6c for the structure of the alkyl intermediate (when L is a nonchelating phosphine) and to rationalize the substituent effects (on L and the olefin) by singling out the factors which control the corresponding energy barrier. Work along these lines is currently in progress.

Acknowledgment. Calculations have been carried out at the Centre de Calcul du CNRS in Strasbourg-Cronenbourg. We thank the staff of the Centre for their cooperation. This work has been supported through A.T.P. No. 3790 of the CNRS.

Registry No. **1** (L = PPh_3), 14694-95-2; **2**, 72152-06-8; **3a**, 71213-98-4; **3b**, 71213-97-3; **3c**, 71171-41-0; **4a**, 72152-07-9; **4b**, 72173-73-0; **4c**, 72173-74-1; **4d**, 72173-75-2; **4e**, 72173-76-3; **4f**, 72173-77-4; **4g**, 72173-78-5; **4h**, 72173-79-6; **4i**, 72173-80-9; **5a**, 72152-08-0; **5b**, 72257-15-9; **5c**, 72257-16-0; **5d**, 72257-17-1; **5e**, 72257-18-2; **5f**, 72257-19-3; **6a**, 72152-09-1; **6b**, 72173-81-0; **6c**, 72173-82-1; **6d**, 72173-83-2; **6e**, 72173-84-3; **6f**, 72173-85-4; **6g**, 72173-86-5; **6h**, 72173-87-6; **6i**, 72173-88-7; **6j**, 72173-89-8.

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Octakis(alkylthio)tetraazaporphyrins

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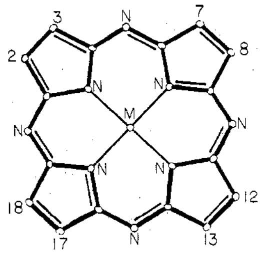
Received July 30, 1979

Free-base and metal-substituted 2,3,7,8,12,13,17,18-octakis(methylthio)tetraazaporphyrins have been synthesized and characterized. The Mg, Ni, and Cu derivatives are discussed. The method of preparation presents a synthetic procedure for a range of (alkylthio)- or (arylthio)tetraazaporphyrins. Electron paramagnetic resonance measurements are reported for copper octakis(methylthio)tetraazaporphyrin ($g_{\parallel} = 2.14$, $g_{\perp} = 2.06$, $\langle a_{Cu} \rangle = 95$; $A_{\parallel}^{Cu} = 215$; $A_N = 19.9$, $C_N = 15.0$) and for the $S = 1$ dimer ($D = 400$ G).

The template reaction, in which four molecules of phthalonitrile condense about a divalent metal ion to form a metallophthalocyanine, M(Pc), is well-known. Metallotetraazaporphyrins, M(TAP), can be prepared by the analogous template condensation of maleonitrile.[2] However, peripherally substituted tetraazaporphyrins are synthesized much more conveniently than the parent macrocycle because disubstituted maleic dinitriles are more stable than the parent compound. Since the substituted tetraazaporphyrins may prove valuable as pigments[3] or catalysts,[4] a convenient route to a diverse set of such complexes is desirable.

The action of alkyl or aryl iodides or diiodides on disodium maleonitrile, $Na_2(mnt)$,[5] yields a wide variety of cis-substituted maleic dinitriles. These provide a rich source of starting materials for the synthesis of substituted tetraazaporphyrins. A few cis-substituted maleic dinitriles, notably 1,2-dicyano-3,6-dithiacyclohexene[6] and 1,2-dicyano-3,6-dithia-4-phenylcyclohexene,[7] have been condensed to form substituted tetraazaporphyrins, respectively the free base and copper derivatives. However, preparations of such relatively unstable metal derivatives as the magnesium macrocycle from free-base tetraazaporphyrin or of any other metal derivative from the stable copper complex are not trivial procedures. Thus, the above syntheses do not present a convenient route to the full variety of metal-substituted tetraazaporphyrins.

