in [Cl₂GaN(H)SiMe₃]₂ with bromine atoms has little effect on the structural features of the trans dimer or the trans–cis isomerization of the dimer.

Registry No. *trans*-[Br₂GaN(H)SiMe₃]₂, 120263-15-2; *cis*-[Br₂GaN-(H)SiMe₃]₂, 120329-66-0; (Me₃Si)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 μ-Phenoxo Manganese(II) Dimer

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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-

Table I. Crystallographic and Data Collection Parameters

formula: Mn₂C₄₀H₅₂N₁₀O₁₂Cl₂	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: P2₁/c
β, = 98.80 (2)°	μ = 7.84 cm⁻¹
V = 2253 (2) Å³	data range: 3 ≤ θ ≤ 25°
NO = 1631 (>3σ)	radiation: Mo Kα
T = 21 °C	data collcd: ±h,+k,+l

Table II. Positional Parameters for [Mn(bpeap)(THF)]₂(ClO₄)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)

(tetrahydrofuran)dimanganese(II) perchlorate, [Mn(bpeap)-(THF)]₂(ClO₄)₂ (**1**).

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 O₂ and H₂O.

Bis(*o*-(bis(2-(1-pyrazolyl)ethyl)amino)phenolato)bis(tetrahydrofuran)dimanganese(II) Perchlorate, [Mn(bpeap)(THF)]₂(ClO₄)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(ClO₄)₂·6H₂O in a minimum amount of CH₃OH. 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 C₄₀H₅₂Cl₂Mn₂N₁₀O₁₀: 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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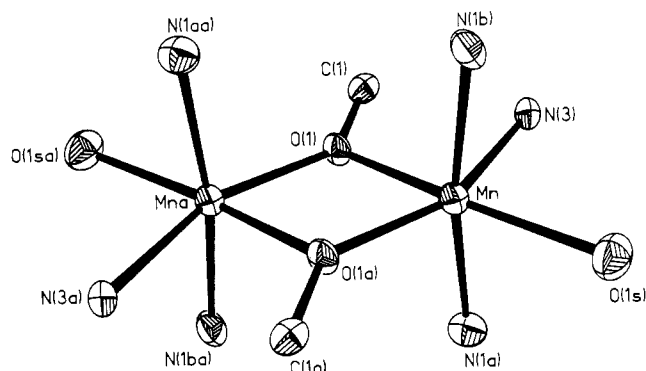
Figure 1. Inner coordination sphere around the manganese(II) centers in the [Mn(bpeap)(THF)]$_2^{2+}$ cation. Atoms O(1s) and O(1sa) are the THF oxygen atoms.
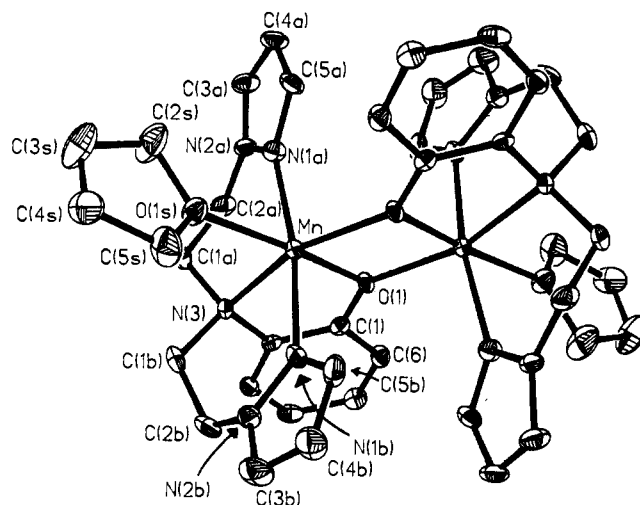
Table III. Principal Bond Lengths (Å) in [Mn(bpeap)(THF)]$_2$(ClO$_4$)$_2$

