ciated with all the methyl carbon atoms (consistent with the low decomposition temperature of **1**), a resolvable rotational disorder could only be found for the methyls on P(2). On the basis of relative peak heights, occupancy factors of 0.5 (50%) were assigned carbon atoms C(4)–C(6) and C(4)′–C(6)′. The occupancy factors were not refined. Due to the disorder and high thermal motion of the carbon atoms, the hydrogen atoms could not be located and were not included in the final refinement. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.038$ and $R_w = 0.050$. A final difference Fourier showed no feature greater than 0.3 e$^-$ Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table V.[31]

X-ray Data Collection, Structure Determination, and Refinement for *trans*-[Mo(C_2H_4)$_2$(PMe$_3$)$_4$] (3). Single crystals of the compound were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 36°$) accurately centered on the diffractometer are given in Table IV. Systematic absences defined the space group as $P2_1/n$.

Data were collected as described for the previous compound. The intensities were corrected for Lorentz and polarization effects but not for absorption. Neutral atom scattering factors were obtained as noted above, and that of molybdenum was corrected for the real and imaginary components of anomalous dispersion.

The position of the molybdenum atom was revealed by the inspection of a Patterson map, and the subsequent calculation of a difference Fourier map allowed the location of the remaining non-hydrogen atoms. Refinement with isotropic thermal parameters led to a reliability index of $R = 0.078$. The hydrogen atoms were located with the aid of a difference Fourier map and included in the final refinement with fixed contributions. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.043$ and $R_w = 0.048$. A final difference Fourier showed no feature greater than 0.3 e$^-$/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table VI.[31]

X-ray Data Collection, Structure Determination, and Refinement for *trans,mer*-[Mo(C_2H_4)$_2$(CO)(PMe$_3$)$_3$] (4). The data were collected and treated as described above. Final lattice parameters from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 42°$) accurately centered on the diffractometer are given in Table IV. The space group, uniquely determined from systematic absences, is $P2_1/n$.

The molybdenum atom position was revealed by the inspection of a Patterson map, and the remaining non-hydrogen atoms located on a difference Fourier map. Refinement with isotropic thermal parameters led to $R = 0.097$. Location of the hydrogen atoms on a difference Fourier map, inclusion with fixed contributions, and anisotropic refinement of the non-hydrogen atoms led to final values of $R = 0.037$ and $R_w = 0.043$. A final difference Fourier showed no feature greater than 0.3 e$^-$/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table VII.[31]

Acknowledgment. We are very grateful to R. D. Priester and to Dr. Peter Edwards for recording the high-field and variable-temperature NMR spectra. Early ^{31}P NMR spectra of **3**, recorded by Dr. A. Sânchez-Delgado are also gratefully acknowledged. This work was supported by the Spanish C.A.I.C.Y.T (E.C.) and Ministerio de Educaciôn y Ciencia (J.M.M. and M.L.P.) and the U.S.N.S.F. (J.L.A.). Some of this work originated at Imperial College, London, and we thank Prof. G. Wilkinson for his help and for valuable suggestions.

Supplementary Material Available: Tables of thermal parameters and observed and calculated structure factors for **1**, **3**, and **5** (47 pages). Ordering information is given on any current masthead page.

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(31) See paragraph at the end of paper regarding supplementary material.

Steric and Electronic Influences of Methyl Substitution on Transition-Metal Complexes of Tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecine

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Received August 2, 1982

Abstract: Transition-metal complexes of a tetraaza macrocyclic ligand obtained from Schiff base condensations of 2-amino-5-methylbenzaldehyde were synthesized and characterized (M(MeTAAB)$^{2+}$, M = Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, and Pt^{2+}). The crystal structure of [Cu(MeTAAB)(NO$_3$)][NO$_3$] was determined by using X-ray crystallographic techniques. The complex crystallizes in the space group $P2_1/c$ with unit cell dimensions $a = 13.136$ (6) Å, $b = 17.294$ (7) Å, $c = 17.391$ (4) Å, and $\beta = 127.66$ (2)°. The coordination sphere of the copper ion is six-coordinate, N$_4$O$_2$, with a symmetrically bidentate nitrate making the overall geometry a bicapped square pyramid. The macrocyclic ligand is, as expected, distinctly saddle shaped, with S_4 symmetry.

The propensity of *o*-aminobenzaldehyde for self-condensation has been found to be extremely sensitive to the chemical environment. The nature of the products formed was first clarified as early as 1926 by Seidel[1,2] and later, in the 1960s, by McGeachin[3] and Melson and Busch.[4-7] Since then numerous studies of condensation reactions of *o*-aminobenzaldehyde in the presence of a variety of transition-metal ions have been made.[8-14] It is now well substantiated that in the absence of metal ions various polycyclic derivatives of condensates of *o*-aminobenzaldehyde are formed.[1-3,15] On the other hand, transition-metal ions have the ability to act as templates, whereby closed-ring macrocyclic ligands can be isolated as their metal complexes. A

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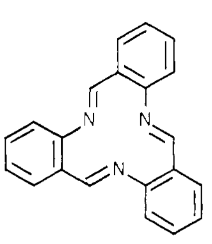
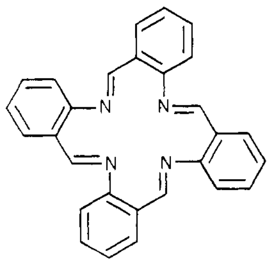
trimeric and/or tetrameric condensate, known as TRI (I) and



I



II

TAAB (II), respectively, can be isolated in this manner depending on the metal ion and reaction conditions. More recently, in this laboratory, an intermediate condensate of *o*-aminobenzaldehyde was isolated and characterized by using platinum(II) ion as a template.[16]

In view of the sensitivity of *o*-aminobenzaldehyde to media influences, the condensation reactions should also be susceptible to electronic effects generated by ring substituents. Investigations using substituted *o*-aminobenzladehydes have unfortunately been limited to a chloro derivative.[17] In reactions of 2-amino-5-chlorobenzaldehyde with nickel(II) ion, only the trimeric condensate ClTRI was isolated as its nickel(II) complex,[17] with no evidence of ClTAAB. Thus it was postulated that the electron-withdrawing effect of the chloro group deactivated the molecule toward condensation. Extended studies in this laboratory using a variety of metal ions have yielded analogous results.[18] In order to examine further the sensitivity of these condensation reactions to substituent effects, 2-amino-5-methylbenzaldehyde was synthesized. It was anticipated, based on the studies involving the 5-chloro derivative, that the electron-donating effects of the methyl group would activate the amine so that both trimeric and tetrameric condensates could be obtained with a variety of metal ions. The synthesis of 2-amino-5-methylbenzaldehyde and its reactivity are discussed below.