We find that the template condensation of disubstituted maleonitriles in the presence of magnesium propoxide leads directly to the magnesium derivative of the octasubstituted tetraazaporphyrins and that these materials provide a convenient route to the preparation of parent macrocycle and thence to other metal derivatives. Several disubstituted maleonitriles have been condensed by this procedure: 1,2-dicyano-3,6-dithiocyclohexane, 1,2-dicyano-3,6-dithiocyclopentane, and 1,2-dicyano-1,2-bis(methylthio)ethylene. We illustrate the technique by presenting the synthesis and properties of metal 2,3,7,8,12,13,17,18-octakis(methylthio)tetraazaporphyrin, M(OMTTAP), where M = Mg, "H_2", Cu, or Ni.



M(OMTTAP)

Experimental Section

All solvents and chemicals used in the experiments were obtained commercially and were of reagent grade. They were used without further purification except for drying with molecular sieves.

Visible spectra were recorded on a Beckman ACTA III spectrophotometer in the range of 350–750 nm. X-Band electron paramagnetic resonance, EPR, measurements were carried out by using a highly modified Varian E-4 X-band EPR spectrometer, with 100-kHz field modulation. For **g**-tensor measurements, 2,2-diphenyl-1-picrylhydrazyl (DPPH, $g = 2{,}0036$) was used to provide absolute field calibration. The cavity resonance frequency was measured to an accuracy of 5 ppm by a transfer oscillator technique.

Elemental analyses were performed by Miss H. Beck, Northwestern Analytical Services Laboratory.

Synthesis. $C_6H_6N_2S_2$. 1,2-Dicyano-1,2-bis(methylthio)ethylene (**I**) was prepared by reacting methyl iodide with Na_2mnt by the method of Bähr et al.[8]

Mg(OMTTAP). Magnesium, 1.0 g (41 mmol), was dissolved in 20 mL of refluxing 1-propanol during 8 h with the aid of a crystal of iodine as initiator. To the resulting magnesium propoxide suspension was added 3.5 g (21 mmol) of I as a slurry in 40 mL of 1-propanol. The combined mixture was refluxed for 18 h. The reaction mixture was filtered hot. The residual solid was discarded after washing with

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Table I. Electronic Spectra Band Maxima and Molar Extinction Coefficients of the M(OMTTAP) Complexes and Some M(TAP), M(Pc), and M(TPP) Complexes

	OMTTAP		TAP[g]		Pc[h]		TPP[i]	
	max, nm	$10^{-3}\epsilon$	max, nm	$10^{-3}\epsilon$	max, nm	$10^{-3}\epsilon$	max, nm	$10^{-3}\epsilon$
Mg	672	75.2[a]	584	50.3[b]	674	49.4[d]	603	10
	620	26.5	536	41.7	647	43.9	562	22
	500	12.9			610	44.5	521	2.5
	375	68.9	326	47.9	347	47.3	427	600
H_2	709	35.0[a]	617	47.5[a]	698	52.1[e]	647	3.4[f]
	637	25.5	545	46.0	665	51.8	592	5.3
	515	20.0			638	46.2	548	8.1
					602	44.3	515	18.7
	367	42.3	333	47.0	350	47.4	419	478
Ni	660	42.2[a]	577	47.7[c]	671	51.0[e]	529	17.1[f]
	482	18.6	530	41.4	643	44.7	490	3.5
						45.1		
	347	39.9	345	45.0	351	45.7	416	233
Cu	667	48.4[a]	578	49.8[c]	678	53.4[e]	580	2.19
	610	19.9	531	41.3	648	45.1	540	20.4
	497	14.8			611	45.6	505	3.65
	363	36.2	334	45.7	350	47.6	417	447

[a] In C_6H_5Cl. [b] In CH_3OH. [c] In $C_6H_4Cl_2$. [d] In C_5H_5N. [e] In $C_{10}H_7Cl$. [f] In C_6H_6. [g] Reference 2. [h] Reference 1. [i] Reference 9.

several portions of acetone. The combined 1-propanol filtrate and acetone washings were taken to dryness under reduced pressure. The resulting blue solid was then recrystallized from acetone to yield reddish purple platelets (yield about 60%).

