2224 *Inorg. Chem.* **1989**, *28*, 2224-2226

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# Synthesis and Characterization of ((Trimethylsilyl)amido)gallium Dibromide[1]

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*Received October 17, 1988*

An equilibrium mixture of the trans trimer and the cis and trans dimers of ((trimethylsilyl)amido)gallium dichloride has been observed in a toluene solution. When a methyl group is substituted for the hydrogen atom on the nitrogen, only the cis and trans dimers of (methyl(trimethylsilyl)amido)gallium dichloride were found in solution.[3] Substituted aminogallanes exhibit a similar trend.[4a] (Methylamino)gallane is trimeric in solution while (dimethylamino)gallane exists as a dimer. Apparently, the introduction of a second substituent on the nitrogen atom creates sufficient steric strain to prohibit the formation of the trimer.

The effect of the substituents bonded to the nitrogen on the degree of association and the conformational properties of aminogallanes has been examined extensively in these and other studies.[4] However, the manner in which the substituents on the gallium atom influence the trimer–dimer equilibrium and the isomerization of the dimer has not been characterized fully. We have begun an investigation of a series of substituted ((trimethylsilyl)amino)gallanes and report here on the results of our study of ((trimethylsilyl)amido)gallium dibromide.

## Experimental Section

**Materials and General Procedures.** Gallium tribromide was purchased from Alfa Products and sublimed prior to use. Bis(trimethylsilyl)amine (PCR Research Chemicals) was distilled at atmospheric pressure. The solvents diethyl ether and benzene were refluxed over sodium/benzophenone ketyl and calcium hydride, respectively, and distilled into storage flasks. Toluene-$d_8$ (Aldrich Chemical Co.) was refluxed over calcium hydride and distilled into a storage flask. All experiments were performed under an oxygen-free, dry-nitrogen or argon atmosphere by using Schlenk and glovebox techniques.[5]

The $^1$H (80.07 MHz), $^{13}$C (20.13 MHz), and $^{29}$Si (15.91 MHz) NMR spectra were obtained from toluene-$d_8$ solutions with an IBM NR-80B spectrometer. Standard broad-band proton noise-modulated decoupling was used where appropriate, and standard variable-temperature accessories were employed with an estimated accuracy of ±0.5 °C. Field-frequency stabilization was provided by locking to the $-CD_3$ deuterium resonance of the deuterated solvent in the 5-mm sample tube ($^1$H, $^{13}$C) or in a 10-mm tube in which the 5-mm tube was placed coaxially and the annular space between the two tubes was filled with the same deuterated solvent ($^{29}$Si). All NMR sample tubes (5 mm) were sealed under vacuum.

The $^1$H, $^{13}$C, and $^{29}$Si chemical shifts are reported in parts per million (ppm) with respect to $Me_4Si$ at 0.0 ppm. A positive chemical shift denotes a resonance to lower shielding (higher frequency). The $^1$H chemical shifts were measured from the $^1$H resonance of the residual $CHD_2C_6D_5$ ($\delta$ 2.09) solvent impurity, and the chemical shifts in the $^{13}$C NMR spectra were determined from the methyl $^{13}$C resonance of the $CD_3C_6D_5$ solvent ($\delta$ 20.4). The $^{29}$Si chemical shift was measured with respect to 50% $Me_4Si$ in toluene-$d_8$ by sample replacement. The spectrum was acquired by using a refocused INEPT pulse sequence.[6]

**Table I.** Experimental Data from the X-ray Diffraction Study

| | |
|---|---|
| cryst syst | orthorhombic |
| space group | *Pbca* (No. 61) |
| cell dimens[a] | |
| $a$, Å | 9.451 (2) |
| $b$, Å | 18.319 (4) |
| $c$, Å | 11.621 (2) |
| $V$, Å$^3$ | 2012.0 (7) |
| $Z$ | 4 |
| MW | 635.5 |
| $\rho$(calcd), g cm$^{-3}$ | 2.097 |
| radiation ($\lambda$, Å) | Mo K$\bar{\alpha}$ (0.710 69) |
| monochromator | graphite |
| $2\theta$ range, deg | 4–50 |
| scan type | $\omega$ |
| scan speed, deg min$^{-1}$ | 3.91–29.3 |
| scan width, deg | 1 |
| std reflcns | 080, 600, 006 |
| no. of unique data | 1508 |
| no. of unique data with $F_o^2 > 3\sigma(F_o^2)$ | 982 |
| $R$[b] | 0.0795 |
| $R_w$[c] | 0.0648 |
| weighting scheme | $w = 1.4868/\sigma^2(F_o)$ |

[a] Unit cell parameters were derived from a least-squares refinement of 15 reflections (19.32° ≤ $\theta$ ≤ 26.32°). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}]$.