Experimental Section

General. All chemicals were reagent grade. Proton NMR spectra were recorded on a Varian EM-360 CW spectrometer at 60 MHz. Mass spectra were obtained on a Varian MAT CH-5 spectrometer. Infrared spectra were recorded from 4000 to 400 cm^{-1} on a Perkin-Elmer Model 421 grating spectrophotometer as KBr pellets. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, IL, and at the Microanalytical Laboratory, University of Kansas, by Dr. Tho Nguyen.

Preparation of 5-Methyl-2-[(triphenylmethyl)amino]benzoic Acid (1). A solution of 2-amino-5-methylbenzoic acid (2.0 g, 13 mmol) and triphenylmethyl chloride (6.0 g, 22 mmol) was heated in 50 mL of pyridine on a steam bath for 5 min and allowed to sit at room temperature overnight. The resulting solution was filtered and the filtrate was evaporated in vacuo at room temperature. The crude product was purified by washing with 300 mL of water followed by recrystallization from chloroform to give 5.8 g (12.4 mmol, 95%) of the benzene solvate of **1**. The product decomposes at 229 °C: ^1H NMR (Me_2SO-d_6) δ 1.97 (s, 3 H), 5.83–6.57 (m, 3 H), 7.05–7.20 (m, 21 H), 7.52 (s, 1 H), 9.47(s, 1 H); IR (cm^{-1}) 3140, 3060, 1660, 1580, 1515, 1490, 1445, 1235, 695; mass spectrum, *m/e* 393 (calcd = obsd). Anal. Calcd for $C_{27}H_{23}NO_2{\cdot}C_6H_6$: C, 84.08; H, 6.16; N, 2.97. Found: C, 84.44; H, 6.30; N, 2.98.

5-Methyl-2-[(triphenylmethyl)amino]benzyl Alcohol (2). $LiAlH_4$ (1.0 g, 30 mmol) was dissolved in 200 mL of absolute ether in a 500-mL, three-necked round-bottom flask, fitted with a condenser and a stopper. In the third neck **1** (4.49 g, 9 mmol) was added in small portions with stirring. When the addition was complete, the third neck was stoppered and the reaction mixture was stirred at room temperature for 1.5 h during which the color of the solution changed from gray to green and back to gray. The reaction was quenched with ethyl acetate and water until a white precipitate formed, which was filtered and rinsed with ether (200 mL) and chloroform (100 mL). The filtrate was dried over anhydrous magnesium sulfate and the solvent removed in vacuo. The resulting oil was crystallized from methanol, yielding a pale-yellow solid (3.36 g, 91% based on **1**), mp 178 °C; ^1H NMR ($CDCl_3$) δ 2.05 (s, 3 H), 4.55 (s, 2 H), 5.82–6.61 (m, 4 H), 7.20 (m, 15 H); IR (cm^{-1}) 3570, 3430, 1630, 1595, 1510, 1490, 1450, 1310, 805, 745, 695, 630. Anal. Calcd for $C_{27}H_{25}NO$: C, 85.45; H, 6.64; N, 3.69. Found: C, 85.09; H, 6.70; N, 3.69.

Table I. Elemental Analyses for $M(MeTAAB)^{n+}$ Complexes

complex		% C	% H	% N
$[Co(MeTAAB)Br][Br]_2{\cdot}H_2O$	calcd	48.95	3.85	7.13
	found	48.47	3.80	6.90
$[Ni(MeTAAB)][BF_4]_2{\cdot}HBF_4$	calcd	48.72	3.70	7.10
	found	49.63	4.08	7.44
$[Ni(MeTAAB)][ClO_4]_2{\cdot}2H_2O$	calcd	50.43	4.23	7.35
	found	49.66	3.83	7.51
$[Cu(MeTAAB)][BF_4]_2{\cdot}0.5HBF_4$	calcd	51.27	3.83	7.47
	found	50.85	3.92	7.57
$[Zn(MeTAAB)][BF_4]_2$	calcd	54.32	3.99	7.92
	found	53.98	4.00	7.80
$[Pd(MeTAAB)][BF_4]_2$	calcd	51.34	3.77	7.48
	found	51.76	3.86	7.64
$[Pt(MeTAAB)][BF_4]_2$	calcd	46.29	2.55	6.75
	found	46.38	3.00	6.60

5-Methyl-2-[(triphenylmethyl)amino]benzaldehyde (3). To a solution of **2** (4.7 g, 12 mmol) in 250 mL of dry ether was added 50 g of activated MnO_2.[19] The resulting slurry was refluxed for 5 h and filtered, and the MnO_2 was rinsed with ether. The filtrate was evaporated in vacuo. The resulting bright-yellow oil could be solidified upon the addition of methanol to give the aldehyde (3.3 g, 70% based on **2**), mp 170 °C; ^1H NMR ($CDCl_3$) δ 2.10 (5, 3 H), 5.99–6.88 (m, 9 H), 7.25 (m, 15 H), 9.82 (s, 1 H), 9.91 (s, 1 H); IR (cm^{-1}) 3290, 1660, 1585, 1515, 1490, 1445, 1390, 1330, 1230, 1155, 810, 745, 695. Anal. Calcd for $C_{27}H_{23}NO$: C, 85.91; H, 6.14; N, 3.71. Found: C, 86.30; H, 6.20; N, 3.65.

Diacid Salt of the Tetrameric Condensate of 2-Amino-5-methylbenzaldehyde, $[H_2(MeTAAB)][BF_4]_2$. To a solution of **3** (1.0 g, 3 mmol) in 60 mL of acetonitrile were added 20 drops of 48% HBF_4. The solution slowly turned red upon stirring at room temperature for several hours. Upon evaporation of the solvent, followed by rinsing with ether, the diacid salt was obtained in nearly quantitative yields as a red powder. Anal. Calcd for $C_{32}H_{30}N_4B_2F_8{\cdot}H_2O$: C, 58.04; H, 4.87; N, 8.46. Found: C, 57.74; H, 4.80; N, 8.30. The infrared spectrum is given in Table II.