Anal. Calcd for $MgC_{16}N_8(SCH_3)_8$: C, 40.88; H, 3.41; N, 15.89. Found: C, 40.59; H, 3.84; N, 15.50.

H_2(OMTTAP). Mg(OMTTAP) was dissolved in a minimum of concentrated sulfuric acid and poured slowly over ice, precipitating H_2(OMTTAP). The suspension was carefully neutralized with aqueous ammonia and filtered. The solid H_2(OMTTAP) was washed with distilled water until the washings were neutral. Recrystallization from benzene yielded olive green crystals (yield about 65%).

Anal. Calcd for $H_2C_{16}N_8(SCH_3)_8$: C, 42.18; H, 3.54; N, 16.41. Found: C, 42.47; H, 3.79; N, 15.70.

Ni(OMTTAP) and Cu(OMTTAP). Direct synthesis of other metal derivatives from Mg(OMTTAP) by refluxing with the metal acetate was unsuccessful. However, M(OMTTAP) with, e.g., M = Ni and Cu can be prepared via the metal-free material. A solution of 0.5 g of H_2(OMTTAP) (0.68 mmol) and a 10 molar excess of the appropriate anhydrous metal acetate in 25 mL of chlorobenzene was refluxed for 24 h. The solution was filtered hot, and the residual solid was discarded after washing with benzene. The combined filtrates were taken to dryness, and the resultant blue solid was washed successively with dilute hydrochloric acid and distilled water to remove any residual metal salts (yield about 65% Ni(OMTTAP) and 80% Cu(OMTTAP)).

Anal. Calcd for $NiC_{16}N_8(SCH_3)_8$: C, 38.95; N, 15.15; H, 3.27. Found: C, 38.61; N, 14.26; H, 3.82. Calcd for $CuC_{16}N_8(SCH_3)_8$: C, 38.70; N, 15.05; H, 3.25. Found: C, 38.81; N, 12.71; H, 3.09.

Results and Discussion

Electronic Spectra. The absorption maxima of the visible absorption spectra of the M(OMTTAP) complexes studied are listed in Table I. The table includes band positions for some M(TAP),[2] M(Pc),[1] and metallotetraphenylporphyrins, M(TPP),[9] for comparison. In all cases these macrocycles show two sets of intense absorptions. The well-known metalloporphyrin Soret peak, near 400 nm, and visible bands near 550 nm are respectively blue and red shifted and much intensified in the aza-bridged macrocycles. In all cases the longer wavelength absorption patterns have more lines in the lower symmetry (D_{2h}) parent macrocycle than in the more symmetrical (D_{4h}) metal derivatives.

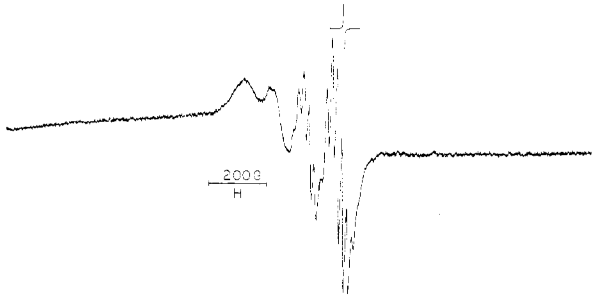

Figure 1. Fluid-solution electron paramagnetic resonance spectrum of Cu(OMTTAP) (10^{-3} M) in benzene at room temperature. DPPH provides an absolute field calibration.