The infrared spectrum of a Nujol mull was recorded on a Perkin-Elmer Model 283 spectrophotometer. Absorption intensities are reported with the abbreviations vw (very weak), w (weak), m (medium), s (strong), and vs (very strong). The molecular weight was determined cryoscopically in benzene with an apparatus similar to that described by Dilts and Shriver.[7] The elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

**((Trimethylsilyl)amido)gallium Dibromide.** Bis(trimethylsilyl)amine (5.82 g, 36.1 mmol) was added to a stirred solution of $GaBr_3$ (9.57 g, 30.9 mmol) in 30 mL of diethyl ether. After the solution was allowed to reflux for 13 h, the liquid portion was removed by vacuum distillation, leaving a crystalline solid. Recrystallization of the solid from ether gave $[Br_2GaN(H)SiMe_3]_2$ (6.02 g, 61.3% yield): mp 170–172 °C; $^1$H NMR (toluene-$d_8$, 0.075 mol/L based on MW 635) $\delta$ 0.17 (s, $CH_3Si$), 0.12 (s, $CH_3Si$); $^{13}$C NMR (toluene-$d_8$) $\delta$ 1.36 (s, $CH_3Si$), 1.22 (s, $CH_3Si$); $^{29}$Si NMR (toluene-$d_8$) $\delta$ 21.81 (s, $CH_3Si$); IR (cm$^{-1}$) 3195 (s), 1276 (m), 1258 (vs), 1131 (s), 976 (w), 912 (s), 845 (vs), 762 (m), 728 (s), 699 (m), 630 (w), 521 (m), 491 (m), 311 (m), 291 (w), 265 (w), 244 (w). Anal. Calcd for $C_3H_{10}Br_2GaNSi$: C, 11.34; H, 3.17; Br, 50.30; Ga, 21.94; N, 4.41; Si, 8.84. Found: C, 11.29; H, 3.22; Br, 50.26; Ga, 21.64; N, 4.49; Si, 7.55. Molecular weight for $C_3H_{10}Br_2GaNSi$: calcd, 317.7; found, 636 (calcd molality based on MW 635: 0.0648).

**Thermodynamic Studies.** The equilibrium constants [$K$ (standard deviation), temp in °C: 0.799 (4), 10; 0.886 (6), 20; 0.951 (7), 41; 0.997 (7), 50; 1.023 (3), 60; 1.070 (2), 70] for the isomerization of *trans*-$[Br_2GaN(H)SiMe_3]_2$ to *cis*-$[Br_2GaN(H)SiMe_3]_2$ were obtained from the ratios of the intensity of the signal (0.17 ppm) for the cis isomer to the intensity of the signal (0.12 ppm) for the trans isomer in the $^1$H NMR spectra.[8] The sample was maintained at each temperature for a minimum of 4 h prior to the collection of the spectral data. Four spectra were acquired at each temperature.

**Collection of Crystallographic Data.** Colorless crystals of $[Br_2GaN(H)SiMe_3]_2$ were grown by slowly cooling a saturated diethyl ether solution, and a suitable crystal was mounted in a capillary tube under a nitrogen atmosphere. The determination of the unit cell parameters and the orientation matrix as well as the collection of the intensity data were made on a Syntex P2$_1$ four-circle diffractometer.[9] The diffractometer was equipped with a graphite monochromator (Bragg $2\theta$ angle 12.2°). Unit cell parameters and details of the data collection are given in Table I. Absorption corrections were applied to the intensity data by using $\psi$ scans for four reflections with $2\theta$ values between 10 and 32°.[10]

**Structure Determination and Refinement.** The positions of the gallium atoms were obtained from a Patterson map, and the positions of the Br, C, N, and Si atoms were taken from various Fourier maps. After several

