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Metal Ion Binding to Octakis(dimethylamino)porphyrazine: Core Coordination of Mn(III) and Peripheral Coordination of Pd(II)

David P. Goldberg,[†] Antonio Garrido Montalban,[‡] Andrew J. P. White,[‡] David J. Williams,[‡] Anthony G. M. Barrett,[*,‡] and Brian M. Hoffman[*,†]

Departments of Chemistry, Northwestern University, Evanston, Illinois 60208, and Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, U.K.

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The synthesis and X-ray structural characterization of two manganese(III) porphyrazine (tetraazaporphyrin) complexes are reported: [Mn(Et_2dtc)ODMAPz] (**1**) and [Mn(Cl)ODMAPz] (**2**) (Et_2dtc = diethyldithiocarbamato; ODMAPz = 2,3,7,8,12,13,17,18-octakis(dimethylamino)porphyrazinato). In both **1** and **2**, the Mn(III) ion sits ~0.3 Å out of the plane of the pyrrolic nitrogen atoms toward the axial ligand. The structural data reveal that for both **1** and **2** the Mn(III) ions are isolated from each other, simplifying the interpretation of the magnetic behavior of these compounds. Cyclic voltammetry shows that the peripheral dimethylamino groups make these metalloporphyrazines extremely electron-rich, with the Mn(III)/Mn(II) couple at −1.3 V (versus ferrocenium/ferrocene), shifted approximately 0.6−0.9 V more negative than those of related manganese macrocycles. Temperature-dependent magnetic susceptibility measurements show that the ground state is $S = 2$ with axial zero-field splitting, and $|D| = 3.1{-}3.3\ \mathrm{cm}^{-1}$ for both **1** and **2**. These bulk magnetic measurements are compared to the magnetic behavior of Mn(III) porphyrin-type complexes, as well as recent direct resonance measurements on **1** and **2** by high-field EPR spectroscopy. The related metalloporphyrazine NiODMAPz, with an internally bound Ni(II) ion, coordinates 4 equiv of $PdCl_2$ to the peripheral dimethylamino sites to give [Ni(ODMAPz)-($PdCl_2$)$_4$] (**5**). Compound **1** crystallizes in $C2/c$, with $a = 22.480(3)$ Å, $b = 20.128(2)$ Å, $c = 19.423(3)$ Å, $\beta = 102.97(1)°$, $V = 8564(2)$ Å^3, and $Z = 8$ ($R_1 = 0.074$, w$R_2 = 0.169$). Compound **2** crystallizes in $P\bar{1}$ with $a = 10.216(6)$ Å, $b = 13.426(8)$ Å, $c = 15.683(14)$ Å, $\alpha = 114.59(5)°$, $\beta = 96.82(6)°$, $\gamma = 101.87(5)°$, $V = 1863(2)$ Å^3, and $Z = 2$ ($R_1 = 0.067$, w$R_2 = 0.183$).

Introduction

Phthalocyanines and related macrocycles[1−3] modified by attachment of substituents at the periphery have long been widely studied. The Mn(III) complexes of such molecules have received recent attention as building blocks for molecular magnetic materials.[4,5] This report describes the syntheses, characterizations, and X-ray crystal structures of two manganese(III) complexes: [Mn(Et_2dtc)ODMAPz] (Et_2dtc = diethyldithiocarbamato; ODMAPz = octakis(dimethylamino)porphyrazinato) (**1**) and [Mn(Cl)ODMAPz] (**2**) with the porphyrazine ligand (tetraazaporphyrin) H_2ODMAPz (**3**).[6] Few such manganese(III) complexes, whether of porphyrins, phthalocyanines, or porphyrazines, have been crystallographically characterized.[7−9] We define the ground spin states of these molecules with magnetic susceptibility measurements and compare the results to those of precise high-field EPR measurements.[10] The peripheral dimethylamino groups make the ODMAPz macrocycle extremely electron-rich. As a result, the free-base form, H_2ODMAPz, is readily oxidized, making it an excellent choice for the preparation of charge-transfer salts with potentially novel conducting properties.[11] Electrochemical measurements of the manganese compounds **1** and **2** now show that the electron-rich Mn^{II}ODMAPz is an extremely strong reductant. Thus, **1** and **2** are good candidates for the preparation of donor−acceptor (D−A) molecule-based magnets.[4,11,12] More recently, there have been increased efforts in the preparation of porphyrazine-, phthalocyanine-, and porphyrin-type molecules with substituents linked directly to the β-carbon atoms of the pyrrole rings, including those that provide metal-binding sites on the periphery.[13−19] The utility of the dimethylamino groups as peripheral bidentate chelation sites is demonstrated by the coordination of four $PdCl_2$ units by NiODMAPz (**4**)[6] to give [$PdCl_2$]$_4$[NiODMAPz] (**5**).

[†] Northwestern University.

[‡] Imperial College of Science, Technology and Medicine.

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Experimental Section

Reagents and solvents were purchased commercially and used as received unless otherwise noted. According to the method of Ciampolini et al.,[20] $Mn(Et_2dtc)_2$ was prepared as a yellow, microcrystalline solid (1.25 g, 70%). Methylene chloride and acetonitrile were distilled over calcium hydride. The porphyrazines H_2ODMAPz and NiODMAPz were prepared according to published procedures.[6] Electronic absorption spectra were recorded using a Hewlett-Packard HP8452A diode-array spectrophotometer. Fast-atom bombardment (FAB) and electric ionization (EI) mass spectra were obtained by Mr. John Barton and Dr. Doris Hung using a VG-70-250E and a VG AutoSpec Q. Elemental analyses were performed by Oneida Research Services, Inc. (Whitesboro, NY) or by the microanalytical laboratory at Imperial College.