(Tetrakis(5-methylbenzo)[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohecadecine)-metal(II), $M(MeTAAB)^{2+}$ (M = Ni, Cu). Method A. A solution of 5-methyl-2-[(triphenylmethyl)amino]benzaldehyde (0.5 g, 1.3 mmol) in 5 to 10 mL of acetonitrile was brought to reflux and a 1:4 molar ratio of the metal salt was added as a solid. Condensation was immediately obvious by a color change. In this way $Ni(MeTAAB)^{2+}$ (orange) and $Cu(MeTAAB)^{2+}$ (olive green) could be obtained. The complexes were isolated by evaporating the solvent nearly to dryness and rinsing the residue with ether. The extreme solubilities of the complexes in most organic solvents made purification difficult. The cobalt(II) complex could also be prepared this way, but air sensitivity and difficulty in purification hampered analysis. Elemental analyses for these and the other metal complexes (often consistent with H_2O or HBF_4 of crystallization) are given in Table I. Corresponding infrared spectra are listed in Table II.

Method B. To a refluxing solution of $[H_2(MeTAAB)][BF_4]_2$ (0.2 g, 0.3 mmol) in acetonitrile was added a 1:1 molar ratio of the metal acetate as a solid. The color changed from the deep red of the diacid salt to the characteristic color of the complex. Nickel(II) and copper(II) complexes as their tetrafluoroborate salts were obtained in this way. Isolation was accomplished as described in method A.

$[Zn(MeTAAB)][BF_4]_2$. Method B using $Zn(OAc)_2{\cdot}2H_2O$ (0.07 g, 0.3 mmol) was employed. The mixture was refluxed for 24 h. Upon cooling the solution to 0 °C, a bright-yellow precipitate formed. Additional complex could be obtained by reducing the volume of the acetonitrile and adding ether.

$[Pd(MeTAAB)][BF_4]_2$. A modification of method B was used. To a refluxing solution of $[H_2(MeTAAB)][BF_4]_2$ (0.2 g, 0.3 mmol) in 5 mL of acetonitrile was added $Pd(benzonitrile)_2Cl_2$[20] (0.12 g, 0.30 mmol) dissolved in 10 mL of acetonitrile. A small portion of sodium acetate was added to neutralize the diacid salt. The solution turned dark-yellow immediately, and within 1 h a yellow precipitate formed in a red solution. The yellow solid was filtered, rinsed with ethanol and ether, and dried in vacuo.

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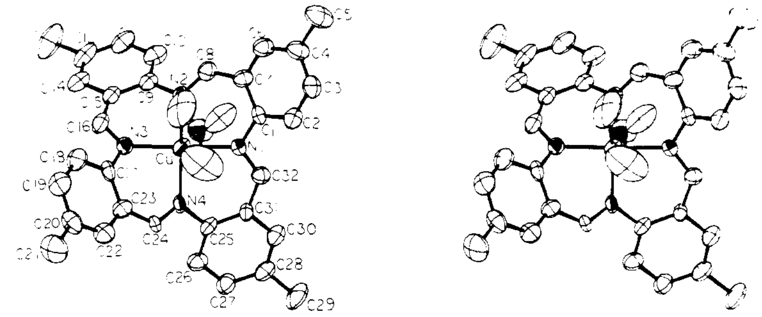

Figure 1. Overhead stereoview showing ellipsoids of 50% probability and numbering scheme for the macrocyclic ligand.

Table II. Comparison of Predominant Infrared Absorption Bands for MeTAAB and TAAB Complexes and Diacid Salts[a]

complex	ν_{CH} w[b]	$\nu_{C=N}$ s	$\nu_{C=C}$ ring modes
$[Co(MeTAAB)Br][Br]_2$	3015, 2918	1574	1614 s, 1501 m, 1450 w
$[Ni(TAAB)][ClO_4]_2$	3020, 2925	1570	1614 vs, 1591 vs, 1492 m, 1448 m
$[Ni(MeTAAB)][BF_4]_2$	3020, 2920	1570	1616 s, 1500 m, 1455 w
$[Cu(MeTAAB)][NO_3]_2$	3020, 2920	1570	1613 s, 1500 m, 1450 w
$[Zn(MeTAAB)][BF_4]_2$	3010, 2920	1570	1620 s, 1500 m, 1453 w
$[Pd(TAAB)][BF_4]_2$	3020, 2900	1567	1612 vs, 1588 vs, 1492 m, 1448 m
$[Pd(MeTAAB)][BF_4]_2$	3010, 2865	1570	1609 s, 1501 w, 1454 w
$[Pt(TAAB)][BF_4]_2$	3020, 2900	1564	1605 vs, 1588 vs, 1492 m, 1448 m
$[Pt(MeTAAB)][BF_4]_2$	3008, 2860	1572	1609 s, 1501 w, 1452 w

diacid salts	$\nu_{C=N}$ m	$\nu_{C=N}$ s	$\nu_{C=C}$ ring modes
$[H_2(TAAB)][BF_4]_2$	3340	1563	1630 s, 1590 sh, 1495 w, 1480 s
$[H_2(MeTAAB)][BF_4]_2$	3340	1560	1630 s, 1595 m, 1480 m

[a] Given as cm^{-1}. [b] Key: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

Table III. Crystal Data for $[Cu(MeTAAB)(NO_3)][NO_3]\cdot H_2O$

formula	$CuN_6O_7C_{32}H_{30}$
M_r	674.19
cell parameters	
a, Å	13.136 (6)
b, Å	17.294 (7)
c, Å	17.391 (4)
β, deg	127.66 (2)
Z	4
ρ_{calcd}, g cm^{-3}	1.398
ρ_{obsd}(flotation, hexane/CCl_4), g cm^{-3}	1.40 (1)
space group	$P2_1/c$
crystal dimens, mm	0.35 × 0.35 × 0.05
temp, K	298
radiatn	Mo Kα
diffractometer	Syntex P$\bar{1}$
μ, cm^{-1}	7.70
check reflections	1,3,1;2,2,2;1,0,6
2θ range, deg	2.0–45.0
no. of indep reflections	3165
no. with $I > 3\sigma(I)$	2327
final R_1	0.052
final R_2	0.052