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**Table II.** Final Positional Parameters

| atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Br(2) | 0.4075 (4) | 0.0015 (2) | 0.7733 (2) |
| Br(1) | 0.2341 (3) | −0.1134 (2) | 0.5414 (3) |
| Ga | 0.4054 (3) | −0.0298 (2) | 0.5820 (2) |
| N | 0.6017 (20) | −0.0530 (9) | 0.5291 (13) |
| Si | 0.6573 (9) | −0.1444 (4) | 0.4947 (6) |
| C(1) | 0.5443 (34) | −0.1869 (18) | 0.3819 (25) |
| C(2) | 0.8502 (32) | −0.1437 (21) | 0.4482 (28) |
| C(3) | 0.6446 (33) | −0.1996 (15) | 0.6289 (25) |

**Table III.** Intramolecular Distances (Å), Bond Angles (deg), and Selected Dihedral Angles (deg)

| | | | |
|---|---|---|---|
| | Distances | | |
| Ga···Ga′ | 2.832 (5) | N···N′ | 2.815 (35) |
| Ga–Br(1) | 2.278 (4) | Ga–Br(2) | 2.296 (4) |
| Ga–N | 2.000 (18) | Ga–N′ | 1.993 (16) |
| N–Si | 1.801 (18) | Si–C(1) | 1.861 (27) |
| Si–C(2) | 1.902 (28) | Si–C(3) | 1.862 (26) |
| | Angles | | |
| Ga–N–Ga′ | 90.4 (7) | N–Ga–N′ | 89.6 (7) |
| Br(1)–Ga–Br(2) | 112.0 (2) | Br(1)–Ga···Ga′ | 124.6 (2) |
| Br(2)–Ga···Ga′ | 123.4 (2) | Br(1)–Ga–N | 116.9 (5) |
| Br(1)–Ga–N′ | 110.7 (5) | Br(2)–Ga–N | 110.0 (5) |
| Br(2)–Ga–N′ | 115.9 (5) | Si–N···N′ | 142.0 (12) |
| Si–N–Ga | 122.5 (10) | Si–N–Ga′ | 125.0 (8) |
| C(1)–Si–N | 112.2 (12) | C(2)–Si–N | 109.7 (14) |
| C(3)–Si–N | 107.5 (10) | C(1)–Si–C(2) | 110.6 (14) |
| C(1)–Si–C(3) | 107.0 (14) | C(2)–Si–C(3) | 107.7 (15) |
| | Dihedral Angles | | |
| Br(1)–Ga–Ga′–N′ | 85.2 (7) | Br(1)–Ga–Ga′–N | −94.8 (7) |
| Br(2)–Ga–Ga′–N′ | −94.7 (7) | Br(2)–Ga–Ga′–N | 85.3 (7) |
| Si–N–N′–Ga | 87.4 (18) | N′–N–Si–C(1) | −0.3 (23) |
| N′–N–Si–C(2) | 123.1 (20) | N′–N–Si–C(3) | −120.2 (20) |
| Ga–N–Si–C(1) | 56.6 (15) | Ga–N–Si–C(2) | −180.0 (12) |
| Ga–N–Si–C(3) | −63.2 (14) | Br(1)–Ga–N–Si | −20.0 (1) |
| Br(2)–Ga–N–Si | 109.2 (9) | | |

cycles of a full-matrix least-squares refinement with all nonhydrogen atoms anisotropic, the methyl hydrogen atoms were generated at calculated positions (C–H = 1.08 Å; H–C–H = 109.5°) with rigid-geometry pivoting around the $C_3$ axis. Additional cycles of refinement led to convergence.

All calculations were performed on the Prime 750 computer using SHELX-76[11] and ORFFE4.[12] Scattering factors for all atoms included real and imaginary anomalous dispersion components.[13] In all least-squares refinements the quantity minimized was $\sum w(|F_o| - |F_c|)^2$. The final positional parameters are found in Table II. The bond lengths, bond angles, and dihedral angles are given in Table III. Tables of observed and calculated structure factors, thermal parameters, and hydrogen coordinates and thermal parameters are available as supplementary material.

