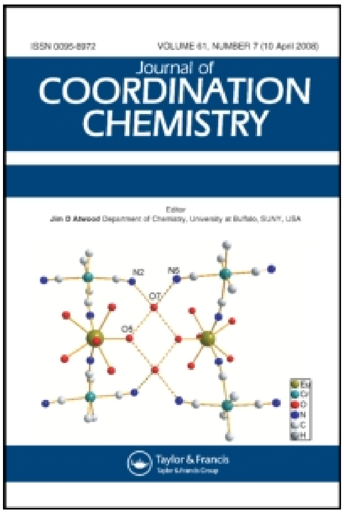

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SYNTHESIS AND PROPERTIES OF NEW DIBENZOTETRAAZA[14] ANNULENES AND ITS METAL CHELATES

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SYNTHESIS AND PROPERTIES OF NEW DIBENZO-TETRAAZA[14] ANNULENES AND ITS METAL CHELATES

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New tetraaza-macrocylic ligands, 6,13-diaryl-1,8-dihydrodibenzo[b,i] [1,4,8,11] tetraazacyclotetradecenes, and its copper(II), nickel(II), cobalt(II) and iron(III) complexes were prepared and characterized. The diimidazole complexes of iron(III) with these N_4-macrocyclic ligands are of low-spin type. ESR and Mossbauer spectral studies led to the conclusion that one unpaired electron lies in the d_{xy} orbital of iron atom for the iron(III) complexes.

INTRODUCTION

A number of macrocyclic complexes have been synthesized and characterized with the dibenzotetraaza[14] annulene framework.[1–4] (cf. Figure 1) Crystallographic studies demonstrated that in the case of $R_1 = R_3 = CH_3$ (cf. Figure 1) the methyl group sterically interact with the benzonoid rings and cause a marked deviation from the planarity for the ligand system leading to a pronounced "saddle shaped" ligand.[5] It was claimed that this peripheral steric constraint is closely connected with the chemical properties observed for the complexes of this ligand.[6]

For the compound of $R_1 = R_2 = R_3 = H$ (cf. Figure 1) the macrocyclic ring is essentially planar,[7] and a considerably unique chemical behavior was observed.[2] In this connection, it is interesting to study the groups of dibenzotetraaza[14] annulene complexes with $R_1 = R_3 = H$ and R_2 = aryl or alkyl.

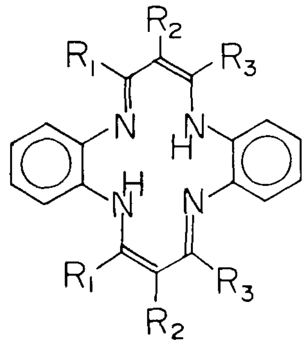


FIGURE 1 Dibenzotetraaza[14] annulenes

TABLE I
Abbreviations of the ligands (cf. Figure 1)

R_1	R_2	R_3	abbreviation	Ref.
H	H	H	H_2(L-a)	2
CH_3	H	CH_3	H_2(L-b)	3
H	$COCH_3$	CH_3	H_2(L-c)	4
H	C_6H_5	H	H_2(L-d)	This work
H	p-CH_3–C_6H_4	H	H_2(L-e)	This work

In this study, we have newly prepared dibenzotetraaza[14] annulenes ($R_1 = R_3 = H$, R_2 = phenyl or p-tolyl) and their metal complexes, and compared the properties of the new compounds with those of the previously reported ones.

EXPERIMENTAL

Preparation of the Ligands:

The general procedure for the preparation of the new ligands with 6,13-diaryl-1,8-dihydrodibenzo[b,i] [1,4,8,11] tetraazacyclotetradecene is as follows.

To the suspension of 4-aryl-1,2-dithiolium hydrogensulfate (0.05 mole) in 300 ml of 1,2-dichloroethane, was added the 1,2-dichloroethane solution (15 ml) containing o-phenylenediamine (10.8 g), drop by drop with stirring, and the solution was refluxed for 7 ~ 8 hours. The resulting red solution was filtered, and evaporated to 10 ml under reduced pressure. The reddish-brown solid that precipitated was filtered and recrystallized from a hot DMF solution.

