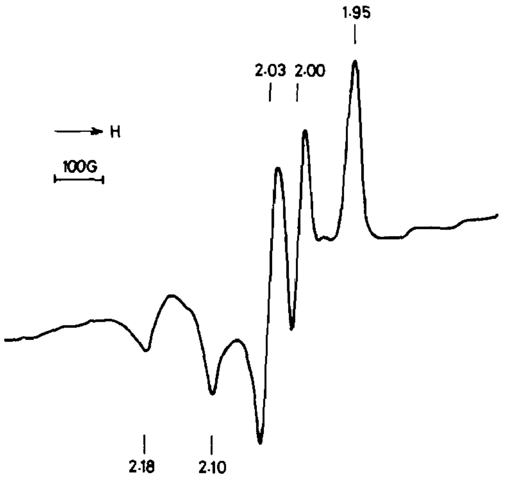

Fig. 3. ESR spectrum of chloroiron(III) complex in N,N-dimethylformamide at 77 K.

to chlorine, and this chloroiron(III) complex becomes a low-spin six-coordinate species from which the ESR signal arises. Similar spectral properties have been observed for intermediate-spin iron(III) complexes derived from tetraaza macrocycles [16].

In conclusion, the nickel(II) complex assumes the square-planar configuration. The iron(III) complex has the N_4Cl-pentacoordination structure in the trivalent state of the nuclear metal and maintains an intermediate-spin state ($S = 3/2$). A strong absorption band in the 581–629 nm region is assigned to the intramolecular CT transition related to the Fe–Cl bond.

Acknowledgement

The authors are indebted to Dr. Seishi Takagi of our college for magnetic susceptibility measurements.

References

1 K. Sakata, M. Hashimoto, N. Tagami and Y. Murakami, *Bull. Chem. Soc. Jpn.*, *53*, 2262 (1980).
2 K. Sakata, H. Nakamura and M. Hashimoto, *Inorg. Chim. Acta*, *83*, L67 (1984).
3 (a) K. M. Smith, 'Porphyrins and Metalloporphyrins', Elsevier, Amsterdam, 1975;
(b) D. Dolphin, 'The Porphyrins, I–V', Academic Press, New York, 1978.
4 V. L. Goedken and Y. Park, *J. Chem. Soc., Chem. Commun.*, 214 (1975).
5 M. C. Weiss, B. Bursten, S. Peng and V. L. Goedken, *J. Am. Chem. Soc.*, *98*, 8021 (1976).
6 M. C. Weiss, G. Gordon and V. L. Goedken, *Inorg. Chem.*, *16*, 305 (1977).
7 E. Lorch and E. Breitmaier, *Chem. Zt.*, *99*, 87 (1975).
8 J. A. VanAllan, *Org. Synth., Coll.*, *4*, 21 (1963).
9 E. Breitmaier and S. Gassenmann, *Chem. Ber.*, *104*, 665 (1971).
10 P. Zeller, F. Bader, H. Lindlar, M. Montavon, P. Muller, R. Ruegg, G. Ryser, G. Saucy, S. F. Schaeren, U. Schwieter, K. Stricker, R. Tamm, P. Zurcher and O. Isler, *Helv. Chim. Acta*, *42*, 841 (1959).
11 R. Ruegg, H. Lindlar, M. Montavon, G. Saucy, S. F. Schaeren, U. Schwieter and O. Isler, *Helv. Chim. Acta*, *42*, 847 (1959).
12 J. A. Riddick and W. B. Bunger, 'Organic Solvents', Wiley Interscience, New York, 1970.
13 S. Sullivan, P. Hambright, B. J. Evans, A. Thorpe and J. Weaver, *Arch. Biochem., Biophys.*, *131*, 51 (1970).
14 L. M.Epstein, D. K. Straub and C. Maricondi, *Inorg. Chem.*, *6*, 1720 (1967).
15 D. H. Dolphin, J. R. Sams and T. B. Tsin, *Inorg. Chem.*, *16*, 711 (1977).
16 S. Koch, R. H. Holm and R. B. Frankel, *J. Am. Chem. Soc.*, *97*, 6714 (1975).
17 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam, 1968.