$[Pt(MeTAAB)][BF_4]_2$. To a solution of the protected 2-amino-5-methylbenzaldehyde (0.3 g, 1.0 mmol) (**3**) refluxing in 5 mL of acetonitrile was added K_2PtCl_4 (0.10 g, 0.25 mmol) as a solid. A small amount of water (2 mL) was added to dissolve the platinum salt, as well as one drop of concentrated HCl to catalyze the reaction. Refluxing for 1 day resulted in the formation of a yellow-orange precipitate, which was filtered and rinsed with acetonitrile and ether. The crude $[Pt(MeTAAB)]Cl_2$ could be purified as its tetrafluoroborate salt by dissolving in hot water, filtering, and adding several drops of 48% HBF_4. The tetrafluoroborate salt precipitated immediately as a yellow solid, was washed with ethanol and ether, and was dried in vacuo.

$[Co(MeTAAB)Br_2]Br\cdot H_2O$. Crude $Co(MeTAAB)^{2+}$, prepared according to method A or B, was dissolved in methanol and filtered. Several milliliters of concentrated HBr were added to the green solution and a red-brown precipitate formed. The mixture was stirred in air overnight, filtered, rinsed with methanol and ether, and dried in vacuo.

X-ray Data. Crystals of $[Cu(MeTAAB)(NO_3)][NO_3]\cdot H_2O$ suitable for X-ray analysis were grown by slow evaporation of a methanolic solution of the complex prepared by method B, using $Cu(NO_3)_2\cdot 3H_2O$ as starting material. Crystal data information is given in Table III. Preliminary measurements indicated monoclinic symmetry with systematic absences, $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, unequivocally indicative of space group $P2_1/c$. Unit cell parameters were derived from a least-squares fit of 15 reflections well distributed in reciprocal space. Three standard reflections monitored every 150 reflections showed evidence of decay of 3.8%. Data were collected on a Syntex P$\bar{1}$ automatic diffractometer equipped with a scintillation counter and pulse-height analyzer, using Zr-filtered Mo Kα radiation. Intensity data were collected and treated as previously described.[21] No absorption corrections were applied. The data were corrected for decay and background, and Lorentz and polarization factors were applied to obtain structure factors.[22] Wilson's method was used to bring the F^2 to a relatively absolute scale. The σ_{I}^2 were scaled by increasing the σ_I^2 obtained from counting statistics by $p\sigma_I^2$, where p was chosen as the rms deviation of the standard reflections.[23]

Solution and Refinement. The position of the copper ion was obtained from a Patterson map, and a subsequent Fourier synthesis based on copper phasing revealed the location of the remaining non-hydrogen atoms. Refinement was performed by using full-matrix least-squares techniques during which the function $\sum w(|F_o| - |F_c|)^2$ was minimized. The data were weighted according to $1/\sigma_F = 4L_pI/\sigma_I^2$. Residuals were calculated as $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. Refinement of positional and isotropic thermal parameters resulted in convergence at $R_1 = 0.113$ and $R_2 = 0.118$. At this point, atomic thermal parameters were allowed to vary anisotropically, resulting in convergence at $R_1 = 0.068$ and $R_2 = 0.074$. Hydrogen atom positions were located from a difference map, with the exception of a few methyl hydrogens. These were calculated at a distance of 0.95 Å from the methyl carbon of attachment, with sp^3 geometry fixed by the location of one hydrogen. The hydrogen atoms were assigned temperature factors 1.0 Å^2 greater than the isotropic B of their atom of attachment, and were included, along with positional parameters, as fixed contributors. Final full-matrix least-squares refinement resulted in convergene at $R_1 = R_2 = 0.052$. A final difference map was virtually featureless. In the final

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(22) Programs for data reduction were written by Dr. B. K. Lee, University of Kansas. Programs for structure determination and refinement were local modifications of A. Zalkin's FORDAP for the Fourier summation, W. Busing, K. Martin, and H. Levy's ORFLS and ORFFE-II for least-squares and function and error calculations, and C. K. Johnson's ORTEP-II for the molecular structure drawing. Computations were performed on the Honeywell 66/60 computer at the University of Kansas. Scattering factors were obtained from: Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.2B. Anomalous dispersion corrections for copper were obtained from: Ibers, J. A. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. II, Table 3.3.2C.

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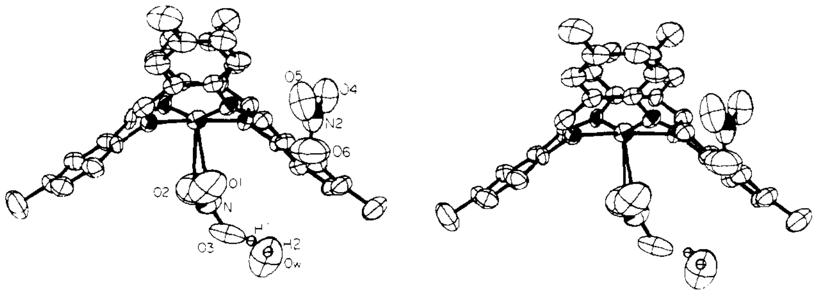

Figure 2. Side stereoview showing ellipsoids of 50% probability and numbering scheme for the nitrate groups.