Mn–Mn(a)	3.256 (2)	N(3)–C(2)	1.471 (6)
Mn–O(1)	2.156 (4)	C(1b)–C(2b)	1.501 (8)
Mn–O(1a)	2.096 (3)	C(3b)–C(4b)	1.357 (9)
Mn–N(1a)	2.188 (5)	C(4b)–C(5b)	1.368 (9)
Mn–N(1b)	2.208 (5)	C(1)–O(1)	1.327 (6)
Mn–N(3)	2.319 (4)	C(1)–C(2)	1.394 (7)
Mn–O(1s)	2.300 (4)	C(1)–C(6)	1.416 (7)
N(1a)–N(2a)	1.348 (6)	C(2)–C(3)	1.381 (7)
N(1a)–C(5a)	1.331 (6)	C(3)–C(4)	1.364 (8)
N(2a)–C(2a)	1.461 (7)	C(4)–C(5)	1.394 (8)
N(2a)–C(3a)	1.334 (7)	C(5)–C(6)	1.371 (7)
C(1a)–C(2a)	1.518 (8)	O(1s)–C(2s)	1.431 (8)
C(3a)–C(4a)	1.350 (8)	O(1s)–C(5s)	1.423 (7)
C(4a)–C(5a)	1.361 (8)	C(2s)–C(3s)	1.422 (9)
N(1b)–N(2b)	1.355 (6)	C(3s)–C(4s)	1.471 (10)
N(1b)–N(5b)	1.331 (8)	C(4s)–C(5s)	1.491 (9)
N(2b)–C(2b)	1.461 (8)	Cl–O(2)	1.342 (6)
N(2b)–N(3b)	1.358 (8)	Cl–O(3)	1.361 (5)
N(3)–C(1a)	1.494 (7)	Cl–O(4)	1.333 (7)
N(3)–C(1b)	1.476 (6)	Cl–O(5)	1.327 (7)

fiber placed on an Enraf-Nonius CAD-4 automatic diffractometer. Cell constants and other data collection parameters are given in Table I.

The location of the one independent manganese atom was deduced from a three-dimensional Patterson function, and the remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. Isotropic refinement of these 33 atoms gave values of the conventional agreement factors $R_1 = 0.095$ and $R_2 = 0.104$; the weighting scheme was that of Ibers and co-workers[17] with the value of $p = 0.02$. Anisotropic refinement reduced these agreement values to 0.069 and 0.076, respectively. The positions of the hydrogen atoms could be deduced from a difference Fourier map computed at this stage, but all hydrogen atoms were included in subsequent calculations in fixed positions calculated on the basis of tetrahedral or trigonal geometry, as appropriate, with C–H distances of 0.95 Å.[18] The final values of the agreement factors were $R_1 = 0.056$ and $R_2 = 0.043$. In the final cycle, no parameter experienced a shift greater than 0.17σ. All computer programs used were those provided by Enraf-Nonius in the CAD-4/SDP package; atomic scattering factors were from ref 19. The refined atomic postional parameters, along with their standard deviations as estimated from the inverse matrix, are collected in Table II. The hydrogen atom coordinates, anisotropic vibrational parameters, and observed and calculated structural amplitudes are available as supplementary material.

Other Measurements. The magnetic susceptibility of a powdered sample of **1** was measured by the Faraday technique in the temperature range 1.5–300 K using equipment described elsewhere.[20,21] The molar susceptibilities were corrected for ligand diamagnetism by using Pascal's constants. X-Band EPR data were recorded at room temperature and at 77 K on a Varian E109 system and at liquid-helium temperature on

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Figure 2. View of a single [Mn(bpeap)(THF)]$_2^{2+}$ cation. Some carbon atoms in the phenyl ring are not labeled, but the numbering scheme is apparent. Hydrogen atoms are omitted for clarity. The right-hand side of the dimer is related to the left side by inversion through the center of the Mn$_2$O$_2$ unit.
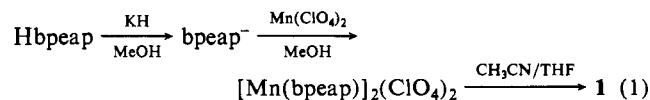
Table IV. Principal Bond Angles (deg) in [Mn(bpeap)(THF)]$_2$(ClO$_4$)$_2$

