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Registry No. Cu(baen·CONH(Ph)), 50520-15-5; Cu(baen·2CONH(Ph)), 50520-21-3; Cu(baen·CONH(Et)), 50520-16-6; Cu(baen·2CONH(Et)), 50495-29-9; Cu(baen·CONH(Me)), 50520-17-7; Cu(baen·2CONH(Me)), 50520-22-4; Cu(baen·CONH(*i*-Pr)), 50520-18-8; Cu(baen·2CONH(*i*-Pr)), 50520-23-5; Cu(baen·CONH(*t*-Bu)), 50520-19-9; Cu(baen·2CONH(*t*-Bu)), 50520-24-6; Cu(baen·CONH(1-naphth)), 50520-14-4; baen, 6310-76-5; baen·CONHPh, 50564-45-9; baen·2CONHPh, 50564-39-1; baen·CONHEt, 50564-46-0; baen·2CONHEt, 50564-40-4; baen·CONHMe, 50564-47-1; baen·2CONHMe, 50564-41-5; baen·CONH-*i*-Pr, 50564-48-2; baen·2CONH-*i*-Pr, 50564-42-6; baen·CONH-*t*-Bu, 50479-45-3; baen·2CONH-*t*-Bu, 50564-43-7; EtNCO, 109-90-0; MeNCO, 624-83-9; *i*-PrNCO, 1795-48-8; *t*-BuNCO, 1609-86-5; 1-naphthNCO, 86-84-0; PhNCO, 103-71-9; Ni(baen·CONH(Et)), 50520-07-5; PhNCS, 103-72-0; IX (R = Ph), 57091-05-1; Cu(baen), 36885-37-7; Ni(baen)·2naphthNCO, 50495-20-0; Ni(baen)·PhNCO, 50495-23-3; Cu(bapn)·2naphthNCO, 57108-97-1; Cu(baen)·NCO$(CH_2)_6$NCO, 57108-96-0; Ni(baen), 36802-27-4; acetoacetanilide, 102-01-2; *N*-methylacetoacetamide, 20306-75-6; *N*-ethylacetoacetamide, 10138-46-2.

References and Notes

(1) Presented in part at the 28th Northwest Regional Meeting of the American Chemical Society, Pullman, Wash., June 14, 1973, see Abstract I.6.

(2) (a) University of Nevada, Reno; (b) China Lake Naval Weapons Center.

(3) J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition-Metal Complexes", Elsevier, New York, N.Y., 1968.

(4) M. M. Jones, "Ligand Reactivity and Catalysis", Academic Press, New York, N.Y., 1968.

(5) D. H. Busch, *Adv. Chem. Ser.*, **No. 37** (1963).

(6) B. J. Luberoff, *Adv. Chem. Ser.*, **No. 70** (1968).

(7) J. R. Collman, *Angew. Chem., Int. Ed. Engl.*, **4**, 132 (1965).

(8) P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1955); D. F. Martin and F. F. Cantwell, *J. Inorg. Nucl. Chem.*, **26**, 2219 (1964).

(9) J. W. Kenney, J. H. Nelson, and R. A. Henry, *J. Chem. Soc., Chem. Commun.*, 690 (1973).

(10) R. W. Kluiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).

(11) L. F. Lindoy, H. C. Lip, and W. E. Moody, *J. Chem. Soc., Dalton Trans.*, 44 (1974).

(12) C. J. Hipp and D. H. Busch, *Inorg. Chem.*, **12**, 894 (1973).

(13) K. S. Bose and C. C. Patel, *J. Inorg. Nucl. Chem.*, **33**, 2947 (1971).

(14) K. Dey and R. L. De, *J. Inorg. Nucl. Chem.*, **36**, 1182 (1974).

(15) Y. Fujii and K. Shinra, *Bull. Chem. Soc. Jpn.*, **43**, 1722 (1970).

(16) I. Masuda, M. Tamaki, and K. Shinra, *Bull. Chem. Soc. Jpn.*, **42**, 157 (1969).

(17) Z. Bukac and J. Sebenda, *Collect. Czech. Chem. Commun.*, **31**, 3315 (1966).

(18) M. Avram and G. H. D. Mateescu, "Infrared Spectroscopy", Wiley-Interscience, New York, N.Y., 1972, p 440 ff.

(19) P. Laszlo and P. Stang, "Organic Spectroscopy", Harper and Row, New York, N.Y., 1971, pp 152–154.

(20) G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2029 (1961).

(21) See ref 19, p 221.

(22) L. Capuano, H. R. Kirn, and M. Kalweit, *Chem. Ber.*, **106**, 3677 (1973).

(23) L. Capuano and R. Zander, *Chem. Ber.*, **106**, 3670 (1973).

(24) K. Ueno and A. E. Martell, *J. Phys. Chem.*, **61**, 257 (1957).

(25) L. A. Funke and G. A. Melson, *Inorg. Chem.*, **14**, 306 (1975).

(26) Anal. Calcd for Ni(baen)·2naphth NCO, $C_{34}H_{32}N_4O_4Ni$: C, 65.96; H, 5.17; N, 9.05; Ni, 9.48. Found: C, 65.91; H, 5.07; N, 9.00; Ni, 9.40; dec pt 238–240°C. Anal. Calcd for Ni(baen)·PhNCO, $C_{19}H_{23}N_3O_3Ni$: C, 57.06; H, 5.76; N, 10.50; Ni, 14.68. Found: C, 57.38; H, 5.83; N, 10.29; Ni, 14.85; dec pt 235–238°C. The infrared spectra were virtually identical with those of the copper analogues.

(27) Anal. Calcd for Cu(bapn)·2naphth NCO, $C_{35}H_{34}N_4O_4Cu$: C, 65.87; H, 5.37; N, 8.78; Cu, 9.96. Found: C, 65.86; H, 5.27; N, 8.14; Cu, 9.31; dec pt 177–179°C.

(28) I. Takagi and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **46**, 3593 (1973).

(29) W. H. Elfring, Jr., and N. J. Rose, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1970.

(30) J. G. Martin and S. C. Cummings, *Inorg. Chem.*, **12**, 1477 (1973).

(31) R. D. Burkhart, personal communication. η reduced in methanol is 0.67 which is indicative of a polymer.