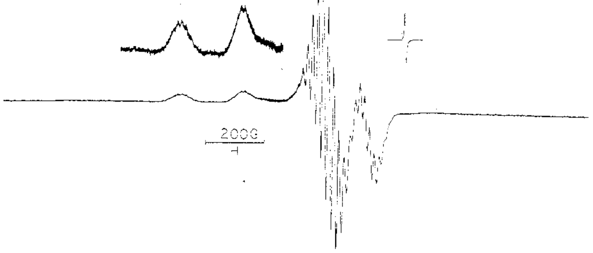

Figure 2. Frozen-solution electron paramagnetic resonance spectrum of Cu(OMTTAP) (10^{-3} M) in concentrated sulfuric acid at 77 K. DPPH provides an absolute field calibration. Inset is at 4× higher gain.

Table II. Electron Paramagnetic Resonance Parameters[a] for Cu(OMTTAP), Cu(TPP), and Cu(Pc)

complex	$g_\parallel$	$g_\perp$	A_{Cu}	B_{Cu}	$\langle a_{Cu} \rangle$	A_N	B_N	$\langle a_N \rangle$
Cu(OMTTAP)	2.14	2.06	215		95	19.9	15.0	16.5
Cu(TPP)[b]	2.19	2.03	209	31.8	89.5	18.9	14.9	15.7
Cu(Pc)[c]	2.18	2.05	198	20.0	81.9	18.6	14.2	15.9

[a] hfs and shfs coupling constants in units of gauss; however, calculations took into account the dependence of splittings in these units on the associated *g* factor.[10] [b] Reference 10. [c] Reference 11.

In particular, H_2(OMTTAP) has two intense peaks at 637 and 709 nm which collapse into a single peak at intermediate wavelength upon metal incorporation (Table I). The M(OMTTAP) have an additional broad, weak band in the region of 500 nm. Interestingly the substituted tetraazaporphyrins in general show a distinct broadening and red shift of their absorption bands in comparison with the corresponding unsubstituted tetraazaporphyrins. The band positions are in fact more comparable to those of the corresponding M(Pc) complexes.

Paramagnetic Resonance. The electron paramagnetic resonance spectrum of Cu(OMTTAP) in a benzene fluid solution is shown in Figure 1; all common organic solvents which dissolve the complex give similar spectra. There are four lines of equal intensity, but unequal width, split by the isotopically weighted hyperfine coupling to the ^{63,65}Co nucleus of the monomeric macrocycle, $\langle a_{Cu} \rangle$ = 95 G. Further hyperfine splittings from the four equivalent ligating ^{14}N are resolvable in the two high-field lines, $\langle a_N \rangle$ = 16.5 G.

Figure 2 displays the frozen-solution spectrum of Cu(OMTTAP) in concentrated sulfuric acid at 77 K. It is characteristic of a monomeric square-planar Cu(II) complex with axial **g** tensor and ^{63,65}Cu hyperfine (hfs) tensor.[10,11]

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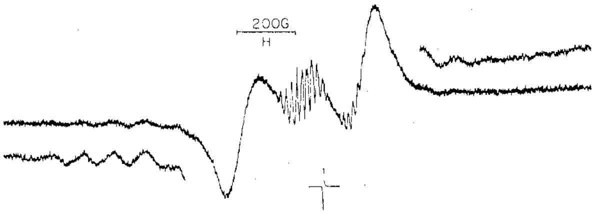

Figure 3. Frozen-solution electron paramagnetic resonance spectrum of Cu(OMTTAP) (10^{-3} M) in 1-chloronaphthalene at 77 K. The spectrum is almost completely due to the $S = 1$ dimer, $[\mathrm{Cu(OMTTAP)}]_2$; only the weak, sharp lines in the center come from monomers. DPPH provides an absolute field calibration. Inset is at 3× higher gain.

Tensor values are listed in Table II.