Preparation of the Metal Complexes

$M(C_{30}H_{22}N_4)$ and $M(C_{32}H_{26}N_4)$; M = Cu(II), Ni(II), Co(II): These complexes were obtained from a boiling DMF solution (30 ml) of the ligand (0.001 mole) and the metal acetate (0.001 mole). The complexes thus obtained were recrystallized from a boiling DMF solution.

Iron(III) complexes: Two types of the new iron(III) complexes were obtained, one is of the formula, Fe H(L-d) Cl_2 (cf. Table 2), and the other, $[Fe(L\text{-}d)(im)_2]^+$, where im represents imidazole. The complex, Fe H(L-d) Cl_2 was obtained by two different methods as described below.

(a) A DMF solution (20 ml) containing anhydrous iron(III) chloride (0.001 mole) and the ligand (0.001 mole) was refluxed for 3 hours. When the solution was cooled to room temperature, black crystals deposited. The yield was very low (less than 10%).

(b) To the iron(II) acetate solution, obtained by dissolving the iron powder in acetic acid, the ligands (0.001 mole) and sodium chloride (200 mg) were added. The solution was refluxed for ca. 3 hours. Upon cooling the solution, black crystals were obtained. These complexes were found to be identical with those obtained by the method (a), as shown in Table 2.

$[Fe(L\text{-}d)(im)_2]Bph_4\cdot CH_3OH$: To a suspension of Fe H(L-d) Cl_2 in DMF, a slight excess of triethylamine was added to obtain a clear green solution. It was evaporated to dryness. The residue was dissolved in a methanol solution of imidazole (500 mg) and filtered. To the filtrate was added $NaBph_4$ (500 mg). After standing one day, green crystals separated from the solution.

Measurements:

ESR spectra were obtained with a JEOL ESR apparatus model JES-3X-ME using an X-band. DPPH was used as a standard marker. The absorption spectra were measured with a Shimadzu Multipurpose MPS-5000 at room temperature. The infrared spectra were obtained with a Hitachi Infrared Spectrophotometer model 215 at room temperature. Magnetic susceptibilities were measured by Faraday method, Pascal's constant being used for diamagnetic correction. The effective magnetic moments were calculated from the expression, $\mu_{eff} = 2.828\sqrt{T\cdot\chi_A}$, where χ_A is the susceptibility per gram atom of iron. The Mossbauer spectra were obtained according to the method described in the separate paper.[8]

RESULTS AND DISCUSSION

Characterization of the New Complexes:

The analytical and mass spectral data of the new compounds are summarized in Table II. As seen in the

TABLE II
Analytical data of the new compounds

compounds	C(%) calcd.	C(%) found	H(%) calcd.	H(%) found	N(%) calcd.	N(%) found
H_2(L-d)[*1]	81.79	(81.52)	5.49	(5.56)	12.72	(12.79)
H_2(L-e)[*1]	82.02	(81.67)	6.02	(6.00)	11.96	(12.23)
[Co(L-d)]	72.43	(72.71)	4.46	(4.54)	11.26	(11.42)
[Ni(L-d)]	72.47	(72.31)	4.46	(4.46)	11.27	(11.30)
[Cu(L-d)]	71.77	(71.75)	4.42	(4.49)	11.16	(11.43)
[Co(L-e)]	73.12	(73.54)	4.99	(5.06)	10.66	(10.34)
[Ni(L-e)]	73.17	(73.46)	4.99	(5.17)	10.67	(11.01)
[Cu(L-e)]	72.50	(72.21)	4.94	(5.03)	10.57	(10.50)
Fe H(L-e) Cl_2[*2]	64.67	(65.07)	4.58	(4.45)	9.43	(9.55)
Fe H(L-e) Cl_2[*3]	64.67	(64.98)	4.58	(4.51)	9.43	(9.23)
Fe H(L-d) Cl_2[*2]	63.63	(63.18	4.09	(3.86)	9.89	(9.59)
$[Fe(L\text{-}d)(im)_2]Bph_4\cdot CH_3OH$[*4]	74.64	(74.65)	5.37	(5.54)	11.47	(11.41)
$[Fe(L\text{-}e)(im)_2]Bph_4\cdot CH_3OH$[*5]	74.92	(74.46)	5.79	(5.70)	11.09	(11.18)