[Mn(Et_2dtc)ODMAPz] (1). In a nitrogen-filled glovebox, a sample of $Mn(Et_2dtc)_2$ (0.160 g, 0.455 mmol) was added to a purple suspension of H_2ODMAPz (0.300 g, 0.456 mmol) in methanol (10 mL). The homogeneous deep blue solution that immediately formed was stirred for 12 h. The solution was filtered, and the supernatant was evaporated to dryness in vacuo. The solid dark blue residue was dissolved in a minimum amount of toluene, and this solution was layered with hexanes and allowed to stand for 5 days. Removal of the supernatant afforded 0.150 g (40%) of a dark blue crystalline solid. UV−vis (MeOH): λ_{max} 336, 470, 602, 780 nm. FABMS (MW = 860): *m/z* 711 ($M^+ - Et_2$-dtc). Anal. Calcd for [Mn(Et_2dtc)ODMAPz] ($MnC_{37}H_{58}N_{17}S_2$): C, 51.67; H, 6.80; N, 27.69. Found: C, 51.47; H, 6.94; N, 26.93.

[Mn(Cl)ODMAPz] (2). A sample of anhydrous $MnBr_2$ (0.033 g, 0.154 mmol) was added to a purple suspension of H_2ODMAPz (0.100 g, 0.152 mmol) in DMF (5 mL), and the mixture was heated at 80 °C for 24 h under N_2. The reaction mixture was cooled and filtered through Celite, and the Celite was washed with methylene chloride. The filtrate was washed with brine (3×10 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure to give a dark blue solid. The crude product was purified by silica gel chromatography (hexane/EtOAc (9/1), then acetone), affording 0.057 g (50%) of a dark blue crystalline solid. UV−vis (CH_2Cl_2): λ_{max} 342, 466, 607, 780 nm. HRMS (FAB), *m/z*: calcd for $MnC_{32}H_{48}N_{16}Cl$ (M^+), 746.3319; found, 746.3330. Anal. Calcd for [Mn(Cl)ODMAPz] ($MnC_{32}H_{48}N_{16}Cl$): C, 51.44; H, 6.47; N, 29.99. Found: C, 51.71; H, 6.26; N, 25.01. Numerous attempts at obtaining a better fit for the nitrogen content using crystalline material failed, and we believe this problem is likely due to difficulties in combustion of the sample rather than to the presence of impurities.

[Ni(ODMAPz)($PdCl_2$)$_4$] (5). Ni(ODMAPz) (0.200 g, 0.280 mmol) and $PdCl_2$ (0.400 g, 2.25 mmol) were combined in $CH_3CN/CHCl_3$ (3/1 v/v) (12 mL); the mixture was heated at 100 °C for 4 h and stirred an additional 12 h at 60 °C. The reaction mixture was cooled and filtered to give a blue solid. After washing with CH_3CN, $CHCl_3$, and Et_2O, 0.280 g (70%) of a blue solid was obtained. UV−vis (DMF): λ_{max} 321, 606 nm. Anal. Calcd for $C_{32}H_{48}N_{16}Cl_8NiPd_4$: C, 26.98; H, 3.40; N, 15.73. Found: C, 26.89; H, 3.72; N, 15.18.

Magnetic Susceptibility Studies. Solid-state magnetic susceptibility measurements on **1** and **2** were made by using a Quantum Design MPMS SQUID susceptometer operating in the temperature range 1.9−300 K and equipped with a 5.5 T magnet. Polycrystalline samples were loaded in gel caps and compressed by fitting one half of the cap into the other half and sealing them together with glue. The susceptibility of the sample holder was measured in the same temperature range and field to provide an accurate correction for its contribution to the total magnetic susceptibility. A diamagnetic correction of -5.00×10^{-4} cm^3/mol was estimated from Pascal's constants[21,22] and used for both **1** and **2**.

Table 1. Crystallographic Data for **1** and **2**[a]

	1	**2**
formula	$C_{37}H_{58}N_{17}S_2Mn$	$C_{32}H_{48}N_{16}ClMn$
fw	860.1	747.3
color, habit	thin black plates	black prisms
cryst size/mm	$0.30 \times 0.25 \times 0.03$	$0.23 \times 0.13 \times 0.08$
lattice type	monoclinic	triclinic
space group, no.	*C*2/*c*, 15	$P\bar{1}$, 2
a/Å	22.480(3)	10.216(6)
b/Å	20.128(2)	13.426(8)
c/Å	19.423(3)	15.683(14)
α/deg		114.59(5)
β/deg	102.97(1)	96.82(6)
γ/deg		101.87(5)
V/Å^3	8564(2)	1863(2)
Z	8	2
D_c/g cm^{-3}	1.334	1.332
F(000)	3648	788
radiation used	Cu Kα[b]	Cu Kα
μ/mm^{-1}	3.82	3.92
θ range/deg	3.0−50.0	3.2−60.0
no. of unique reflns		
measd	4389	5172
obsd, $\lvert F_o \rvert > 4\sigma(\lvert F_o \rvert)$	2948	3977
abs cor	face-indexed numerical	
max, min transm	0.906, 0.509	
no. of variables	531	452
R_1[c]	0.074	0.067
wR_2[d]	0.169	0.183
weighting factors *a*, *b*[e]	0.075, 54.974	0.108, 3.157
largest diff peak, hole/e Å^{-3}	0.55, −0.38	0.45, −0.50