(32) Anal. Calcd for Cu(baen)·NCO$(CH_2)_6$NCO, $C_{20}H_{30}N_4O_4Cu$: C, 53.00; H, 6.61; N, 12.6; Cu, 14.00. Found: C, 52.99, H, 6.77; N, 12.07; Cu, 14.53. The infrared spectrum shows ν_{NH} (3210 cm^{-1}) and $\nu_{C=O}$ (1615 cm^{-1}) and the absence of the methine ν_{CH} ($\sim$1140) and ν_{NCO} suggesting that the polymer terminates with the complex and not with NCO groups. This material is flammable with difficulty in an open flame and burns with a copper green flame.

(33) We thank a referee for this suggestion: L. F. Lindoy and W. E. Moody, *J. Am. Chem. Soc.*, **97**, 2276 (1975).

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Manganese and Zinc Complexes Incorporating an Unsaturated Cyclic Schiff Base Ligand

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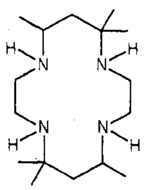
A number of manganese(II) and -(III) as well as two zinc(II) complexes with the conjugated cyclic Schiff base, $H_2[14]12eneN_4$, have been synthesized and fully characterized. The high-spin Mn(III) complexes have the stoichiometry Mn(III)$[14]12eneN_4X$, where X is Cl^-, Br^-, SCN^-, and N_3^-. The compounds are intensely colored and exhibit a number of electronic transitions which appear to be associated with the ligand framework. The reduced magnetic moment of the azide derivative suggests that for this complex the Mn(III) ions are linked via an azide bridge in the solid state. Manganese(II) and zinc(II) form five-coordinate complexes with $H_2[14]12eneN_4$ having stoichiometry M(II)$[14]12eneN_4$(amine), where amine is triethyl- or tri-*n*-propylamine. NMR studies on the diamagnetic zinc(II) complexes indicate that the sterically hindered tertiary amine is axially coordinated to the metal ion. The distorted five-coordinate geometry is attributed to the mismatch between the relatively large high-spin d^5 and d^{10} metal ions and the hole provided by the macrocyclic ligand. The chemical reactivity of the complexes is also discussed.

Introduction

Although a considerable effort has been expended on the study of manganese–porphyrin complexes,[1] examples of synthetic macrocyclic ligands complexed to manganese are rare. The facile variation of ring size, charge, and unsaturation of cyclic Schiff bases and their analogues[2,3] permit the exploration of structure–function relationships which cannot be readily examined in metalloporphyrin chemistry. In an effort to explore the properties of manganese complexes containing synthetic macrocyclic ligands, we reported the synthesis and characterization of a number of complexes with the saturated uncharged tetraazo macrocyclic ligand *meso*-$[14]aneN_4$ (**1**).[4,5]



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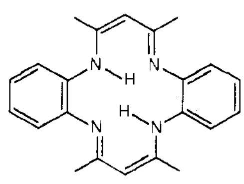

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This report deals with the synthesis and properties of man-

Table I. Analyses for the Macrocyclic Complexes

		Calcd %				Found %			
Compd	Axial ligand[a]	C	H	N	Other	C	H	N	Other
$\mathrm{H_2[14]12eneN_4}$		76.71	7.02	16.27		76.51	7.14	16.34	
$\mathrm{Zn(II)[14]12eneN_4}$	$\mathrm{N(Et)_3}$	66.02	7.27	13.75		65.50	7.37	13.96	
$\mathrm{Zn(II)[14]12eneN_4}$	$\mathrm{N(\textit{n}\text{-}Pr)_3}$	67.56	7.86	12.70		67.14	7.95	12.87	
$\mathrm{Mn(II)[14]12eneN_4}$	$\mathrm{N(Et)_3}$	67.45	7.48	14.05		67.63	7.76	14.10	
$\mathrm{Mn(II)[14]12eneN_4}$	$\mathrm{N(\textit{n}\text{-}Pr)_3}$	68.88	7.98	12.96		69.07	8.18	13.69	
$\mathrm{Mn(III)[14]12eneN_4}$	$\mathrm{Cl^-}$ [b]	60.83	5.32	14.77	(Cl) 7.48	61.00	5.17	14.60	(Cl) 7.52
$\mathrm{Mn(III)[14]12eneN_4}$	$\mathrm{Br^-}$ [b]	55.56	4.82	13.50		55.45	4.98	13.58	
$\mathrm{Mn(III)[14]12eneN_4}$	$\mathrm{NCS^-}$	60.65	4.83	15.36	(S) 7.02	60.75	4.92	15.91	(S) 6.92
$\mathrm{Mn(III)[14]12eneN_4}$	$\mathrm{N_3^-}$	60.14	5.05	22.31		59.63	5.48	22.38	

[a] Abbreviations: Et is $\mathrm{C_2H_5}$, *n*-Pr is $\mathrm{(CH_2)_2CH_3}$. [b] Crystallizes with one molecule of acetonitrile.

Table II. Physical Properties of the Complexes

			Mass spectra *m/e*		
Complex	Axial ligand[a]	$\mu_{\mathrm{eff}}, \mu_{\mathrm{B}}$	Calcd	Obsd	Infrared spectra cm^{-1}
$\mathrm{Zn(II)[14]12eneN_4}$	$\mathrm{N(Et)_3}$	dia	508	407[b]	1530 (s), 1260 (m), 1175 (s), 1035 (m), 1015 (m), 813 (w), 737 (s)
$\mathrm{Zn(II)[14]12eneN_4}$	$\mathrm{N(\textit{n}\text{-}Pr)_3}$	dia			1530 (s), 1260 (m), 1175 (s), 1015 (m), 910 (w), 737 (s)
$\mathrm{Mn(II)[14]12eneN_4}$	$\mathrm{N(Et)_3}$	5.99	498	397[b]	1540 (s), 1260 (m), 1175 (s), 1150 (m), 1018 (m), 750 (s)
$\mathrm{Mn(II)[14]12eneN_4}$	$\mathrm{N(\textit{n}\text{-}Pr)_3}$	5.86			1540 (s), 1265 (m), 1175 (s), 1020 (m), 750 (s), 740 (s)
$\mathrm{Mn(III)[14]12eneN_4}$	$\mathrm{Cl^-}$ [c]	4.96	473	432[d]	2252 (vw), 1520 (s), 1260 (w), 1185 (w), 1025 (m), 758 (s), 290 (s)
$\mathrm{Mn(III)[14]12eneN_4}$	$\mathrm{Br^-}$ [c]	4.96	518	477[d]	2252 (vw), 1520 (s), 1260 (w), 1185 (w), 1025 (m), 790 (w), 773 (s), 750 (s), 738 (s)
$\mathrm{Mn(III)[14]12eneN_4}$	$\mathrm{SCN^-}$	5.05	455	455	2060 (vs), 1520 (s), 1195 (w), 1025 (m), 980 (w), 792 (w), 758 (s), 750 (s)
$\mathrm{Mn(III)[14]12eneN_4}$	$\mathrm{N_3^-}$	4.78			2054 (vs), 1520 (s), 1191 (w), 1020 (m), 791 (w), 752 (m), 741 (w), 718 (w)