[*1] Mass spectral data are; m/e found for H_2(L-d) 440 (calculated value is 440.20) and 468 found for H_2(L-e) (calculated value is 468.23).

[*2] prepared by method (a) (see text).

[*3] prepared by method (b) (see text).

[*4] μ_{eff} = 2.04 BM (295 K).

[*5] μ_{ff} = 2.02 BM (295 K).

Table, the calculated and experimental values are in satisfactory accordance. The preparative method of the new ligands obtained in this study is similar to those of ethylenediamine and trimethylenedimaine analogues reported by Tang et al.[9]

The new copper(II), nickel(II) and cobalt(II) complexes are likely to be of the planar structure, because the nickel(II) complexes are diamagnetic and the effective magnetic moments, μ_{eff} of the cobalt(II) complexes are in the range 2.28 ~ 2.30 BM.[10]

In Figure 2, the absorption spectra of H_2(L-e) and its nickel(II) complex are shown. The ligand spectrum exhibits several peaks in the range 23000 ~ 26000 cm^{-1}. In the spectrum of the nickel(II) complex, they shift to the lower energy region. A similar behaviour was observed for H_2(L-a) and its nickel(II) chelate.[2]

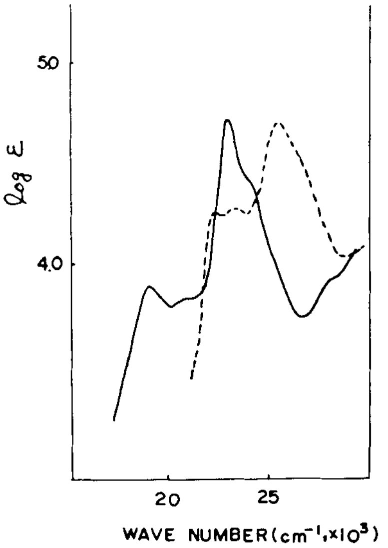


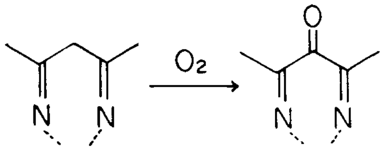
FIGURE 2 Absorption spectra of H_2(L-e) (– – – – –) and [Ni(L-e)] (————) in DMF at room temperature

TABLE III
Infrared spectral data (1200–1700 cm^{-1} region)

H_2(L-d)	1635(s), 1590(s), 1550(s), 1496(s), 1453(m), 1410(s), 1357(s), 1310(s), 1260(m), 1215(s)
[Ni(L-d)]	1632(w), 1607(s), 1598(s), 1580(s), 1490(m), 1466(s), 1442(s) 1300(w), 1380(s), 1348(s), 1207(w)
Fe H(L-d) Cl_2	1592(m), 1572(m), 1540(m), 1500(w), 1452(m), 1430(m), 1372(m), 1300(s), 1253(m), 1202(m), 1190(s)
[Fe(L-d)(im)$_2$]Bph$_4$	1590(m), 1570(w), 1540(w), 1497(m), 1460(s), 1430(m), 1357(s), 1430(s), 1288(m), 1260(w), 1220(s)

The infrared spectral data of H_2(L-d) and its nickel(II) complex are given in Table III. Intense bands were observed at 1635, 1590 and 1550 cm^{-1} for the free ligand, but N–H stretching was not clearly observed. When the ligand complexes with a metal ion, remarkable changes occur in the ranges 1635–1500 and 1280–1320 cm^{-1}. (cf. Table III).