[a] Details in common: graphite-monochromated radiation, ω scans, Siemens P4 diffractometer, 293 K, refinement based on F^2. [b] Rotating-anode source. [c] $R_1 = \sum \lVert F_o \rvert - \lvert F_c \rVert / \sum \lvert F_o \rvert$. [d] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [e] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Crystallography. Table 1 provides a summary of the crystal data and data collection and refinement parameters for [Mn(Et_2dtc)-ODMAPz] (**1**) and [Mn(Cl)ODMAPz] (**2**). Both structures were solved by direct methods and were refined by full-matrix least-squares based on F^2. All of the major-occupancy non-hydrogen atoms of both complexes were refined anisotropically. In compound **1**, two adjacent NMe_2 groups were disordered over two partial occupancy (60:40) orientations, the minor-occupancy atoms of which were refined isotropically. Also in this structure, two discrete positions were identified for each of the terminal methyl groups of the diethyldithiocarbamate ligand (65:35 and 55:45), and the minor occupancy atoms were again refined isotropically. The hydrogen atoms in both structures were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$ [$U(H) = 1.5U_{eq}(C-Me)$], and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL-PC program system.[23]

Electrochemistry. Cyclic voltammetry data were recorded with a Cypress Systems CS-1087 computer-controlled potentiostat. A three-electrode configuration was employed: a platinum disk working electrode, a silver wire counter electrode, and a silver−silver chloride reference electrode. Measurements were made in dichloromethane freshly distilled over calcium hydride. The supporting electrolyte was tetra-*n*-butylammonium hexafluorophosphate. All measurements were calibrated by addition of ferrocene as an internal reference, and $E_{1/2}$ values were calculated from $(E_{pa} + E_{pc})/2$ at a scan rate of 110 mV s^{-1}.

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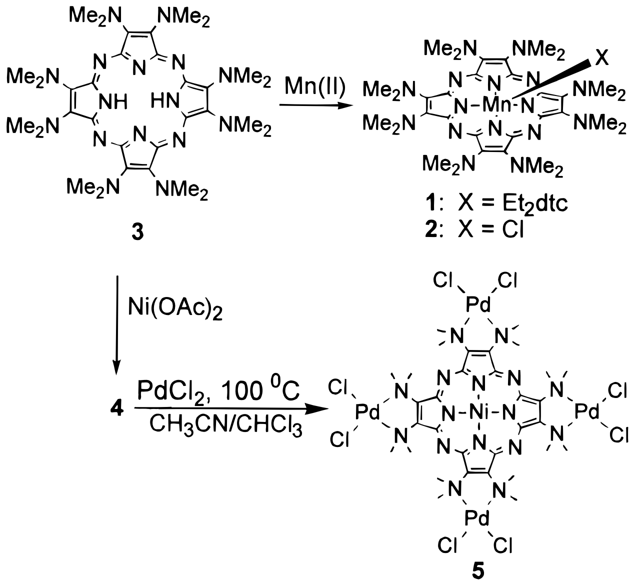
Scheme 1



Results and Discussion

Synthesis and Optical Properties. In principle, a metal ion could coordinate to either the peripheral dimethylamino chelation sites or the central cavity of H_2ODMAPz. Not surprisingly, as shown by X-ray crystallography, the manganese ions were captured by the macrocyclic core to give a manganese(III) porphyrazine with a single axial ligand bound to the metal center, as shown in Scheme 1. Similarly, reaction of H_2-ODMAPz with $NiCl_2$ gave the internally metalated compound **4**.[6] However, the reaction of excess $PdCl_2$ with a centrally metalated ODMAPz, **4**, gives [Ni(ODMAPz)$(PdCl_2)_4$] (**5**), confirming that the peripheral NMe_2 groups can indeed coordinate in a bidentate fashion analogous to tetramethylethylenediamine.

Much work has been reported examining the influence of the properties of the macrocycle on the rate of metal complexation, as well as the effect of the solution conditions,[24−26] but less has been done on the effect of changing the metal salt upon the rates of complexation.[27] Insertion of the metal into the porphyrazine core by the Mn$(Et_2dtc)_2$ reagent is remarkably fast at room temperature, occurring in seconds. This facile metalation contrasts with the more typical reaction of $MnBr_2$, which demanded an extended period of reaction (24 h) at elevated temperatures.[1] This difference parallels the disparity in rates of metalation of H_2TAP (TAP = tetraazaporphyrin) or H_2Pc-^{t}Bu$_4$[25] (H_2Pc^{t}Bu$_4$ = tetra-*tert*-butylphthalocyanine) by Cu$(OAc)_2$ versus $CuCl_2$.

During the synthesis and purification of **1**, the incorporated Mn was oxidized from Mn(II) to Mn(III) even though all steps were performed under an inert atmosphere. This contrasts with the recently described synthesis of Mn^{II}OESPz (OESPz = octakis(ethylsulfanyl)porphyrazine), which was stable in the manganous form unless exposed to air or alkyl halides.[7] The electrochemical data (vide infra) show that the dimethylamino substituents make the ODMAPz macrocycle significantly more electron-rich than other porphyrazines such as OESPz and are consonant with the increased stability of the higher oxidation state of manganese.