[a] Et is $\mathrm{C_2H_5}$, *n*-Pr is $\mathrm{(CH_2)_2CH_3}$. [b] $\mathrm{[M(II)[14]12eneN_4]^+}$. [c] Crystallizes with one molecule of acetonitrile. [d] $\mathrm{[Mn(III)[14]12eneN_4X]^+}$.

ganese(II) and -(III) as well as two structurally related zinc(II) complexes with the macrocyclic Schiff base $\mathrm{H_2[14]12eneN_4}$ (**2**). Since this ligand is a charged, highly conjugated macrocycle, it possesses electronic and structural properties which are significantly different than those associated with **1**. These differences are reflected in the properties of the metal complexes which it forms.

The Cu(II) and Ni(II) complexes of $\mathrm{H_2[14]12eneN_4}$ were first reported by Jager.[6] Later Goedken et al.[7] modified the preparation of the nickel complex and reported the isolation of the free ligand. These workers also described the synthesis of a number of Fe(II) complexes[8] as well as the preparation and single-crystal x-ray analysis of $\mathrm{[Fe(III)[14]12eneN_4(C_6H_5)]}$[9] and $\mathrm{[Fe(II)[14]12eneN_4(CO)(H_2NNH_2)]}$.[7] No manganese or zinc complexes with $\mathrm{H_2[14]12eneN_4}$ have yet been reported.

Experimental Section

Physical Measurements. A Perkin-Elmer 137 or a 521 spectrometer was used for the infrared measurements. Nujol mulls between KBr plates (4000–400 cm^{-1}) or polyethylene plates (400–250 cm^{-1}) were employed. NMR spectra of the $\mathrm{Zn(II)[14]12eneN_4}$(amine) complexes were obtained by dissolving 10–20 mg of the compound in 0.5 ml of degassed benzene-*d*$_6$. A Varian A-60 or a T60-A spectrometer was used for the measurements. All chemical shifts are reported in ppm relative to TMS.

The ability of various coordinating agents to displace the bound amine was examined by adding small amounts of acetonitrile, pyridine, or trimethyl phosphite to the NMR solutions. After the addition of a fivefold molar excess of each reagent, the chemical shift of the amine signals was measured. The resonances were unaffected by acetonitrile or trimethyl phosphite but were shifted to those of the free amine by addition of pyridine (see text for values). The ability of Ni(II)-$\mathrm{[14]12eneN_4}$ to bind the tertiary amine was checked by adding an equal molar amount of triethylamine to the benzene-*d*$_6$ NMR solution. The chemical shifts of the amine signals were identical with those of the free amine in benzene.

Electronic absorption spectra were determined on 10^{-4} *M* solutions using either a Cary 14 or a 118C spectrophotometer. Due to extreme air sensitivity, reliable values of the extinction coefficients for the Mn(II) complexes could not be determined. Solid state mull spectra (4.3–30 kK) were recorded at room temperature using filter paper impregnated with Halocarbon 25-S5 grease and the compound. Since the agreement between the solid and solution spectra was generally good, only the solution data are presented. The conductivity measurements were run at room temperature on 10^{-3}–10^{-4} *M* solutions using a Yellow Springs Instrument Company Model 31 conductivity bridge. All of the complexes are nonconductors in $\mathrm{CH_2Cl_2}$. In addition, the Mn(III) complexes are also nonelectrolytes in acetonitrile. The solvents used for the uv-visible spectral and conductivity measurements were purified by standard techniques.[10]

Magnetic moment measurements at room temperature in the solid state were determined on 10–20 mg of sample using the Faraday method.[11] The diamagnetic correction for $\mathrm{H_2[14]12eneN_4}$ was found to be -215×10^{-6} cgs unit.

ESR spectra of the Mn(II) complexes between 500 and 8500 G were obtained using a Varian E-9 spectrometer. The spectra of the two Mn(II) complexes were recorded under $\mathrm{N_2}$ in the solid state at room temperature and in toluene glasses at 77°K. Low resolution mass spectral measurements were supplied by Cornell University, Mass Spectrometry Service, Ithaca, N.Y. Elemental analyses were performed by Galbraith Labs, Nashville, Tenn., Instranal-Labs, Rennselaer, N.Y., and Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Analytical data for the ligand and the Mn and Zn complexes are presented in Table I. Spectral and other properties are summarized in Tables II–IV.

Syntheses. Although the Mn(III) and Zn(II) complexes are not oxygen sensitive, all of the syntheses were carried out under nitrogen in a drybox. The tertiary amines required for the preparation of the Mn(II) and Zn(II) complexes were dried by distillation off of Na metal.

$\mathbf{H_2[14]12eneN_4}$. The ligand was synthesized via its Ni(II) complex using the method of Goedken et al.[7] For $\mathrm{H_2[14]12eneN_4}$: NMR ($\mathrm{CDCl_3}$): δ 2.18 (s, $\mathrm{CH_3}$), 4.98 (s, CH), 7.20 (s, aro), 13.04 (s, NH); mass spectrum *m/e* calcd 344, obsd 344.