Table IV. Final Positional Parameters for $[Cu(MeTAAB)(NO_3)][NO_3]\cdot H_2O$

atom	*x*	*y*	*z*
Cu	0.33545 (8)	0.22154 (4)	0.35431 (6)
N(1)	0.2330 (5)	0.2220 (3)	0.2121 (4)
C(1)	0.2802 (6)	0.1803 (4)	0.1702 (5)
C(2)	0.2014 (6)	0.1361 (4)	0.0871 (6)
C(3)	0.2498 (7)	0.0964 (4)	0.0475 (5)
C(4)	0.3805 (8)	0.0989 (4)	0.0885 (6)
C(5)	0.4309 (8)	0.0550 (5)	0.0443 (7)
C(6)	0.4591 (6)	0.1426 (4)	0.1732 (6)
C(7)	0.4137 (6)	0.1824 (4)	0.2152 (5)
C(8)	0.5075 (6)	0.2244 (4)	0.3042 (6)
N(2)	0.4906 (5)	0.2510 (3)	0.3639 (5)
C(9)	0.5956 (6)	0.2951 (4)	0.4450 (6)
C(10)	0.6702 (7)	0.3423 (4)	0.4314 (6)
C(11)	0.7742 (7)	0.3823 (4)	0.5119 (7)
C(12)	0.8022 (7)	0.3756 (4)	0.6038 (7)
C(13)	0.9137 (8)	0.4216 (5)	0.6908 (6)
C(14)	0.7281 (6)	0.3293 (4)	0.6166 (5)
C(15)	0.6223 (6)	0.2889 (4)	0.5352 (6)
C(16)	0.5532 (7)	0.2429 (4)	0.5592 (5)
N(3)	0.4382 (5)	0.2123 (3)	0.4956 (4)
C(17)	0.3878 (7)	0.1682 (4)	0.5340 (5)
C(18)	0.4656 (7)	0.1202 (4)	0.6146 (6)
C(19)	0.4176 (8)	0.0800 (4)	0.6530 (6)
C(20)	0.2891 (8)	0.0860 (4)	0.6159 (6)
C(21)	0.2369 (9)	0.0414 (6)	0.6563 (7)
C(22)	0.2105 (7)	0.1322 (4)	0.5334 (6)
C(23)	0.2563 (7)	0.1726 (4)	0.4913 (5)
C(24)	0.1648 (6)	0.2189 (4)	0.4055 (5)
N(4)	0.1821 (5)	0.2487 (3)	0.3473 (4)
C(25)	0.0774 (6)	0.2960 (4)	0.2691 (6)
C(26)	0.0060 (7)	0.3402 (4)	0.2881 (5)
C(27)	−0.0999 (7)	0.3818 (4)	0.2108 (7)
C(28)	−0.1330 (6)	0.3789 (4)	0.1180 (6)
C(29)	−0.2517 (7)	0.4220 (5)	0.0325 (6)
C(30)	−0.0606 (6)	0.3355 (4)	0.0999 (5)
C(31)	0.0489 (6)	0.2942 (4)	0.1777 (6)
C(32)	0.1185 (7)	0.2532 (4)	0.1508 (5)
N(5)	0.3159 (8)	0.0553 (5)	0.3167 (6)
O(1)	0.4158 (8)	0.0875 (5)	0.3659 (5)
O(2)	0.2252 (10)	0.0830 (4)	0.3055 (7)
O(3)	0.3025 (5)	−0.0051 (3)	0.2721 (5)
N(6)	0.8317 (7)	0.2345 (5)	0.3564 (6)
O(4)	0.7441 (5)	0.2778 (4)	0.2928 (4)
O(5)	0.9338 (6)	0.2647 (4)	0.4238 (4)
O(6)	0.8160 (9)	0.1668 (5)	0.3514 (6)
O(w)	0.0677 (7)	−0.0500 (5)	0.0864 (5)

Table V. Interatomic Distances (Å) for $[Cu(MeTAAB)(NO_3)][NO_3]\cdot H_2O$

Cu-N(1)	1.965 (5)	N(3)-C(17)	1.418 (9)
Cu-N(2)	2.006 (6)	C(17)-C(18)	1.395 (8)
Cu-N(3)	1.957 (6)	C(18)-C(19)	1.357 (11)
Cu-N(4)	1.998 (6)	C(19)-C(20)	1.395 (11)
Cu-O(1)	2.503 (8)	C(20)-C(21)	1.465 (11)
Cu-O(2)	2.656 (4)	C(20)-C(22)	1.398 (9)
N(1)-C(1)	1.411 (8)	C(22)-C(23)	1.388 (10)
C(1)-C(2)	1.385 (9)	C(23)-C(24)	1.456 (9)
C(2)-C(3)	1.373 (9)	C(23)-C(17)	1.405 (10)
C(3)-C(4)	1.400 (9)	C(24)-N(4)	1.275 (10)
C(4)-C(5)	1.494 (12)	N(4)-C(25)	1.457 (7)
C(4)-C(6)	1.395 (9)	C(25)-C(26)	1.398 (10)
C(6)-C(7)	1.378 (10)	C(26)-C(27)	1.405 (8)
C(7)-C(8)	1.453 (7)	C(27)-C(28)	1.392 (10)
C(7)-C(1)	1.418 (7)	C(28)-C(29)	1.537 (8)
C(8)-N(2)	1.274 (9)	C(28)-C(30)	1.391 (10)
N(2)-C(9)	1.447 (7)	C(30)-C(31)	1.425 (7)
C(9)-C(10)	1.402 (10)	C(31)-C(32)	1.442 (10)
C(10)-C(11)	1.403 (9)	C(31)-C(25)	1.392 (9)
C(11)-C(12)	1.408 (13)	C(32)-N(1)	1.316 (6)
C(12)-C(13)	1.536 (8)	N(5)-O(1)	1.181 (8)
C(12)-C(14)	1.381 (10)	N(5)-O(2)	1.185 (12)
C(14)-C(15)	1.421 (7)	N(5)-O(3)	1.247 (8)
C(15)-C(16)	1.448 (10)	N(6)-O(4)	1.246 (8)
C(15)-C(9)	1.386 (12)	N(6)-O(5)	1.234 (8)
C(16)-N(3)	1.320 (8)	N(6)-O(6)	1.184 (9)

cycle of refinement, no atom shifted by more than 0.15 of its esd. Final positional parameters are listed in Table IV. Atom numbering is shown in Figures 1 and 2, top and side stereoviews, respectively. Bond lengths are given in Table V and bond angles in Table VI. Available as supplementary material are a list of observed and calculated structure factors, final anisotropic thermal parameters, and positional and thermal parameters for hydrogen atoms.

Results and Discussion

Synthesis. The methyl-substituted *o*-aminobenzaldehyde proved to be a more versatile compound than the analogous 5-chloro derivative[17,18] with respect to metal-assisted self-condensation reactions. The previously unreported synthetic route employs triphenylmethyl protection of the amine, which serves two purposes. First, it prevents oxidation of the amine in the last step. More importantly, however, the protection allows for the isolation and storage of a species that is stable to undesirable self-condensation reactions. Therefore, the necessity of using freshly made samples of *o*-aminobenzaldehyde due to its propensity for self-condensation reactions is circumvented. Triphenylmethyl-protected 2-amino-5-methylbenzaldehyde was found to be stable indefinitely at room temperature and is thus a convenient source of the *o*-aminobenzaldehyde.