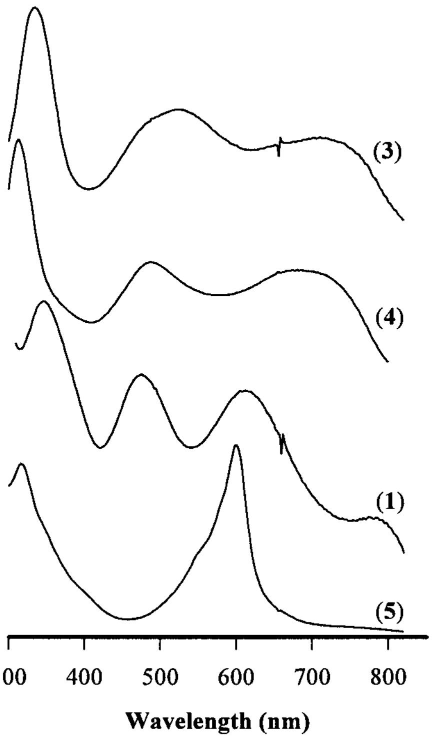


Figure 1. UV−vis spectra (λ_{max}, nm (log ϵ)) for H_2ODMAPz (**3**) [334 (4.57), 531 (4.29), 708 (4.16)], NiODMAPz (**4**) [325 (4.92), 561 (4.42), 704 (4.52)], and [Mn(Et_2dtc)ODMAPz] (**1**) [336 (4.53), 470 (4.47), 602 (4.59), 780 (4.24)] in CH_2Cl_2 and for [Ni(ODMAPz)$(PdCl_2)_4$] (**5**) [321 (4.45), 606 (4.52)] in DMF.

H_2ODMAPz (**3**) exhibits a Soret peak centered at 334 nm and two broad bands at 522 and 705 nm, as can be seen in Figure 1.[28] The peak at 522 nm is assigned to n−π^* transitions from the lone-pair electrons on the external nitrogen atoms into a π^* ring orbital, and the 705 nm peak is assigned to the Q band. The spectrum of NiODMAPz (**4**) is qualitatively the same, with a small blue shift (~20 nm) of all three bands. In contrast, insertion of Mn(III) into the porphyrazine to form **1** and **2** causes striking changes in the absorption spectrum, as seen in Figure 1.[29] Although the Soret band matches that of the free base, the next two peaks are blue-shifted and centered at 467 and 607 nm, with a less intense shoulder near 765 nm. The absorption spectra of Mn(III) porphyrin compounds are well-known to contain other transitions in addition to the normal Q and Soret bands,[30,31] and are not amenable to simple interpretation. We tentatively suggest that the peak at 607 nm is the blue-shifted Q band, and the n−π^* peak is now centered at 467 nm. The shoulder at the red end of the spectrum may be due to an LMCT absorbance of the type a_{2u} (ring) → e_g (metal) as has been described in analogous porphyrin spectra.[30,31] Peaks observed in the near-infrared region (800−1550 nm) for [Mn(OESPz)Cl] have been suggested as arising from LMCT transitions.[7]

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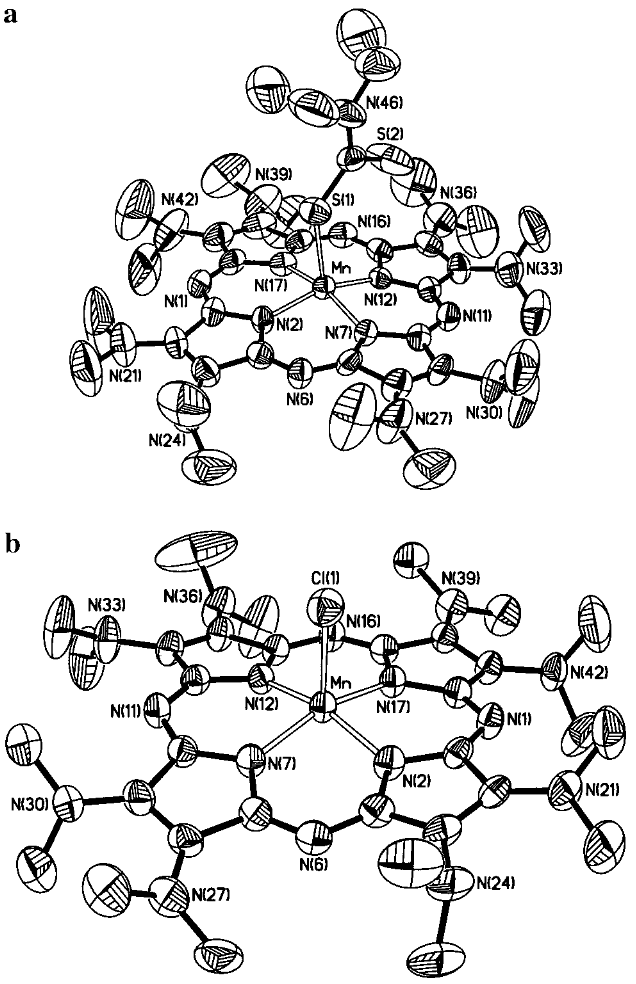

Figure 2. Molecular structures of (a) **1** and (b) **2** shown with 50% probability ellipsoids.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Mn−S(1)	2.505(2)	Mn−N(2)	1.965(6)
Mn−N(7)	1.955(6)	Mn−N(12)	1.938(6)
Mn−N(17)	1.941(6)		
S(1)−Mn−N(2)	90.6(2)	S(1)−Mn−N(7)	98.8(2)
S(1)−Mn−N(12)	109.8(2)	S(1)−Mn−N(17)	99.1(2)
N(2)−Mn−N(7)	88.3(3)	N(2)−Mn−N(12)	159.6(3)
N(2)−Mn−N(17)	88.3(3)	N(7)−Mn−N(12)	88.3(3)
N(7)−Mn−N(17)	161.8(3)	N(12)−Mn−N(17)	88.7(3)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