$\mathbf{[Mn(III)([14]12eneN_4)X]\cdot CH_3CN}$ Where X is $\mathbf{Cl^-}$ and $\mathbf{Br^-}$ and

Table III. Spectral Properties of the Complexes[a]

Compd	Axial ligand[b]	Absorption[c]
$Zn(II)[14]12eneN_4$	$N(Et)_3$	20.4 (sh), 26.8 (10800), 36.2 (2870), 39.3 (sh), 43.5 (sh)
$Zn(II)[14]12eneN_4$	$N(n\text{-}Pr)_3$	20.4 (sh), 26.7 (11900), 36.1 (3150), 39.2 (sh), 43.4 (sh)
$Mn(II)[14]12eneN_4$[d]	$N(Et)_3$	21.5 (sh), 23.8 (sh) 26.3, 27.8 (sh), 33.9 (sh)
$Mn(III)[14]12eneN_4$	Cl^-	14.7 (sh), 16.7 (1480), 17.9 (sh), 21.6 (5880), 22.8 (sh), 25.9 (sh), 27.9 (26800), 32.3 (sh), 35.2 (sh), 36.6 (22500)
$Mn(III)[14]12eneN_4$[e]	Cl^-	15.8, 20.4 (sh), 25.1 (sh), 32.8
$Mn(III)[14]12eneN_4$	Br^-	15.2 (sh), 16.4 (1300), 17.5 (sh), 21.6 (5600), 22.7 (sh), 26.0 (sh), 27.9 (23400), 32.3 (sh), 34.7 (sh), 36.8 (20600)
$Mn(III)[14]12eneN_4$	SCN^-	14.9 (sh), 16.7 (1400), 17.5 (sh), 21.7 (5300), 22.7 (sh), 26.1 (sh), 28.2 (23100), 32.8 (sh), 35.2 (sh), 37.1 (18800)
$Mn(III)[14]12eneN_4$	N_3^-	14.7 (sh), 17.1 (2140), 17.5 (sh), 21.5 (6700), 22.9 (sh), 27.7 (sh), 28.0 (26500), 32.6 (sh), 35.0 (sh), 37.0 (24100)

[a] Unless otherwise noted the spectra were determined in acetonitrile solution. [b] Et is C_2H_5, n-Pr is $(CH_2)_2CH_3$. [c] The absorption maximum in kK is given followed by the molar extinction coefficient in $mol^{-1}\ l\ cm^{-1}$. [d] Toluene solution. The spectrum of the $N(n\text{-}Pr)_3$ derivative is identical with the $N(Et)_3$ analogue. [e] A 10^{-4} M solution of the complex in acetonitrile containing 0.1 M HSO_3CF_3.

Table IV. NMR Spectra of the $Zn(II)[14]12eneN_4$ Complexes

Complex[a]	Chemical shifts
$Zn(II)[14]12eneN_4(N(Et)_3)$	0.82[b] (amine, CH_3), 2.09 (CH_3), 2.22[c] (amine, CH_2), 4.62 (CH), 6.91 (aro)
$Zn(II)[14]12eneN_4(N(n\text{-}Pr)_3)$	0.72[b] (amine, CH_3), 1.5[d] (amine, CH_2), 2.09 (CH_3), 2.11[d] (amine NCH_2), 4.62 (CH), 6.91 (aro)

[a] Et is C_2H_5 and n-Pr is $(CH_2)_2CH_3$. [b] Triplet. [c] Quartet. [d] Center of multiplet.

$[Mn(III)([14]12eneN_4)X]$ Where X is NCS^- and N_3^-. To 50 ml of a refluxing acetonitrile solution containing 0.75 g (2.6 mmol) of $Mn(III)(acac)_2X$[12,13] was added a hot acetonitrile solution of the ligand (0.89 g dissolved in 100 ml). After mixing, the green solution was set aside to cool for 8 hr. The dark green complexes which formed were recovered by filtration, washed with a small amount of acetonitrile, and dried under a stream of N_2 gas. Prior to analysis each complex was dried at room temperature over P_4O_{10} under vacuum (0.01 mm) for 1 day. The yield of each complex was about 0.75 g.

$M(II)([14]12eneN_4)(amine)$ Where M is Mn and Zn and the Amine is $N(C_2H_5)_3$ or $N((CH_2)_2CH_3)_3$ and Attempted Synthesis of $Ni(II)[14]12eneN_4(amine)$. To 2.60 mmol of an acetonitrile metal solvate,[4,14] $M(II)(SO_3CF_3)_2$, dissolved in 100 ml of hot acetonitrile (50°) was added 150 ml of a hot acetonitrile solution containing 0.89 g (2.60 mmol) of $H_2[14]12eneN_4$. After the addition of 5.2 mmol of triethylamine or tri-n-propylamine, the solution was set aside to crystallize for 8 hr. The red-orange zinc and brown manganese complexes were removed by filtration, washed with a small amount of acetonitrile, and dried under a stream of nitrogen gas. The reaction yielded about 0.75 g of each complex.

Working on the above scale the synthesis of $Ni(II)[14]12eneN_4(amine)$ from $Ni(CH_3CN)_6(BF_4)_2$[15] and the free ligand was attempted. The complex crystallized without the amine and had properties identical with those earlier reported for $Ni(II)[14]12eneN_4$.[6] The yield was about 0.6 g.

Protonation of $[Mn(III)[14]12eneN_4Cl]\cdot CH_3CN$. To 3 ml of a 10^{-4} M solution of the complex in acetonitrile was added 50 μl of HSO_3CF_3. The absorption spectrum of the solution from 800 to 250 mn was recorded immediately after acidification. After addition of Et_3N the spectrum was recorded again.

Results and Discussion

General. Initial attempts to synthesize the manganese complexes concentrated on using simple Mn(II) salts in a metal template reaction.[3] For manganese this approach has been successful in at least one other case. Alexander et al.[16] have shown that the pentadentate cyclic Schiff base formed from triethylenetetramine and 2,6-diacetylpyridine could be synthesized in the presence of $MnCl_2$. However, condensation of o-phenylenediamine with acetylacetone in the presence of $MnCl_2$ or $Mn(CH_3CO_2)_2\cdot 4H_2O$ did not lead to $Mn(II)[14]12eneN_4$. Infrared characterization of the solids isolated from the reaction suggested that the cycle was not formed. The approach which ultimately proved successful in the synthesis of the manganese as well as zinc complexes is outlined in eq 1 and 2. These methods rely on the synthesis of the

$$H_2[14]12eneN_4 + Mn(III)(acac)_2X \rightarrow Mn(III)[14]12eneN_4X + 2Hacac \qquad (1)$$

$$(X = Cl^-, Br^-, SCN^-, N_3^-)$$

$$H_2[14]12eneN_4 + Mn(II)(SO_3CF_3)_2 \xrightarrow[N_2]{base} M(II)[14]12eneN_4(base)$$

$$(M = Mn, Zn) \qquad (2)$$

ligand via its nickel complex. Demetalation of $Ni(II)[14]12eneN_4$ in methanolic HCl yields the dihydrochloride salt of the macrocycle which can be neutralized with triethylamine.[7] The free ligand is a stable yellow solid which is soluble in a number of organic solvents.