It was reported that [Ni(L-a)] reacts with molecular oxygen in H_2SO_4 solution, and yields brownish-black powder of the experimental formula, $NiC_{18}H_{10}N_4O_2$.[2] However, [Ni(L-d)] and [Ni(L-e)] did not show such a reactivity. It is known that some macrocyclic cobalt(II) complexes react with O_2 molecule at the γ-carbon atom in the chelate ring to yield a ketone.[11] (see below)



Thus, it can be concluded that the substitution of R_2 for H (cf. Figure 1) bring about a marked difference in the reactivity of the compounds under discussion.

In Figure 3, the ESR spectrum of [Cu(L-d)] is shown, g_{av}, $|A_{av}|$, $g_{//}$ and $|A_{//}|$ being 2.070, 97 x 10^{-4} cm^{-1}, 2.127 and 207 x 10^{-4} cm^{-1}, respectively. The $g_{//}$ values of [Cu(L-d)] and [Cu(L-e)] are smaller than those of copper(II) porphyrins and phthalocyanines.[12] This indicates that the σ-donating ability of dibenzotetraaza[14] annulene is greater than that of porphyrins and phthalocyanine, which may probably be related to the limited charge delocalization of the former ligand; that is, resonance forms for the dibenzotetraaza[14] annulenes place appreciable negative charge on the nitrogen atoms, however it is much more widely dispersed on porphyrins and phthalocyanines.[13]

As shown in our previous paper,[10] the ground state configuration of [Co(L-d)] and [Co(L-e)] is different from those of cobalt(II) porphyrin and phthalocyanine.

Characterization of the Iron(III) Complexes

When the porphyrin (for example, α, β, γ, δ-tetraphenyl-porphyrin) is refluxed with iron(II) acetate and sodium chloride in acetic acid, a five coordinate complex, [Fe(tpp)Cl] is formed. Under the same condition, it was found that the ligands, H_2(L-d) and

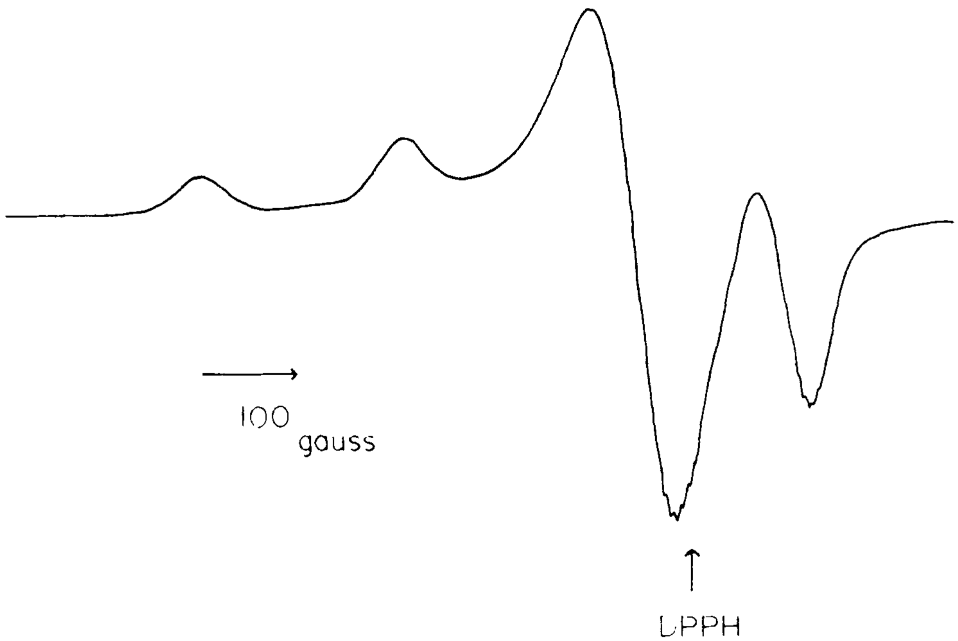


FIGURE 3 ESR spectrum of [Cu(L-d)] (diluted in [Ni(L-d)]) obtained at 77 K

H_2(L-e), give the iron(III) complexes with the experimental formula, Fe H(L-d) Cl_2. For these complexes, two structures can be considered, that is,