The spectrum further shows superhyperfine splitting (shfs) from interaction with the coordinating ^{14}N. ENDOR studies on the related Cu(TPP) show that, within the precision of powder EPR measurements, the ^{14}N shfs tensors will be axial, with the unique tensor value, A_N, corresponding to the Cu–N vector.[10] Thus the splitting of the individual Cu hfs lines in the g-parallel region corresponds not to A_N but to the other ^{14}N hfs values, B_N (Table II). The nine-line shfs of the $g_\perp$ features corresponds to $B_N' = (A_N + B_N)/2$,[10] allowing the determination $A_N = 2B_N' - B_N$ (Table II). This value is in good agreement with that obtained from B_N and the isotropic ^{14}N hfs: $A_N = 3\langle a_N \rangle - 2B_N$.

The **g** and hfs tensor values for Cu(Pc) and Cu(TPP) are also presented in Table II. Comparison of the spin-Hamiltonian parameters for the three related Cu(II) macrocycles shows a curious pattern. One might have anticipated that Cu(OMTTAP) would present values intermediate between those of Cu(TPP) and the larger but aza-bridged Cu(Pc). However, in all the critical parameters Cu(OMTTAP) shows an extreme value, the smallest $g_\parallel$, and the largest A_{Cu}, $\langle a_{Cu} \rangle$, A_N, and $\langle a_N \rangle$. Detailed analysis of the electronic properties of the two aza-bridged macrocycles, for comparison with that recently performed for Cu(TPP),[10] should be quite interesting.

Frozen solutions of Cu(OMTTAP) in organic solvents (Figure 3) show spectra quite different from that in frozen sulfuric acid. The spectra in frozen organic solvents are characteristic of a randomly oriented triplet species ($S = 1$),[12,15] indicating the formation of $[\mathrm{Cu(OMTTAP)}]_2$ dimers upon freezing. It might be expected that coordination of nitrogenous bases to the Cu(II) would disrupt the dimers, but somewhat surprisingly they persist in neat pyridine (10^{-4} M Cu(OMTTAP)).

The separation of the center fields of the two most intense peaks in Figure 3 is 400 G and corresponds to $D_\perp$, the standard zero-field splitting parameter about $g_\perp$.[12-15] Cu hfs for the dimer are resolved for $g_\parallel$, and are most readily discernible in the low-field region of the spectrum. The observed pattern of seven hyperfine lines, with a hyperfine splitting half that observed for the monomer, indicates that exchange coupling is larger than the Larmor energy. For such an exchange-coupled dimer the experimentally determined $D_\perp$ is composed of contributions from the magnetic dipole–dipole interactions and from the pseudodipolar term which originates in spin–orbit coupling. It has been shown, however, that the pseudodipolar term can usually be neglected. Metal–metal distances, R, which are estimated from the zero-field splitting by treating the two d^9 Cu(II) ions as point dipoles are in reasonable agreement with the R for a dimer as determined by other means.[14] Following this approach, $R\ (\text{Å}) = (0.650 g_\perp^2 / D_\perp\ (\text{cm}^{-1}))^{1/3}$. The measured $D_\perp$ for $[\mathrm{Cu(OTMTAP)}]_2$ gives $R = 4.3$ Å. This value suggests that the dimer involves face to face stacking, with a slipped, metal-over-nitrogen arrangement. This distance is roughly in the middle of the range previously reported. Yokoi et al. report on a series of copper β-diketonate dimers with R ranging between 3.73 and 4.50 Å;[13] Collman et al. report that copper "face to face" porphyrins have an R of about 6.5 Å.[15]

The tetraazaporphyrins have been long known but little studied in comparison with their more readily accessible relatives, the metalloporphyrins and M(Pc). With a variety of substituted M(TAP) complexes now readily available, studies of their electronic, electrochemical, and solid-state properties can be pursued. These will be reported later.

Acknowledgment. We thank Dr. Terry E. Phillips for helpful discussions. This work has been supported by the Materials Research Center of Northwestern University (Grant DMR 76-80847-A01).

Registry No. I, 7373-02-6; $\mathrm{H_2(OMTTAP)}$, 72207-07-9; Mg(OMTTAP), 72207-40-0; Ni(OMTTAP), 72207-41-1; Cu(OMTTAP), 72207-42-2.

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