The Manganese(III) Complexes. Marianelli et al.[17,18] have shown that certain five-coordinate bis(acetylacetonato) Mn(III) complexes are sufficiently labile to be used as intermediates in the synthesis of manganese(III) porphyrins. Since **2** is similar to that of the porphyrin ring system (conjugated and coordinates as a dianion) the reaction outlined in eq 1 was employed. However, this approach does not appear to be general for the synthesis of other manganese(III) complexes containing synthetic macrocyclic ligands. The reaction of the saturated ligand, **1**, with $Mn(III)(acac)_2X$ does not give Mn(III) products. Moreover, the use of Mn(III)–acac complexes as a source of the metal ion may be limited by coordination unsaturation. The six-coordinate complex $Mn(III)(acac)_3$ does not appear to react with $H_2[14]12eneN_4$ in acetonitrile solution.

The manganese(III) complexes with $H_2[14]12eneN_4$ were isolated as green crystalline solids from acetonitrile. On the basis of elemental analyses, compounds with two different stoichiometries are formed (Table I). The chloro and bromo derivatives crystallize with a molecule of acetonitrile and have stoichiometry $[Mn(III)[14]12eneN_4X]\cdot CH_3CN$ while the thiocyanate and azide derivatives can be isolated unsolvated. On the basis of conductance measurements all of the complexes are nonelectrolytes in CH_2Cl_2 and CH_3CN. Available evidence for the halide derivatives suggests that the CH_3CN molecule is uncoordinated or at best only weakly bonded to the metal ion. A very weak infrared stretch for CH_3CN can be observed at 2252 cm^{-1} (Table II). Doping small amounts of acetonitrile into the Nujol mull of the complex showed this absorption to be degenerate with that of free acetonitrile. Furthermore, the solvent molecule is easily lost in the gas phase. For both complexes the largest m/e value observed in their mass spectra corresponds to $[Mn(III)[14]12eneN_4X]^+$ (Table II). However, attempts to remove the nitrile molecule by subjecting the solid complexes to a vacuum (0.02 mm) for 2 days were not successful. Elemental analyses before and after exposure to the vacuum were identical. Similar treatment of the macrocyclic complex, $[Fe(II)[14]aneN_4(CH_3CN)_2](BF_4)_2$, which contains coordinated acetonitrile resulted in the facile removal of the axial ligands.[19]

The room-temperature magnetic moments of $Mn(III)[14]12eneN_4X$ are indicative of high-spin d^4 ($S = 2$) systems.

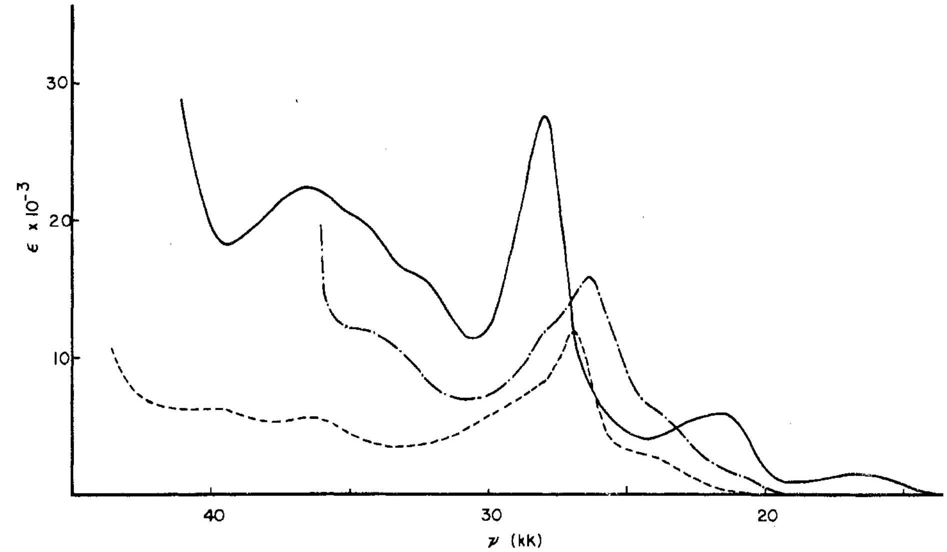


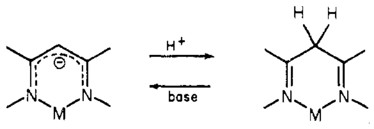
Figure 1. The absorption spectra of the complexes: (a) Mn(III)[14]12eneN$_4$Cl in CH$_3$CN (—); (b) Mn(II)[14]12eneN$_4$(NEt$_3$) in toluene (– · –) (due to the air sensitivity of this complex the value of the extinction coefficient has not been determined); (c) Zn(II)[14]12eneN$_4$(NEt$_3$) in CH$_3$CN (- - -).

The values for the Cl$^-$, Br$^-$, and SCN$^-$ derivatives range from 4.96 to 5.05 μ_B and are consistent with those found for [Mn(III)[14]aneN$_4$X$_2$]$^+$ and a number of Mn(III)–porphyrin complexes.[1,4] The moment for the N$_3^-$ complex, μ_{eff} 4.78 μ_B, is significantly lower than the others. A magnetic moment less than ~4.9 μ_B would be consistent with antiferromagnetically coupled Mn(III) ions via an N$_3^-$ bridge.[13]

All of the complexes display similar infrared spectra (Table II). The thiocyanate derivative gives an intense absorption at 2060 cm^{-1} which is associated with the C≡N stretch of the SCN$^-$ anion. However, the C–S stretching mode of SCN$^-$ is apparently obscured by ligand absorptions. The latter has been shown to be diagnostic of N or S bonded SCN$^-$.[20] A strong absorption due to N$_3^-$ in [Mn(III)[14]12eneN$_4$N$_3$] can be observed at 2054 cm^{-1}.