## Results and Discussion

When $(Me_3Si)_2NH$ was allowed to react with $GaBr_3$ in a 1:1 mole ratio, the colorless crystalline solid ((trimethylsilyl)amido)gallium dibromide was isolated. Cryoscopic molecular weight measurement in benzene indicates that the degree of association is 2.00.

$$GaBr_3 + (Me_3Si)_2NH \rightarrow {}^1\!/_2[Br_2GaN(H)SiMe_3]_2 + Me_3SiBr \quad (1)$$

The observed temperature dependency of the $^1$H NMR spectrum of ((trimethylsilyl)amido)gallium dibromide in toluene is consistent with the existence of an equilibrium between the trans and cis isomers of the dimer. The intensity of the singlet at 0.17 ppm increases with respect to the intensity of the singlet at 0.12 ppm with an increase in temperature. The assignment of the former singlet to the protons of the trimethylsilyl groups in *cis*-$[Br_2GaN(H)SiMe_3]_2$ and the latter singlet to the corresponding protons in *trans*-$[Br_2GaN(H)SiMe_3]_2$ is based on the assumption that the trans isomer is the more thermodynamically stable dimer. The cis and trans isomers of $[Me_2GaN(Me)Ph]_2$ were identified unequivocally in the $^1$H NMR spectrum, and temperature studies of the trans to cis isomerization have shown that the trans isomer is the more stable dimer.[14] The equilibrium constants ($K$ = [cis]/[trans]) for the trans to cis isomerization of $[Br_2GaN(H)SiMe_3]_2$ (eq 2) in toluene were determined at six different

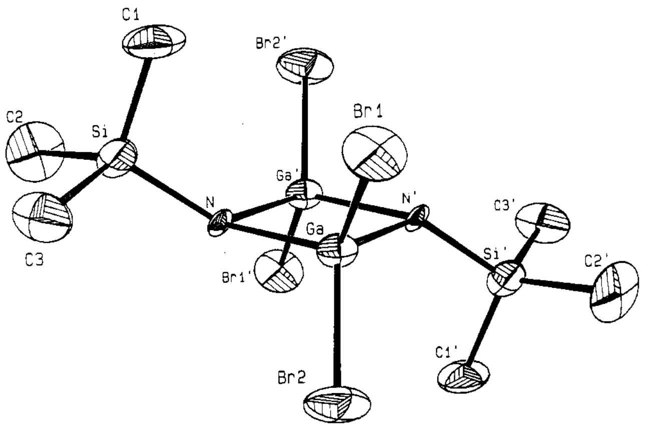

**Figure 1.** ORTEP diagram of $[Br_2GaN(H)SiMe_3]_2$.

$$trans\text{-}[Br_2GaN(H)SiMe_3]_2 \rightleftarrows cis\text{-}[Br_2GaN(H)SiMe_3]_2 \quad (2)$$

temperatures. A least-squares plot of ln $K$ vs $1/T$ gave $\Delta H$ = 3.7 (3) kJ/mol and $\Delta S$ = 11.2 (9) J/(mol K) with a correlation coefficient of 0.988. These values are similar to the values that were reported for the trans–cis isomerization of $[Cl_2GaN(H)SiMe_3]_2$ ($\Delta H$ = 2.4 (2) kJ/mol and $\Delta S$ = 7.1 (6) J/(mol K)).[3]

The narrow melting point range of the $[Br_2GaN(H)SiMe_3]_2$ suggests that only one isomer is present in the solid state. To determine which isomer was isolated, a crystallographic study of a single crystal of the compound was undertaken. The ORTEP diagram of *trans*-$[Br_2GaN(H)SiMe_3]_2$ is shown in Figure 1. A least-squares plane calculation indicates that the four-membered $Ga_2N_2$ ring is very flat with a root-mean-square displacement from the ring of <1.1 × $10^{-6}$ Å for each atom.[15] The plane that is formed by the Si, N, and N′ atoms makes an angle of 87.4 (18)° with the $(GaN)_2$ ring, and the C(1) atoms lie above and below the ring. The plane of the Br(1), Ga, and Br(2) atoms tilts away from the trimethylsilyl groups and forms an angle of 94.8 (7)° with the $(GaN)_2$ ring. A comparison of the bond lengths, bond angles, and dihedral angles common to *trans*-$[Br_2GaN(H)SiMe_3]_2$ and *trans*-$[Cl_2GaN(H)SiMe_3]_2$[3] reveals that the structures of the two dimers are very similar.