a) [Fe(L-d)Cl]·HCl (five-coordinated complex), and

b) [Fe H(L-d) Cl_2] (six-coordinated complex),

as shown in Figure 4. In (b), the ligand system has 14π electrons, whereas, 16π electrons in (a). The infrared spectrum of Fe H(L-d) Cl_2 is greatly different in the range 1500 ~ 1650 cm^{-1} from those of the corresponding nickel(II) complex and $[Fe(L\text{-}d)(im)_2]^{2+}$ (cf. Table III), however it is uncertain that the structure of Fe H(L-d) Cl_2 is of (a) or (b) at present.

The diimidazole complex, $[Fe(L\text{-}d)(im)_2]^+$ is the low-spin type. (cf. Table 2) In Figure 5, the ESR spectrum of $[Fe(L\text{-}d)(im)_2]^+$ is shown. The observed *g*-values are 2.20, 2.12 and 1.97. The absolute value of the quadrupole splitting, $|\Delta E_q|$ is 3.02 mm/sec for $[Fe(L\text{-}d)(im)_2]Bph_4 \cdot CH_3OH$ (at 77 K).

Recently Nishida et al.[14,15] have investigated the relationship among the *g*-values, quadrupole splitting and the ground state configuration of the six-coordinated iron(III) complexes. There are two possible ground state configurations for low-spin iron(III) complexes, i.e., $(d_{xz})^2(d_{xy})^2(d_{yz})^1$ and $(d_{xz})^2(d_{yz})^2(d_{xy})^1$.[15] According to our results, the low-spin iron(III) complexes of the $[FeN_6]$ type with the $(d_{xy})^2(d_{xz})^2(d_{yz})^1$ ground state show the different features of ESR parameters and quadrupole splitting, from those with the $(d_{xy})^1(d_{xz})^2(d_{yz})^2$