Figure 1 shows the absorption spectrum of Mn(III)[14]12eneN$_4$Cl which is typical of the Mn(III) complexes. The bands appear to be associated with the ligand framework and are not of d–d origin as in the case of [Mn(III)[14]aneN$_4$X$_2$]$^+$.[4] Three reasons for this conclusion can be cited. The extinction coefficients of the bands (10^3–10^4 mol^{-1} cm^{-1}l.) are larger than those normally assigned to d–d electronic transitions.[21] In addition, Zn(II)[14]12eneN$_4$(NEt$_3$) and Mn(II)[14]12eneN$_4$(NEt$_3$), which contain a closed shell d^{10} and a high-spin d^5 metal ion, respectively, exhibit absorption spectra which are similar to those of the manganese(III) complexes (Figure 1 and Table III). Finally, the expected crystal field changes associated with the axial anions (*Dq*, N$_3^-$ ~ NCS$^-$ > Cl$^-$ > Br$^-$) are not reflected in the absorption spectra. The spectra for all four Mn(III) derivatives are nearly superimposable (Table III). The band maxima are independent of the coordinating ability of the solvent. The spectra of the Mn(III) complexes in CHCl$_3$, benzene, and acetonitrile except for small changes in the extinction coefficients are identical. This behavior contrasts with the spectra of certain Mn(III)–porphyrin complexes which show some solvent dependence.[22]

The Mn(III) compounds are stable in the solid state for long periods of time under dry nitrogen gas. Exposure to the atmosphere over a period of weeks results in a slow discoloration which is accompanied by an odor characteristic of ligand decomposition. The complexes rapidly decompose in aqueous base (1 *N* NaOH) to give intractable solids. However, in acidic solutions they undergo a reversible protonation. For example, addition of excess anhydrous HSO$_3$CF$_3$ to an acetonitrile solution containing Mn(III)[14]eneN$_4$Cl causes the solution to turn bright green. Immediate addition of triethylamine restores the original color. This process can be repeated a number of times before the characteristic color of the manganese(III) no longer returns. Since the band intensities slowly decrease with time in acidic solution, the protonated complex is probably unstable. Addition of small amounts of water to the acetonitrile–HSO$_3$CF$_3$ solution led to rapid decomposition. Since the ligand framework carries two negative charges the protonation site is probably the olefinic carbon of the β-diketone fragment. Such a protonation would lead to the isolated imine structure 3. A number of nickel(II) macrocyclic complexes have been reported to exhibit this phenomenon.[23] Attempts to isolate the protonated form of Mn(III)[14]12eneN$_4$Cl from acetonitrile–HSO$_3$CF$_3$ solutions yielded green oils which could not be characterized.



3

The Manganese(II) and Zinc(II) Complexes. The complexation of manganese(II) and zinc(II) with the cyclic Schiff base is very sensitive to the source of the metal ion and the base which is present in the reaction solution. Mixing equal molar amounts of anhydrous MnCl$_2$ or MnBr$_2$ with the ligand in acetonitrile under nitrogen yields a straw yellow solution. If triethylamine or pyridine is added, the solution turns a deep brown but crystallization does not occur. Reduction of the solution volume yields H$_2$[14]12eneN$_4$ as the only identifiable product. If the source of the metal ion is Mn(II)(SO$_3$CF$_3$)$_2$, crystallization will occur with the tertiary amine (eq 2) but not with pyridine. Work-up of the reaction involving the latter again yielded H$_2$[14]12eneN$_4$. Similar behavior was observed in the preparation of the zinc(II) compounds.

The reaction of M(II)(SO$_3$CF$_3$)$_2$, M = Mn and Zn, with the ligand in the presence of triethyl- or tri-*n*-propylamine (eq 2) gives complexes with stoichiometry M(II)[14]12eneN$_4$(amine). The compounds are stable in certain solvents and can be recrystallized from hot benzene or toluene under nitrogen without loss of the amine. Chemical analyses before and after recrystallization were identical. This behavior suggests that the tertiary amine is not simply lattice bound

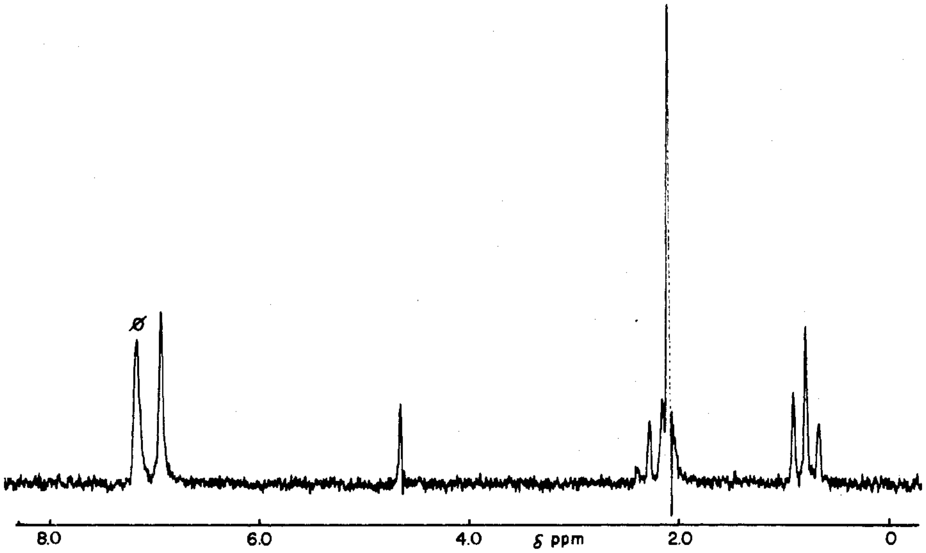


Figure 2. The 60-MHz NMR spectrum of Zn(II)[14]12eneN$_4$(NEt$_3$) in benzene-d_6.

but is in fact bonded to the metal ion. However, attempts to confirm this in the gas phase via mass spectral measurements failed. The largest *m/e* value observed in all cases (Table II) corresponded to that of the cation [M(II)[14]12eneN$_4$]$^+$.