Mn−Cl(1)	2.395(2)	Mn−N(2)	1.942(5)
Mn−N(7)	1.941(5)	Mn−N(12)	1.940(4)
Mn−N(17)	1.956(5)		
Cl(1)−Mn−N(2)	98.2(2)	Cl(1)−Mn−N(7)	101.5(2)
Cl(1)−Mn−N(12)	101.5(2)	Cl(1)−Mn−N(17)	99.2(2)
N(2)−Mn−N(7)	88.7(2)	N(2)−Mn−N(12)	160.3(2)
N(2)−Mn−N(17)	87.9(2)	N(7)−Mn−N(12)	87.7(2)
N(7)−Mn−N(17)	159.4(2)	N(12)−Mn−N(17)	88.8(2)

Crystal Structures of 1 and 2. The X-ray structural analyses reveal that in both **1** and **2** the manganese centers adopt distorted square pyramidal geometries (Figure 2), the basal plane being formed by the octakis(dimethylamino)porphyrazine ring and with, in **1**, the diethyldithiocarbamate ligand and, in **2**, the chlorine atom occupying the apical positions. The metal−ligand coordination distances are unexceptional for both compounds (Tables 2 and 3). The inner C_8N_8 core of the porphyrazine ligand for **1** is planar to within 0.09 Å, but for **2** this core is severely twisted, being planar only to within 0.21 Å. This twisting causes the C_β atoms to be displaced by as much as 0.35 Å out of the metal−N_4 coordination plane. The manganese atom is displaced out of the N_4 coordination plane toward the apical ligand by 0.33 Å (0.34 Å) for **1** (**2**). This out-of-plane deformation is similar to that observed (0.29 Å) in the manganese porphyrazine complex [Mn(OESPz)Cl][7] but contrasts with the 0.26 Å displacement seen in the manganese porphyrin compound [Mn(TPP)Cl][32] (TPP = 5,10,15,20-tetraphenylporphyrinate). This difference in behavior is probably due to the smaller size of the central porphyrazine cavity compared to that in porphyrins. There is a distinct loss of planarity in the porphyrazine ligand of **1** outside this inner core, with two adjacent C_β atoms of one pyrrole ring being displaced by ca. 0.28 Å out of the plane of the inner core on the opposite side to the metal atom. The peripheral dimethylamino groups adopt various skewed conformations with respect to the ligand plane for both **1** and **2**, with torsion angles about the C_β−NMe_2 bonds ranging from 12 to 68°. In solution, however, there is no barrier to rotation among these groups as evidenced by the single methyl resonance at 3.73 ppm in the ^1H NMR spectrum for H_2ODMAPz.

Interpretation of the magnetic susceptibility (vide infra) for **1** and **2** in part depends on structural information concerning nearest-neighbor contacts. Analysis of the packing of the molecules reveals no significant intermolecular interactions other than normal van der Waals contacts. In **1**, the closest approach to the manganese(III) center is a C−H···Mn contact of 3.15 Å trans to the sulfur donor atom (173°), from a *partial-occupancy* carbon atom of the diethyldithiocarbamate ligand of a glide-related molecule. In **2**, the closest intermolecular contact is from the hydrogen atom of a dimethylamino group of one molecule which lies 3.09 Å away from the manganese atom of a C_i related complex, in a position trans to the chlorine ligand (180°). Figure 3 illustrates the weak “stacking/dimer pair” associations observed for these molecules in the crystals. In the latter structure, **2**, the interplanar separation between the core atoms of the “dimer” pair is ca. 4.2 Å.

Electrochemistry. The formal potentials of the reversible redox processes exhibited by compounds **1**−**4** and Cu^{II}-ODMAPz[33] are given in Table 4 together with literature values for some related compounds. The free base **3** exhibits two reversible oxidations centered at −0.061 and −0.269 V (versus ferrocenium/ferrocene), which we assign to the $[H_2Pz]^{2+}/[H_2Pz]^+$ and $[H_2Pz]^+/[H_2Pz]$ couples, respectively.[34] These data can be compared to the single reversible oxidation found for octaethylthio- or octapropyl-substituted porphyrazines in the range +0.65 to +0.70 V.[35] A ring reduction assigned to the $[H_2Pz]/[H_2Pz]^-$ couple is centered at −1.61 V, close to that observed for the reduction of the related octapropyl-[35] or unsymmetrical sulfur-substituted porphyrazines.[13] For Ni^{II}- or Cu^{II}ODMAPz, the first oxidation and reduction waves are centered at values close to those found for the first ring oxidation and reduction of H_2ODMAPz, which indicates that for the Ni^{II}- and Cu^{II}ODMAPz complexes no metal-centered redox activity is observed in the potential window of the experiment.

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(35) Cook, A. S.; Williams, D. B. G.; White, A. J. P.; Williams, D. J.; Lange, S. J.; Barrett, A. G. M.; Hoffman, B. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 760−761.