The methyl diacid salt of the tetrameric condensate is readily obtained from the protected amine. Addition of acid, in addition to promoting the formation of the salt, apparently cleaves the triphenylmethyl group. The analysis of the diacid salt was complicated by its tendency to crystallize with a molecule of H_2O or HBF_4. This behavior is well-known for unsubstituted diacid salts.[13] The infrared spectra of the methyl diacid salt and the unsubstituted compound are compared in Table II. The similarities in the spectra are readily apparent for the characteristically deep-red compounds. In contrast to the chloro-substituted derivative,[18] the diacid salt provides a convenient route to MeTAAB–metal complexes. All of the reported complexes, with the exception of zinc(II), can also be synthesized directly from the triphenylmethyl-protected 2-amino-5-methylbenzaldehyde in template condensations with the metal ions. The MeTAAB complexes are identical when prepared by either method and are readily soluble in many organic solvents. Metathesis reactions in water or methanol can be used to form complexes with a variety of anions such as PF_6^-, NO_3^-, Cl^-, Br^-, and BF_4^-.

In an attempt to isolate intermediate condensates, 2-amino-5-methylbenzaldehyde was reacted with platinum(II) ion in aqueous solution. The analogous reaction with the unsubstituted analogue

Table VI. Bond Angles (deg) for $[Cu(MeTAAB)(NO_3)][NO_3]\cdot H_2O$

N(1)–Cu–N(2)	89.1 (2)	Cu–N(2)–C(9)	122.0 (6)
N(1)–Cu–N(3)	175.5 (2)	N(2)–C(9)–C(15)	119.6 (6)
N(2)–Cu–N(3)	91.7 (2)	N(2)–C(9)–C(10)	119.4 (9)
N(2)–Cu–N(4)	151.7 (2)	C(15)–C(9)–C(10)	121.0 (5)
N(3)–Cu–N(4)	89.6 (1)	C(9)–C(10)–C(11)	118.3 (8)
N(4)–Cu–N(1)	91.8 (2)	C(10)–C(11)–C(12)	120.8 (8)
O(1)–Cu–N(1)	92.1 (2)	C(11)–C(12)–C(13)	120.4 (7)
O(1)–Cu–N(2)	82.6 (2)	C(11)–C(12)–C(14)	120.6 (4)
O(1)–Cu–N(3)	83.7 (2)	C(13)–C(12)–C(14)	118.9 (6)
O(1)–Cu–O(2)	46.5 (2)	C(12)–C(14)–C(15)	118.8 (6)
O(1)–Cu–N(4)	125.6 (1)	C(14)–C(15)–C(9)	120.5 (6)
O(2)–Cu–N(1)	77.4 (2)	C(14)–C(15)–C(16)	112.7 (5)
O(2)–Cu–N(2)	125.7 (3)	C(9)–C(15)–C(16)	126.8 (4)
O(2)–Cu–N(3)	98.6 (2)	C(15)–C(16)–N(3)	125.1 (6)
O(2)–Cu–N(4)	81.9 (2)	C(16)–N(3)–Cu	125.3 (6)
Cu–N(1)–C(1)	118.0 (4)	Cu–N(3)–C(17)	118.3 (2)
N(1)–C(1)–C(7)	119.2 (6)	N(3)–C(17)–C(23)	119.9 (4)
N(1)–C(1)–C(2)	122.5 (6)	N(3)–C(17)–C(18)	121.8 (7)
C(7)–C(1)–C(2)	118.3 (7)	C(23)–C(17)–C(18)	118.2 (6)
C(1)–C(2)–C(3)	121.3 (7)	C(17)–C(18)–C(19)	121.6 (5)
C(2)–C(3)–C(4)	121.9 (7)	C(18)–C(19)–C(20)	122.0 (4)
C(3)–C(4)–C(5)	120.8 (7)	C(19)–C(20)–C(21)	121.9 (7)
C(3)–C(4)–C(6)	116.2 (8)	C(19)–C(20)–C(22)	116.3 (6)
C(5)–C(4)–C(6)	122.9 (4)	C(21)–C(20)–C(22)	121.6 (8)
C(4)–C(6)–C(7)	123.3 (6)	C(20)–C(22)–C(23)	122.9 (5)
C(6)–C(7)–C(1)	119.0 (6)	C(22)–C(23)–C(17)	118.8 (5)
C(6)–C(7)–C(8)	117.0 (5)	C(22)–C(23)–C(24)	117.7 (6)
C(1)–C(7)–C(8)	124.0 (8)	C(17)–C(23)–C(24)	123.5 (6)
C(7)–C(8)–N(2)	126.3 (7)	C(23)–C(24)–N(4)	126.8 (6)
C(8)–N(2)–Cu	121.0 (4)	C(24)–N(4)–Cu	121.3 (3)
Cu–N(4)–C(25)	122.0 (4)	C(30)–C(31)–C(32)	114.2 (7)
N(4)–C(25)–C(26)	118.3 (7)	C(25)–C(31)–C(32)	126.8 (6)
N(4)–C(25)–C(31)	119.7 (6)	C(31)–C(32)–N(1)	125.1 (7)
C(31)–C(25)–C(26)	122.0 (6)	C(32)–N(1)–Cu	125.9 (6)
C(25)–C(26)–C(27)	118.0 (6)	Cu–O(1)–N(5)	98.7 (5)
C(26)–C(27)–C(28)	121.1 (7)	Cu–O(2)–N(5)	90.9 (6)
C(27)–C(28)–C(29)	121.2 (8)	O(1)–N(5)–O(2)	119.3 (8)
C(27)–C(28)–C(30)	120.6 (6)	O(1)–N(5)–O(3)	121.2 (9)
C(29)–C(28)–C(30)	118.2 (8)	O(2)–N(5)–O(3)	119.4 (7)
C(28)–C(30)–C(31)	119.2 (5)	O(4)–N(6)–O(5)	117.9 (8)
C(30)–C(31)–C(25)	119.0 (6)	O(4)–N(6)–O(6)	120.2 (8)
		O(5)–N(6)–O(6)	121.8 (8)

was found to produce a dimeric condensate intermediate on the way to the fully cyclized TAAB species.[16] Neither dimeric nor other intermediate condensates could be isolated by using the methyl-substituted derivative, however. (On the other hand, reaction of 2-amino-5-chlorobenzaldehyde with platinum(II) does afford the dimeric condensate.[18]) Evidently the electron-donating methyl substituent does activate the condensation so that the reaction readily proceeds to the fully cyclized MeTAAB complex.