The trimer–dimer equilibrium that is present in a toluene solution of ((trimethylsilyl)amido)gallium dichloride[3] is absent in the toluene solution of ((trimethylsilyl)amido)gallium dibromide. Only resonances associated with the cis and trans isomers of $[Br_2GaN(H)SiMe_3]_2$ were observed in the $^1$H and $^{13}$C NMR spectra, and the degree of association was found to be 2.00. Although the van der Waals radii of the chlorine and bromine atoms (1.70–1.90 and 1.80–2.00 Å)[16] differ only slightly, the increase in the steric requirements of the bromine atoms as compared with the chlorine atoms is sufficient to prohibit the formation of the trimer, $[Br_2GaN(H)SiMe_3]_3$. The steric strain between the substituents in the dimer is considerably less than in the trimer,[17] and thus, the replacement of the chlorine atoms

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in $[Cl_2GaN(H)SiMe_3]_2$ with bromine atoms has little effect on the structural features of the trans dimer or the trans-cis isomerization of the dimer.

**Acknowledgment.** The partial support of this research by The Camille and Henry Dreyfus Foundation and Davidson College is gratefully acknowledged. We are indebted to Dr. Donald VanDerveer for his helpful discussions. F.K. and J.D.O. gratefully acknowledge the financial support from the National Science Foundation (Grant CHE80-13694).

**Registry No.** *trans*-$[Br_2GaN(H)SiMe_3]_2$, 120263-15-2; *cis*-$[Br_2GaN(H)SiMe_3]_2$, 120329-66-0; $(Me_3Si)_2NH$, 999-97-3.

**Supplementary Material Available:** Listings of hydrogen coordinates and temperature factors and of anisotropic temperature factors (1 page); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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## Synthesis, Structure, and Magnetic Behavior of a New $\mu$-Phenoxo Manganese(II) Dimer

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*Received August 12, 1988*

There has been significant recent interest in the chemistry of binuclear and tetranuclear complexes of manganese. Much of this interest stems from the involvement of such species in a wide variety of biological redox processes, including the water-oxidizing enzyme in photosystem II.[2] Binuclear complexes with oxygen bridges are also of intrinsic magnetic and chemical interest and may be of use as electrocatalysts in chemical redox processes. For these reasons, we[3,4] and others[5-11] have synthesized and examined series of complexes that contain this bridging network; other workers have examined systems that contain carboxylate bridges in addition to oxo bridges.[12,13] Here, we report the synthesis, structure, and magnetic properties of the binuclear manganese complex bis(*o*-(bis(2-(1-pyrazolyl)ethyl)amino)phenolato)bis(tetrahydrofuran)dimanganese(II) perchlorate, $[Mn(bpeap)(THF)]_2(ClO_4)_2$ (**1**).

**Table I.** Crystallographic and Data Collection Parameters

| | |
|---|---|
| formula: $Mn_2C_{40}H_{52}N_{10}O_{12}Cl_2$ | $Z = 2$ |
| $a = 9.731$ (2) Å | $D_c = 1.542$ g cm$^{-3}$ |
| $b, = 18.104$ (4) Å | $D_o = 1.51$ (2) g cm$^{-3}$ |
| $c = 12.939$ (5) Å | space group: $P2_1/c$ |
| $\beta, = 98.80$ (2)° | $\mu = 7.84$ cm$^{-1}$ |
| $V = 2253$ (2) Å$^3$ | data range: $3 \le \theta \le 25°$ |
| NO = 1631 ($>3\sigma$) | radiation: Mo K$\alpha$ |
| $T = 21$ °C | data collcd: $\pm h,+k,+l$ |