Direct evidence for metal bound triethyl- or tri-*n*-propylamine in solution for the diamagnetic zinc complexes is provided by NMR. The 60-MHz NMR spectrum of Zn(II)[14]12eneN$_4$(N(Et)$_3$) in benzene-d_6 is shown in Figure 2 and the data are tabulated in Table IV. The macrocyclic ligand resonances of this complex occur at δ 6.91 (s, aro), 4.62 (s, olefinic), and 2.09 (s, CH$_3$). The resonances of the bound triethylamine ligand are found at δ 0.82 (t, CH$_3$) and 2.22 (q, CH$_2$) and are shifted to higher field relative to those of the free amine in benzene (δ, 0.95 (CH$_3$) and 2.37 (CH$_2$)). Stepwise addition of small amounts of triethylamine to the NMR solution causes both an intensification of the ethyl signals and a gradual shift of the signals to lower field.[24] Thus, the exchange between free and complexed amine appears to be rapid on the NMR time scale. Addition of a competing ligand such as pyridine causes the immediate and total displacement of the amine while trimethyl phosphite or acetonitrile have little effect on amine displacement. The same behavior was observed for Zn(II)[14]12eneN$_4$(N(*n*-Pr)$_3$). The chemical shifts for unbound tri-*n*-propylamine occur at δ 0.87 (CH$_3$) and 2.30 (NCH$_2$) and thus are at lower field than the bound amine (Table IV).

In view of the coordination similarity of high-spin d^5 and d^{10} metal ions the Zn(II) and Mn(II) complexes are probably isostructural.[25] The Mn(II) compounds are paramagnetic and give a very broad ESR absorption at $g_{\text{eff}} \sim 2.0$ in the solid state at room temperature. In toluene at 77 K the triethylamine adduct exhibits a number of transitions each having six-line hyperfine patterns (coupling with the $I = {}^5/_2$ Mn nucleus). However, these transitions, which occur at g_{eff} of 2 and 6, are not reproducible suggesting that the material is slowly decomposing or otherwise altering its structure.

Molecular models show that the divalent complexes have a square pyramidal geometry with the metal ion displaced from the macrocyclic ligand plane (Figure 3). Coordination of tertiary amines is relatively rare and to our knowledge has not been previously observed in metallo macrocyclic chemistry. The "front strain"[26] associated with tertiary amines strongly influences their coordinating ability. Assuming a M–N bond distance of 2.0–2.3 Å for the amine[27] as well as an in-plane metal ion, severe steric interactions between the alkyl groups of the amine and macrocyclic framework can develop. These interactions can be minimized by displacement of the metal ion from the ligand plane. It is our contention that for the Mn(II) and Zn(II) complexes, significant metal ion displacement is the most important factor leading to the binding of the amine.

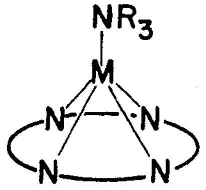


Figure 3. The proposed coordination geometry of M(II)[14]12eneN$_4$(NR$_3$), where M is Mn and Zn and R is C$_2$H$_5$ and (CH$_2$)$_2$CH$_3$.

It is important to point out that the Ni(II)[14]12eneN$_4$ shows no propensity to bind either triethyl- or tri-*n*-propylamine. The synthesis of this complex in a manner similar to that employed for the Mn(II) and Zn(II) analogues did not yield the amine adducts. Furthermore, NMR studies indicated that triethylamine will not bind to the nickel complex in benzene solution. The chemical shifts of the amine signals are uneffected by the presence of the nickel(II) macrocyclic complex.

The different coordination geometries found for the Mn(II) and Zn(II) complexes as compared to their Ni(II)[6] and possibly Fe(II)[8] analogues appear to be related to the hole size of the cyclic Schiff base. Manganese(II), high-spin d^5, and Zn(II), d^{10}, are both larger than Ni(II).[28] Since Goedken et al.[9] have shown that the hole size of H$_2$[14]12eneN$_4$ is smaller than that of the porphyrins, it appears that the five-coordinate geometries for Mn(II)[14]12eneN$_4$(amine) and Zn(II)-[14]12eneN$_4$(amine) are a direct result of the mismatch between the metal ion radius and the hole size of the cyclic ligand.

The five-coordinate Mn(II) complexes are generally more reactive than their Mn(III) counterparts. Purging toluene or benzene solutions of Mn(II)[14]12eneN$_4$(amine) with dry oxygen gas yields a dark amorphous solid. The isolated material exhibits a simple infrared spectrum and is probably an oxide of manganese (possibly MnO$_2$). The Mn(II) complexes are easily oxidized by chloroform. Gently warming Mn(II)[14]12eneN$_4$(amine) in this solvent under nitrogen gives the green complex Mn(III)[14]12eneN$_4$Cl. Although the Zn(II) analogues are oxygen insensitive, they demetalate in chloroform. NMR solutions of Zn(II)[14]12eneN$_4$(amine) in chloroform-d_1 slowly decompose (hours) to give the dideuterated form of the ligand, D$_2$[14]12eneN$_4$, and a white solid (possibly ZnCl$_2$).

Both the manganese and zinc complexes are sensitive to alkylating agents. Addition of excess CH$_3$X, where X is I$^-$ and FSO$_3^-$, to benzene solutions containing the complexes leads to their destruction. However, the only alkylated product which could be identified from the reaction mixture was [CH$_3$NR$_3$]X. Attempts to isolate the alkylated form of the ligand lead to hygroscopic yellow solids which could not be characterized. The compounds are easily decomposed by aqueous strong mineral acids, e.g., HCl and HClO$_4$. Unlike the Mn(III) derivatives addition of Et$_3$N will not restore the original complex. However, if anhydrous HSO$_3$CF$_3$ is added to acetonitrile suspensions of the compounds under nitrogen a dissolution accompanied by a color change occurs. Addition of triethylamine results in the regeneration of M(II)[14]12eneN$_4$(amine) (eq 2).

The synthesis and properties of manganese complexes containing other unsaturated tetraaza and mixed N–O donor ligands will be subsequently reported.

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Registry No. H$_2$[14]12eneN$_4$, 56276-51-8; Zn(II)[14]12eneN$_4$(N(Et)$_3$), 56943-15-8; Zn(II)[14]12eneN$_4$(N(*n*-Pr)$_3$), 56943-16-9; Mn(II)[14]12eneN$_4$(N(Et)$_3$), 56943-17-0; Mn(II)[14]12eneN$_4$(N(*n*-Pr)$_3$), 56943-18-1; Mn(III)[14]12eneN$_4$(Cl), 56943-19-2; Mn(III)[14]12eneN$_4$(Br), 56943-20-5; Mn(III)[14]12eneN$_4$(NCS), 56943-21-6; Mn(III)[14]12eneN$_4$(N$_3$), 56943-23-8; Mn(III)(acac)$_2$Cl, 51197-21-8; Mn(III)(acac)$_2$Br, 51147-59-2; Mn(III)(acac)$_2$(NCS), 52242-31-6; Mn(III)(acac)$_2$(N$_3$), 52242-29-2.