The chemistry of MeTAAB complexes appears to be similar to that of the corresponding TAAB complexes. Solubilities in most solvents are greater, but $[Co(MeTAAB)Br]Br_2$ is as insoluble as its unsubstituted analogue. Nucleophilic attack on the azomethine carbon by bases as observed in TAAB complexes is also apparent, although no complexes have been isolated.

Spectral Data. Selected absorptions from the infrared spectra of the MeTAAB complexes for the different metal ions are listed in Table II along with band assignments. With the exception of differences in anion absorption, the spectra are similar and are diagnostic for MeTAAB, particularly in the 1700–1500-cm^{-1} region. Assignments are based largely on similar assignments in TAAB complexes,[14] with which there is observed to be a strong correlation, evident by comparison with the representative $Ni(TAAB)^{2+}$ also included in the Table II. The major difference in the spectra of MeTAAB vs. TAAB is the absence of an assigned phenyl ring vibration typically found at 1590 cm^{-1} in TAAB complexes. This difference can be attributed to different ring modes for trisubstituted vs. disubstituted phenyl rings. Hence, two strong bands at 1610 and 1570 cm^{-1} are apparently characteristic for MeTAAB, while three bands are observed in that region for TAAB.

Structure of $[Cu(MeTAAB)(NO_3)][NO_3]\cdot H_2O$. The complex consists of the cation $[Cu(MeTAAB)(NO_3)]^+$, the anion NO_3^-, and a water molecule of crystallization. An overhead stereoview shows the numbering scheme for the macrocycle (Figure 1) and a side view the nitrate numbering (Figure 2). The coordination sphere of the copper is six-coordinate N_4O_2, with a symmetrically bidentate nitrate providing the two oxygen donor atoms and the macrocycle the additional four nitrogens. The overall geometry can best be described as a bicapped square pyramid. The stereochemistry involves the [4 + 2] coordination which is derived from a cis-distorted octahedral configuration. Apparently this is the first example of such a geometry in a copper macrocyclic ligand complex with a symmetrically bidentate nitrate ion.

Table VII. Selected Least-Squares Planes and Atom Displacements (Å) for $[Cu(MeTAAB)(NO_3)][NO_3]\cdot H_2O$

atom	displacement	atom	displacement
A. Cu-N(1)-N(2)-N(3)-N(4)			
$0.013x - 0.999y - 0.042z = -4.190$			
Cu	0.165	N(3)	0.242
N(1)	0.242	N(4)	−0.324
N(2)	−0.324		
B. N(5)-O(1)-O(2)-O(3)			
$0.327x + 0.530y - 0.782z = -2.628$			
N(5)	−0.019	O(2)	0.006
O(1)	0.006	O(3)	0.006
C. N(6)-O(4)-O(5)-O(6)			
$0.847x - 0.079y - 0.526z = 3.141$			
N(6)	0.000	O(5)	0.000
O(4)	0.000	O(6)	0.000
D. C(1)-C(2)-C(3)-C(4)-C(7)-C(8)			
$0.230x + 0.800y - 0.554z = 1.619$			
C(1)	0.011	C(4)	0.009
C(2)	−0.003	C(5)	0.000
C(3)	−0.007	C(7)	−0.010
E. C(9)-C(10)-C(11)-C(12)-C(14)-C(15)			
$-0.593x + 0.776y - 0.214z = 0.823$			
C(9)	−0.005	C(12)	0.000
C(10)	0.002	C(14)	−0.003
C(11)	0.000	C(15)	0.005
F. C(17)-C(18)-C(19)-C(20)-C(22)-C(23)			
$0.202x - 0.778y - 0.595z = -6.736$			
C(17)	−0.018	C(20)	−0.019
C(18)	0.001	C(22)	0.002
C(19)	0.018	C(23)	0.016
G. C(25)-C(26)-C(27)-C(28)-C(30)-C(31)			
$-0.568x - 0.792y - 0.225z = -3.853$			
C(25)	0.015	C(28)	0.006
C(26)	−0.002	C(30)	0.006
C(27)	−0.008	C(31)	−0.017

As found for previously reported TAAB structures,[24-26] the geometry of the macrocyclic ligand is distinctly saddle shaped, with S_4 symmetry. The cavity size, the perpendicular distance from the mean plane of coordinated nitrogens to the farthest carbon atoms in the benzo groups, averages 2.50 Å (3.2 Å to the methyl carbons). This compares to a distance of 2.68 Å in $[Pd(TAAB)][I_8]$[26] and 2.70 Å in $[Pd(TAAB)][BF_4]_2$.[24] The dihedral angle of the mean planes of the four benzo groups with the CuN_4 mean plane averages 141.9°, while the corresponding average is 138.1° in $[Pd(TAAB)][I_8]$ and 137.3° in $[Pd(TAAB)][BF_4]_2$ (mean plane calculations are given in Table VII). These differences indicate that the MeTAAB ligand is more planar than TAAB with a corresponding reduction in cavity size. It is not evident if this is a result of intermolecular steric repulsion or electronic effects of the methyl substitution.

Also different from previously reported TAAB structures, the macrocyclic coordination sphere is slightly distorted from the expected square-planar configuration toward tetrahedral geometry.

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This is evident in an N(2)–Cu–N(4) angle of 151.7 (2)° and an N(1)–Cu–N(3) angle of 175.5 (2)°. In comparison, [Pd(TAAB)][I_8] shows only a slight tetrahedral distortion about the palladium (167.8 (3) and 168.0 (3)°).[26] The extent of the tetrahedral distortion is obviously restricted by the geometry of the macrocyclic ligand and, particularly in the palladium(II) and platinum(II) cases, the desire of the metal ion for square-planar geometries. The coordinated bidentate nitrate undoubtedly is primarily responsible for this distortion rather than the methyl substitution.