Table 4. Comparison of Half-Wave Potentials (V vs Fc$^+$/Fc) for Compounds **1**−**4**

compound	Pz(0)/ Pz(1−)	Pz(1−)/ Pz(2−)	Mn^{III}Pz(2−)/ Mn^{II}Pz(2−)	Pz(2−)/ Pz(3−)	ref
H_2ODMAPz (**3**)	−0.061	−0.269		−1.61	35
NiODMAPz (**4**)		−0.284		−1.75	33
CuODMAPz		−0.289		−1.76	33
[Mn(Et_2dtc)ODMAPz] (**1**)		−0.069^a	−1.28		this work
[Mn(Cl)ODMAPz] (**2**)		−0.077^a	−1.32		this work
Mn^{II}Pc			−0.4 to −0.5		36
[Mn(TPP)(Cl)(H_2O)]			−0.5 to −0.7		31, 38

[a] May be the Mn(IV)/Mn(III) couple; see text.

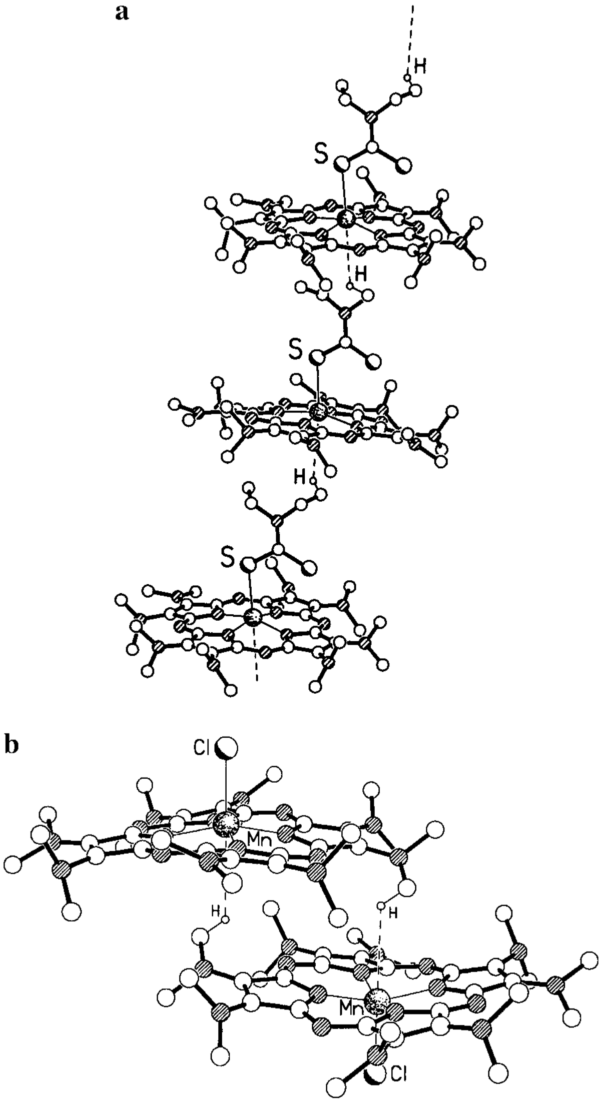

Figure 3. Packing diagrams showing the weak intermolecular contacts present in (a) the chainlike structure of **1** and (b) the dimeric structure of **2**. The nonbonded Mn···Mn contacts are 9.92 and 7.21 Å, respectively.

The Mn(III)/Mn(II) reduction waves for **1** and **2** (the [Mn^{3+}Pz^{2-}]$^+$/[Mn^{2+}Pz^{2-}] couple) occur at ≈−1.3 V (vs Fc$^+$/Fc). This is a dramatic cathodic shift compared to literature values for other Mn macrocycles (Table 4). Thus, the Mn(III)/Mn(II) couple has a potential of −0.40 to −0.5 V for Mn^{II}Pc,[36,37] while for [Mn(TPP)(Cl)(H_2O)] and related porphyrin compounds, the analogous half-wave potential lies between ca. −0.5 and −0.7 V.[31,38,39] Clearly, the eight dimethylamino groups make the macrocycle extremely electron-rich, destabilizing the Mn(II) oxidation state and making Mn^{II}ODMAPz an exceptionally strong reductant.

No reversible couples were observed up to −2.0 V, suggesting that the ring reductions either are no longer reversible or have been shifted by metalation with manganese to potentials more negative than this limit. The couple at −0.07 mV for **1** and **2** we tentatively assign as metal-centered, [Mn^{4+}Pz^{2-}]$^{2+}$/[Mn^{3+}Pz^{2-}]$^+$, rather than as ring-based, [Mn^{3+}Pz$^-$]$^{2+}$/[Mn^{3+}Pz^{2-}]$^+$, because it occurs some 200 mV more positive than the first ring oxidation in the H_2, Ni(II), or Cu(II) porphyrazines. No reversible oxidation waves are observed at potentials more positive.

Reports of the Mn(IV)/Mn(III) couple for phthalocyanines are scarce, but Lever et al. have given an $E_{1/2}$ of ca. +0.5 V for the [Mn^{4+}Pz^{2-}]$^{2+}$/[Mn^{3+}Pz^{2-}]$^+$ couple.[37] A recent electrochemical study of manganese tetraphenylporphyrins in aqueous solution placed the Mn(IV)/Mn(III) couple between +0.3 and +0.7 V, depending upon the pH of the solution.[40] The shift to more negative potentials for both the Mn(III)/Mn(II) and Mn(IV)/Mn(III) couples for these manganese porphyrazines again is attributed to the strong electron-donating ability of the dimethylamino groups, making the ODMAPz macrocycle significantly more electron-rich than its phthalocyanine or porphyrin relatives.