**Table II.** Positional Parameters for $[Mn(bpeap)(THF)]_2(ClO_4)_2$

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Mn | 0.0049 (1) | 0.00252 (8) | 0.12627 (8) |
| Cl | 0.3532 (2) | 0.3587 (1) | 0.0472 (2) |
| O(1) | 0.0632 (4) | −0.0677 (2) | 0.0055 (3) |
| O(1s) | −0.0565 (5) | 0.0593 (3) | 0.2716 (4) |
| O(2) | 0.4731 (7) | 0.3385 (4) | 0.1058 (8) |
| O(3) | 0.3114 (9) | 0.3098 (4) | 0.9689 (5) |
| O(4) | 0.2594 (9) | 0.3574 (7) | 0.1122 (6) |
| O(5) | 0.3443 (12) | 0.0727 (4) | 0.5104 (6) |
| N(1a) | −0.1931 (6) | −0.0559 (3) | 0.1198 (4) |
| N(2a) | −0.2136 (6) | −0.1269 (3) | 0.1449 (4) |
| N(1b) | 0.2042 (6) | 0.0625 (4) | 0.1609 (4) |
| N(2b) | 0.3151 (6) | 0.0471 (3) | 0.2345 (4) |
| N(3) | 0.1174 (6) | −0.0960 (3) | 0.2175 (4) |
| C(1a) | 0.0141 (8) | −0.1424 (5) | 0.2624 (5) |
| C(2a) | −0.0974 (8) | −0.1762 (4) | 0.1813 (6) |
| C(3a) | −0.3479 (8) | −0.1450 (5) | 0.1252 (6) |
| C(4a) | −0.4190 (7) | −0.0843 (5) | 0.0875 (6) |
| C(5a) | −0.3207 (7) | −0.0311 (4) | 0.0856 (6) |
| C(1b) | 0.2162 (8) | −0.0673 (4) | 0.3064 (5) |
| C(2b) | 0.3406 (7) | −0.0262 (4) | 0.2808 (6) |
| C(3b) | 0.4044 (9) | 0.1052 (5) | 0.2480 (7) |
| C(4b) | 0.3478 (9) | 0.1598 (5) | 0.1832 (6) |
| C(5b) | 0.2263 (8) | 0.1313 (5) | 0.1312 (6) |
| C(1) | 0.1503 (7) | −0.1222 (4) | 0.0382 (5) |
| C(2) | 0.1858 (6) | −0.1394 (4) | 0.1439 (5) |
| C(3) | 0.2789 (7) | −0.1954 (4) | 0.1762 (5) |
| C(4) | 0.3402 (8) | −0.2357 (4) | 0.1068 (6) |
| C(5) | 0.3077 (8) | −0.2198 (4) | 0.0005 (6) |
| C(6) | 0.2141 (7) | −0.1649 (4) | −0.0329 (5) |
| C(2s) | −0.1814 (10) | 0.0474 (6) | 0.3150 (7) |
| C(3s) | −0.1660 (10) | 0.0807 (6) | 0.4156 (7) |
| C(4s) | −0.0501 (9) | 0.1335 (6) | 0.4231 (7) |
| C(5s) | 0.0130 (10) | 0.1199 (5) | 0.3268 (7) |

### Experimental Section

All solvents were purified by published procedures[14] and deoxygenated with pure dinitrogen in an inert-atmosphere box. All reagents were purchased commercially; potassium hydride was washed three times with hexanes to remove dispersion oil. The ligand Hbpeap was prepared as described.[15] All chemicals were stored in a Vacuum Atmospheres Dri-Lab operating at <1 ppm of $O_2$ and $H_2O$.

**Bis(*o*-(bis(2-(1-pyrazolyl)ethyl)amino)phenolato)bis(tetrahydrofuran)dimanganese(II) Perchlorate, $[Mn(bpeap)(THF)]_2(ClO_4)_2$ (1).** In an inert-atmosphere box, a solution of 418 mg (1.41 mmol) of the ligand Hbpeap was allowed to stir with 57 mg (1.42 mmol) of KH dissolved in a minimum amount of methanol. To the resulting orange solution was slowly added a solution of $Mn(ClO_4)_2 \cdot 6H_2O$ in a minimum amount of $CH_3OH$. A beige precipitate formed immediately. The mixture was allowed to stir for 3.5 h. The solution was filtered, and the solid was dissolved in a minimum volume of acetonitrile. Crystals were grown by vapor diffusion of THF into the latter solution. The transparent beige prisms were allowed to dry for several weeks in the inert atmosphere. Anal. Calcd for $C_{40}H_{52}Cl_2Mn_2N_{10}O_{10}$: C, 44.40; H, 4.56; N, 14.38. Found: C, 44.47; H, 4.70; N, 13.91.

**X-ray Data Collection.** The X-ray data were collected and reduced in the usual manner[16] using a coffin-shaped crystal mounted on a glass

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