No disorder in the macrocyclic ligand is observed in Cu(MeTAAB)$^{2+}$, and bond lengths and angles within the macrocyclic ligand correlate well with those in unsubstituted TAAB structures. C–C_{methyl} bond lengths average 1.508 (10) Å, typical for a C–C single bond.[27] Interior angles of the benzo groups average 120.0 (7)°, as expected. Cu–N bond lengths average 1.982 (6) Å, in good agreement with an average of 2.008 Å in [Cu(bipy)$_2$(NO_3)][NO_3][28] and other copper(II) macrocyclic ligand complexes.[29,30]

The bidentate coordination of the nitrate is the most interesting aspect of the structure. The infrared spectrum shows one broad nitrate band, which makes the assignment of this band to ionic or coordinated nitrate modes difficult. Other bands expected for ionic and coordinated nitrates overlap with macrocyclic ligand vibrations and also cannot be assigned with certainty. Thus the bidentate nature of the coordination is only discernible from X-ray crystallographic techniques. The nitrate is bonded to the copper through O(1) and O(2) at 2.503 (8) and 2.656 (4) Å, respectively. Previous studies have delineated two types of bidentate nitrate coordination, unsymmetrical or symmetrical, determined by the difference in the two metal–oxygen bond lengths. The Cu–O bond-length difference in the MeTAAB complex (0.15 Å) is less than the minimum suggested as the limit of an unsymmetrical bidentate (0.2 Å),[31] and thus the coordinated nitrate can be considered to be symmetrically bidentate. The average Cu–O bond length of 2.580 (8) Å is 0.6 Å greater than the average in-plane Cu–N distance, typical of the [4 + 2] semicoordination[32] in six-coordinate copper(II). The nitrates are both planar (Table VII). The plane of the coordinated nitrate is tilted with respect to the CuN_4 mean plane at an angle of 60.5°, in the direction of N(1) and N(2).

Structural aspects of this regular bicapped square pyramid can be compared to the geometrically analogous (*N,N,N′N′*-tetrakis(2-benzimidazylmethyl)ethane-1,2-diamine)copper(II) complex ([Cu(tben)][BF_4]$_2$),[33] in which the hexadentate ligand occupies all six coordination sites. A regular bicapped square pyramid results, with four Cu–N distances averaging 2.10 Å and two (cis-distorted) bonds at 2.50 Å. The macrocyclic portion of the [Cu(MeTAAB)(NO_3)]$^+$ cation is substantially less distorted toward a tetrahedral configuration than is the in-plane coordination sphere of [Cu(tben)][BF_4]$_2$ as seen in the N–Cu–N angles of 142.9 and 165.6° in the [Cu(tben)]$^{2+}$ complex compared to those previously cited for [Cu(MeTAAB)]$^{2+}$. The cis distorted N–Cu–N angle of 70.3° in [Cu(tben)][BF_4]$_2$ corresponds to the O(1)–Cu–O(2) angle of 46.5(2)° in the MeTAAB complex. A range of 46–56° has been observed for this angle in bidentate nitrates;[28,34] for example, a bite angle of 46° is found for [Cu(bipy)$_2$(NO_3)][NO_3], which has an unsymmetrically bidentate nitrate.[28] The differences in the geometries of the two symmetrical bicapped pyramids are undoubtedly the result of the less-flexible coordination of the MeTAAB ligand, which would place more restraints on the overall configuration in that complex.

The average N–O bond length (1.213 (9) Å) and O–N–O angle (120 (8)°) in this structure agree well with other nitrate structures.[21,28] An anomaly is observed, however, in the bond lengths of the coordinated nitrate of [Cu(MeTAAB)(NO_3)]$^+$. While the O–N(4)–O bond angles do not vary significantly from 120° in the coordinated nitrate, N(5)–O(1) and N(5)–O(2) are significantly shorter than the terminal N(5)–O(3) bond (averaging 1.183 (10) Å vs. 1.247 (8) Å). A possible explanation for the somewhat shortened N(4)–O(1) and N(4)–O(2) bonds and the longer N(4)–O(3) bond is the presence of hydrogen bonding of O(3) with the lattice water molecule (O(3)–O(w) = 2.894 (9) Å). In the uncoordinated nitrate, one slightly shorter bond is also observed (N(6)–O(6) = 1.184 (9) Å), with no apparent explanation.

Acknowledgment. K.B.M. acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Kansas General Research Allocation No. 3780-XO-0038 for support of this work. The authors also wish to express their gratitude to Professor Byungkook Lee, who has provided a revised and improved X-ray crystallographic program package.

Registry No. 1, 85167-27-7; **2**, 85167-28-8; **3**, 85167-29-9; [H_2(MeTAAB)][BF_4]$_2$, 85135-57-5; [Co(MeTAAB)Br][Br]$_2$, 85167-30-2; [Ni(MeTAAB)][BF_4]$_2$, 85167-32-4; [Ni(MeTAAB)][ClO_4]$_2$, 85167-33-5; [Cu(MeTAAB)][BF_4]$_2$, 85135-59-7; [Zn(MeTAAB)][BF_4]$_2$, 85167-35-7; [Pd(MeTAAB)][BF_4]$_2$, 85167-37-9; [Pt(MeTAAB)][BF_7]$_2$, 85167-39-1; [Cu(MeTAAB)(NO_3)][NO_3]·H_2O, 85167-42-6; [Ni(TAAB)][ClO_4]$_2$, 36539-87-4; [Pd(TAAB)][BF_4]$_2$, 69799-66-2; [Pt(TAAB)][BF_7]$_2$, 72573-56-9; Pd(benzonitrile)$_2$$Cl_2$, 14220-64-5; triphenylmethyl chloride, 76-83-5; 2-amino-5-methylbenzoic acid, 2941-78-8.

Supplementary Material Available: Table i, listing of observed and calculated structure factors for [Cu(MeTAAB)(NO_3)][NO_3]·H_2O, Table ii, final anisotropic thermal parameters, and Table iii, final hydrogen atom positional and isotropic thermal parameters (15 pages). Ordering information is given on any current masthead page.

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