Magnetic Susceptibility. A plot of the product of the molar magnetic susceptibility and temperature ($\chi_M T$) versus temperature for **2** is shown in Figure 4; the data for **1** are similar and are not shown. The $\chi_M T$ curve exhibits a plateau region between 300 and 10 K with a magnetic moment of 2.8−2.9 cm^3 mol^{-1} K, indicative of simple Curie behavior for a high-spin d^4 $S = 2$ ground state, as seen for both Mn(III) phthalocyanine[41] and porphyrin complexes.[31] At low temperatures, the $\chi_M T$ data quickly decrease to a minimal value of 2.0 cm^3 mol^{-1} at 1.9 K for both **1** and **2**. This downturn in $\chi_M T$ could be due to either zero-field splitting of the $S = 2$ ground state or a weak antiferromagnetic exchange interaction between neighboring Mn(III) ions. The latter effect is ruled out because the crystallographic data for compounds **1** and **2** show no reasonable pathways for mediating antiferromagnetic coupling between manganese centers (vide supra). Thus, for interpreting the magnetic phenomena, we used the well-known expression for the molar susceptibility of an $S = 2$ system that exhibits an axial zero-field splitting, characterized by the conventional zfs

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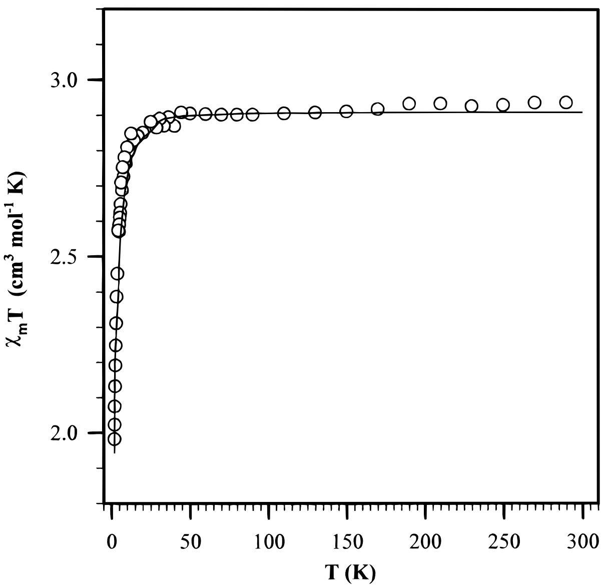

Figure 4. Plot of the product of the molar magnetic susceptibility times temperature ($\chi_M T$) versus temperature for a polycrystalline sample of **2**. The solid line represents the best fit by using the model given in eq 1, with $|D| = 3.30$ cm^{-1} and $g = 1.96$.

Table 5. Magnetic Parameters for Mn(III) Porphyrinic Compounds[a]

compound	D/cm^{-1}	g[c]	technique[e]	ref
[Mn(Et_2dtc)ODMAPz]	±3.3(1)	1.96	magn susc	this work
	−2.625(5)	1.983	HFEPR	10
[Mn(Cl)ODMAPz]	±3.1(1)	2.04	magn susc	this work
	−2.326(5)	1.984	HFEPR	10
Mn(TPP)Cl	−2.3(2)	2[d]	magn susc	42
	−2.273(5)	1.822	HFEPR	10
Mn(TPP)ClO_4·$2H_2O$[b]	−2.3(1)	2.00	magn susc	45
Mn(OEP)Cl·H_2O[b]	−1.6(1)	2.02	magn susc	45
Mn(OEP)ClO_4·H_2O[b]	−2.3(1)	1.96	magn susc	45
Mn(DP−IX-DME)Cl	−2.53(2)	2[d]	far-IR abs	47

[a] Abbreviations used: TPP = 5,10,15,20-tetraphenylporphyrinato; OEP = octaethylporphyrinato; DP-IX-DME = deuterioporphyrin IX dimethyl ester. [b] The effect of small exchange coupling (J) was explored, and a negative sign of D was assumed. [c] An isotropic g value is assumed in all cases. [d] The g value was not determined here but assumed equal to 2. [e] Pure powder samples were used for all measurements.

parameter, D. An averaged value of the $\chi_{\|}$ and $\chi_{\perp}$ components for the susceptibility was used as described in eq 1, where $x =$

$$\chi_M = \frac{C}{3}\left[\frac{2\exp(-x) + 8\exp(-4x)}{1 + 2\exp(-x) + 2\exp(-4x)}\right] + \frac{2C}{3}\left[\frac{(6/x)(1 - \exp(-x)) + (4/3x)(\exp(-x) - \exp(-4x))}{1 + 2\exp(-x) + 2\exp(-4x)}\right] \tag{1}$$

D/kT and $C = Ng^2\mu_B{}^2/kT$.[22] A best fit, displayed in Figure 4, was obtained with $|D| = 3.30$ cm^{-1} and $g = 1.96$ (Table 5); the sign of D cannot be determined by this fitting procedure.[42−44] Similar results were obtained by fitting the susceptibility data for **1** (data not shown), and a best fit gave final parameters of $|D| = 3.1$ cm^{-1} and $g = 2.04$. We recently probed the ground states of **1** and **2** through high-field EPR (HFEPR) spectroscopy.[10] Although these compounds are EPR-silent at conventional microwave frequencies (X or Q band), measurements at high frequency (200−500 GHz) and high field (0−14 T) yield strong EPR signals arising from within the $S = 2$ manifold. By collecting spectra at multiple frequencies, we were able to determine the magnitude of D to high precision, and to obtain its sign, and these results are listed in Table 5 for comparison.