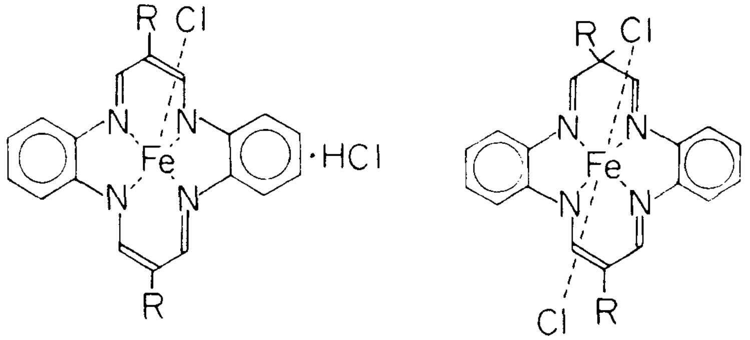


FIGURE 4 Two possible structures for Fe H(L-d) Cl_2 and Fe H(L-e) Cl_2

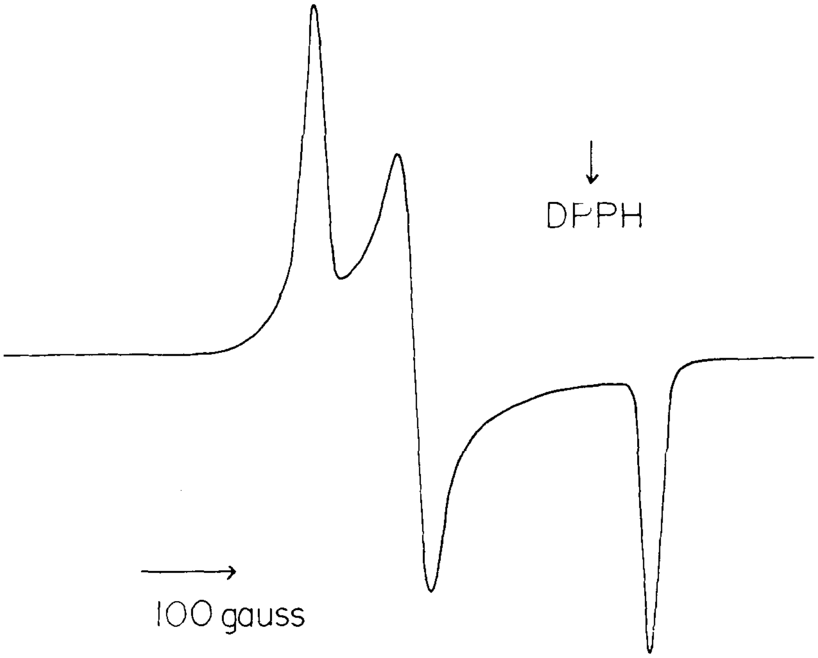


FIGURE 5 ESR spectrum of $[Fe(L\text{-}d)(im)_2]Bph_4$ obtained at 77 K in DMF frozen solution

ground state. That is, the smaller anisotropy of *g*-values and the larger absolute values of ΔE_q (about $|\Delta E_q| \sim 3.0$ mm/sec) are observed for the complexes with the $(d_{xy})^1(d_{xz})^2(d_{yz})^2$ ground state configuration.[15] Therefore we can assume that an unpaired electron in $[Fe(L\text{-}d)(im)_2]^+$ complex lies in the d_{xy} orbital of the iron atom.

As shown in Table IV, the ground state configuration of the $[Fe(L')(im)_2]^+$ complexes (where L′ represents various N_4-macrocyclic ligands) is $(d_{xz})^2(d_{yz})^2(d_{xy})^1$, except for porphyrins. The most important factor to determining the ground state configuration of these low-spin iron(III) complexes seems to be the π-interaction between metal $d_\pi(= d_{xz}, d_{yz})$ and ligand π-orbitals, because d_{xy} orbital is assumed to be non-bonding orbital in these complexes.[16,17] If the interaction between metal d_π and ligand π-orbital is stronger than that of $d_\pi - \pi^*$, the ground state must be $(d_{xy})^2(d_{xz})^2(d_{yz})^1$, and vice versa. The extent of the interaction between $d_\pi - \pi$ orbitals may be determined by the ionization potentials of these orbitals in the metal complexes. The ionization potential of the *d*-orbitals in metal complexes is mainly determined by the σ-donating ability of the N_4-macrocyclic ligands.[18] According to our recent ESR studies on the copper(II) complexes with various N_4-macrocyclic ligands,[19] the σ-donor ability of porphyrin is found to be much smaller than those of 14-membered N_4-macrocyclic ligands listed in Table IV. Therefore, the results in Table IV can be understood in the following manner. In the porphyrin complexes, the ionization potential of *d*-orbital is larger than those of complexes with other N_4-macrocyclic ligands, because of its weaker σ-donating ability, resulting the stronger interaction between d_π and π-orbitals than that of d_π and π^*-orbitals. In the case of other 14-membered N_4-macrocyclic ligands, the *d*-orbitals are destabilized

TABLE IV
ESR and Mossbauer data of $[Fe(L')(im)_2]$ complexes

L′	ESR parameter	$\lvert\Delta E_q\rvert$ (mm/sec)	Ref.
porphyrin	$g_z = 2.91, g_x = 1.53, g_y = 2.26$	2.12	22
[14] tetraeneN_4	$g_1 = 2.10, g_2 = 2.04, g_3 = 1.99$	–	21
dimethylglyoxime	$g_\perp = 2.28, g_\parallel = 1.96$	2.84	15
[14] hexaeneN_4	$g_1 = 2.20, g_2 = 2.12, g_3 = 1.97$	3.02	This work

due to their stronger σ-donor ability, therefore the interaction between d_π and π^*-orbitals is stronger than that of $d_\pi-\pi$ interaction. A similar discussion as described above may be applied to elucidate the ground state configuration of the square planar cobalt(II) complexes with various N_4-macrocyclic ligands.[20]

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