References and Notes

(1) L. J. Boucher, *Coord. Chem. Rev.*, 7, 289 (1972).
(2) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 3 (1974).
(3) L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, **6**, 1 (1971).
(4) P. S. Bryan and J. C. Dabrowiak, *Inorg. Chem.*, **14**, 296 (1975).
(5) P. S. Bryan and J. C. Dabrowiak, *Inorg. Chem.*, **14**, 299 (1975).
(6) E. G. Jager, *Z. Anorg. Allg. Chem.*, **364**, 177 (1969).
(7) V. L. Goedken, J. Molin-Case, and Y. A. Whang, *J. Chem. Soc., Chem. Commun.*, 337 (1973); V. L. Goedken, to be published.
(8) V. L. Goedken and Y. Park, *J. Chem. Soc., Chem. Commun.*, 214 (1975).
(9) V. L. Goedken, S. Peng, and Y. Park, *J. Am. Chem. Soc.*, **96**, 284 (1974).
(10) A. Weissberger, "Techniques of Chemistry", Vol. II, Wiley-Interscience, New York, N.Y., 1970.
(11) V. Katovik, L. Lindoy, and D. H. Busch, *J. Chem. Educ.*, **49**, 117 (1972).
(12) G. H. Cartledge, *J. Am. Chem. Soc.*, **74**, 6015 (1952).
(13) B. R. Stults, R. S. Marianelli, and V. W. Day, *Inorg. Chem.*, **14**, 722 (1975).
(14) Although the preparation of Zn(II)(SO$_3$CF$_3$)$_2$ is not specifically described in ref 4 it can be prepared in a manner identical with the Mn salt which is therein described.
(15) B. J. Hathaway, D. J. Holah, and A. E. Underhill, *J. Chem. Soc.*, 2444 (1962).
(16) M. D. Alexander, A. VanHeuvelen, and H. G. Hamilton, Jr., *Inorg. Nucl. Chem. Lett.*, **6**, 445 (1970).
(17) B. R. Stults, V. W. Day, E. L. Tasset, and R. S. Marianelli, *Inorg. Nucl. Chem. Lett.*, **9**, 1259 (1973).
(18) V. W. Day, B. R. Stults, E. L. Tasset, R. O. Day, and R. S. Marianelli, *J. Am. Chem. Soc.*, **96**, 2650 (1974).
(19) J. C. Dabrowiak, P. H. Merrell, and D. H. Busch, *Inorg. Chem.*, **11**, 1979 (1972).
(20) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, N.Y., 1970, p 187.
(21) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, New York, N.Y., 1968.
(22) L. J. Boucher, *J. Am. Chem. Soc.*, **90**, 6640 (1968).
(23) C. J. Hipp, L. F. Lindoy, and D. H. Busch, *Inorg. Chem.*, **11**, 1988 (1972).
(24) The chemical shifts of the triethylamine signals in benzene are essentially concentration independent.
(25) A recent x-ray analysis of Mn(II)[14]12eneN$_4$(NEt$_3$) has confirmed the presence of five-coordinate Mn(II): V. L. Goedken, personal communication.
(26) R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965); H. C. Brown and R. B. Johannescn, *ibid.*, **75**, 16 (1953).
(27) S. Koda, S. Ooi, H. Kuroya, Y. Nishikawa, Y. Nakamura, and S. Kawaguchi, *Inorg. Nucl. Chem. Lett.*, **8**, 89 (1972); T. J. Kistenmacher, *Acta Crystallogr., Sect. B*, **28**, 1302 (1972); M. Zocchi, A. Albinati, and G. Tieghi, *Cryst. Struct. Commun.*, **1**, 135 (1972).
(28) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).

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Carbon-13 Nuclear Magnetic Resonance of Substituted Tetraphenyl Porphyrins and Their Complexes with Ruthenium, Indium, and Titanium

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^{13}C NMR spectra of H$_2$P and MPXY (P = tetrakis(*p*-trifluoromethylphenyl)porphyrin, tetrakis(*p*-isopropylphenyl)porphyrin, and tetrakis(*o*-tolyl)porphyrin, M = Ru, X = CO, Y = tetrahydrofuran, 4-*tert*-butylpyridine, or CO; M = In, X = Cl; M = Ti, X = O; P = octaethylporphyrin, M = Ru, X = CO, Y = tetrahydrofuran; M = In, X = Cl) and RuPX$_2$ (P = tetrakis(*p*-trifluoromethylphenyl)porphyrin), X = trimethyl phosphite and *tert*-butyl isocyanide) are reported and interpreted. Chemical shift differences for nonequivalent sites and ring current effects are compared for ^{1}H and ^{13}C NMR spectra. Significant dependence of porphyrin chemical shifts on the metal is observed.

Introduction

Recently, increasing effort has been applied to understanding and using ^{13}C NMR to elucidate the chemistry of porphyrins and metalloporphyrins. These studies have concerned the apparent electron delocalization pathway in natural porphyrins,[1] biosynthesis,[2] identification of type isomers,[3] isotropic shifts in paramagnetic iron(III) porphyrins,[4] ring current effects on the porphyrin resonances and on the resonances of other coordinated ligands,[5,6] assignment of spectra of tetrapyrroles,[7] and Cd(II), Hg(II), and Tl(III) complexes of tetraphenylporphyrin.[3c] We now report the ^{13}C NMR spectra of Ru(II), (TiO)$^{2+}$, and In(III) complexes of substituted tetraphenylporphyrins. The compounds chosen for study provide comparison of the relative ^{1}H and ^{13}C chemical shift differences for sites which are nonequivalent due to restricted phenyl ring rotation.[8] These compounds also provide an indication of the effect of complexed metal on porphyrin chemical shifts.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol or halocarbon mulls on a Perkin-Elmer 710 grating spectrometer. Visible spectra were obtained in chloroform solution on a Beckman Acta V spectrometer. Data are given below with wavelengths in nanometers and log ε in parentheses. ^{1}H NMR spectra were run at