A variety of methods, including magnetic susceptibility,[42,43] variable-field magnetization,[43,45,46] and far-infrared spectroscopy,[47] have been used to determine the magnetic behavior of analogous Mn(III) porphyrin molecules. In all of these studies the ground state was found to be $S = 2$, with 1.0 cm^{-1} < $|D|$ < 3.0 cm^{-1}, and these data are summarized in Table 5. Changing the identity of either the porphyrin macrocycle or the axial ligand does not effect large changes in D (i.e., several wavenumbers). More subtle changes are evident from the HFEPR data, and the axial sulfur-donating Et_2dtc ligand gives the largest $|D|$ value in Table 5. Reports on the magnetism of Mn(III) phthalocyanine compounds are scarce; the one study of Mn(Cl)Pc assigned it as having an $S = 2$ ground state but made no attempt at discerning zfs effects.[41] The only other Mn(III) porphyrazine complex, prepared by Ricciardi et al., was examined by magnetic susceptibility measurements.[8] The high-temperature data showed that the ground state is $S = 2$. The data were interpreted in terms of an exchange-coupled model that found the Mn centers to be weakly antiferromagnetically coupled ($J = 1.58$ cm^{-1}, $H = JS_1 \cdot S_2$), and no attempt was made to take zfs effects into account.

Peripheral Metalation. Experiments to examine peripheral chelation employed NiODMAPz (**4**), which has the porphyrazine central cavity occupied by Ni(II).[48] The reactions of several metal salts with **4**, including Mn(Et_2dtc)$_2$, Mn(acac)$_2$, $CuCl_2$, $CuBr_2$, and Cu(OAc)$_2$, were monitored by UV−vis spectroscopy and TLC (silica gel). When 4 equiv of $CuCl_2$ was reacted with **4**, the solution gave an optical spectrum with peaks at 305 and 650 nm and a dark green solid was obtained, but numerous attempts failed to give crystals suitable for an X-ray diffraction measurement. Analogous reactions with $CuBr_2$ gave a dark brown precipitate that was insoluble in common organic solvents, making purification and characterization impractical. Optical spectroscopy and TLC data suggested that **4** does not react with Cu(OAc)$_2$ Mn(Et_2dtc)$_2$, or Mn(acac)$_2$.

Reaction of **4** with $PdCl_2$ (Scheme 1) gave an immediate precipitate which could be isolated by filtration and washed carefully to yield an analytically pure solid of formula [Ni(ODMAPz)($PdCl_2$)$_4$] (**5**). This solid proved insoluble in most common organic solvents but was soluble in DMF. The formation of the peripherally metalated *star*-porphyrazine **5** depicted in Scheme 1 is indicated not only by the stoichiometry as defined by elemental analysis but also by the optical spectrum shown in Figure 1.[49] In this case the Soret band is found at 316 nm, slightly blue-shifted from the spectra of H_2ODMAPz (**3**) or NiODMAPz (**4**), and the Q band is now dramatically sharpened to a single peak at 602 nm, implying 4-fold symmetry for the macrocycle. The position of this sharp band lends

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credence to the assignment of the Q band as the peak found at the same position for **1** and **2**. The n−π* peaks are lost completely because the lone pairs of all the dimethylamino nitrogen atoms in **5** are bound to Pd(II), making them inaccessible for charge transfer into the porphyrazine π system. Analogous changes in the UV−vis spectrum occur upon binding of metals to dithiolato-[50] and crown-functionalized porphyrazines.[51] Work is in progress with the more soluble products formed between metal caps such as $PdCl_2$ and an unsymmetrical porphyrazine bearing only one dimethylamino chelate and will be reported in due course.[52]

Conclusions

We have successfully carried out the syntheses and determined the X-ray crystal structures of two new Mn(III) porphyrazine complexes. Metalation of the central cavity by manganese(III) causes several distinct changes in the optical spectrum as compared to those of the free base and Ni(II) forms, including a blue shift in the Q band and the appearance of a shoulder near 800 nm that may be an LMCT transition. The Ni(II) form of ODMAPz chelates four $PdCl_2$ units, and the dramatic changes in the optical spectra caused by this peripheral metalation are consistent with the palladium ions binding to the bidentate dimethylamino groups. Examination of these compounds by electrochemical methods has yielded the fact that they are markedly easier to oxidize than other manganese(III) porphyrazine, phthalocyanine, or porphyrin compounds, thus indicating that the dimethylamino groups donate significant electron density into the macrocycle.

Compounds **1** and **2** provide rare examples in which Mn(III) ions are coordinated in a porphyrin-type core and are truly isolated from nearest-neighbor interactions. Often, complications in fitting magnetic data for this type of macrocycle arise from intermolecular interactions caused by close stacking of the ring systems. In this case, it was possible to study the single-ion spin ground states in detail by magnetic susceptibility measurements and obtain good theoretical fits of the data. These complexes provide initial structural and magnetic information that we may be able to use in engineering magnetic properties applicable to problems in materials science as well as biomedical imaging, as part of our wider efforts in synthesizing a new family of metalloporphyrazine complexes.

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Supporting Information Available: Tables giving complete X-ray experimental details, fractional atomic coordinates including those of the hydrogen atoms, equivalent isotropic displacement parameters, bond lengths, bond angles, and isotropic displacement parameters for compounds **1** and **2** (15 pages). Ordering information is given on any current masthead page.

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