O(1)–Mn–O(1a)	80.1 (1)	O(1)–Mn–N(1a)	90.8 (1)
O(1)–Mn–N(1b)	96.7 (2)	O(1)–Mn–N(3)	76.1 (1)
O(1)–Mn–O(1s)	170.2 (1)	O(1a)–Mn–N(1a)	94.3 (2)
O(1a)–Mn–N(1b)	92.7 (2)	O(1a)–Mn–N(3)	155.9 (1)
O(1a)–Mn–O(1s)	108.9 (1)	N(1a)–Mn–N(1b)	170.5 (2)
N(1a)–Mn–N(3)	89.5 (2)	N(1a)–Mn–O(1s)	84.9 (1)
N(1b)–Mn–N(3)	86.7 (2)	N(1b)–Mn–O(1s)	86.8 (1)
N(3)–Mn–O(1s)	95.1 (1)	Mn–O(1)–Mn(a)	99.9 (1)
Mn–N(1a)–N(2a)	127.9 (4)	Mn–N(1a)–C(5a)	128.3 (5)
N(2a)–N(1a)–C(5a)	103.7 (5)	Mn–N(1b)–N(2b)	128.5 (4)
Mn–N(1b)–C(5b)	125.3 (5)	N(2b)–N(1b)–C(5b)	104.4 (6)
Mn–N(3)–C(1a)	109.7 (3)	Mn–N(3)–C(1b)	109.1 (3)
Mn–N(3)–C(2)	107.9 (3)	C(1a)–N(3)–C(1b)	107.0 (4)
C(1a)–N(3)–C(2)	110.4 (4)	C(1b)–N(3)–C(2)	112.8 (4)
N(1a)–N(2a)–C(2a)	121.6 (5)	N(1a)–N(2a)–C(3a)	111.4 (5)
C(2a)–N(2a)–C(3a)	126.8 (5)	N(1b)–N(2b)–C(2b)	122.8 (5)
N(1b)–N(2b)–C(3b)	110.9 (6)	C(2b)–N(2b)–C(3b)	125.8 (6)
N(3)–C(1a)–C(2a)	114.2 (5)	N(2a)–C(2a)–C(1a)	114.3 (5)
N(2a)–C(3a)–C(4a)	107.6 (6)	C(3a)–C(4a)–C(5a)	105.1 (5)
N(1a)–C(5a)–C(4a)	112.2 (6)	N(3)–C(1b)–C(2b)	117.0 (5)
N(2b)–C(2b)–C(1b)	116.7 (5)	N(2b)–C(3b)–C(4b)	107.0 (6)
C(3b)–C(4b)–C(5b)	105.6 (7)	N(1b)–C(5b)–C(4b)	112.1 (7)
C(2s)–O(1s)–C(5s)	106.6 (6)	O(1s)–C(2s)–C(3s)	108.6 (7)
C(2s)–C(3s)–C(4s)	108.0 (7)	C(3s)–C(4s)–C(5s)	104.3 (7)
O(1s)–C(5s)–C(4s)	108.8 (7)	O(2)–Cl–O(3)	112.2 (4)
O(2)–Cl–O(4)	105.0 (6)	O(2)–Cl–O(5)	117.5 (5)
O(3)–Cl–O(4)	107.6 (6)	O(3)–Cl–O(5)	110.3 (4)
O(4)–Cl–O(5)	103.3 (6)		

a Bruker ESP 300 spectrometer. Electronic absorption spectra were taken on a Hewlett-Packard 8450A rapid-scanning spectrophotometer.

Results and Discussion

The synthesis of **1** is summarized by eq 1. The crystalline product is stable toward O$_2$ although solutions of **1** change color, giving uncharacterized substances.

$$\text{Hbpeap} \xrightarrow[\text{MeOH}]{\text{KH}} \text{bpeap}^- \xrightarrow[\text{MeOH}]{\text{Mn(ClO}_4)_2}$$

$$[\text{Mn(bpeap)}]_2(\text{ClO}_4)_2 \xrightarrow{\text{CH}_3\text{CN/THF}} \mathbf{1} \quad (1)$$

(A) Description of Structure. The structure consists of binuclear [Mn(bpeap)(THF)]$_2^{2+}$ units, which are well separated from the anions. The inner coordination geometry of the metal ions is shown in Figure 1, and a view of the entire cation is presented in Figure 2. The principal bond lengths and angles in the structure are listed in Tables III and IV, respectively.

The geometry about each manganese(II) center is approximately octahedral. The bpeap ligand binds through three nitrogen

atoms and the phenolate oxygen atom, which also bridges between the metal ions. The sixth coordination site is occupied by the oxygen atom of a THF molecule. The Mn–N(pyrazole) distances of 2.188 (5) and 2.208 (5) Å are significantly shorter than the Mn–N(3) distance of 2.319 (4) Å. The long Mn–N(3) bond is presumably the result of strain in the N(3)–Mn–O(1) moiety induced by the binding of the two metal centers in a binuclear fashion with a Mn–Mn separation of only 3.256 Å. It is also the result of the low basicity of the arylamino groups relative to the pyrazole nitrogen atom. It is noteworthy in this regard that the O(1)–Mn–N(3) angle of 76.1 (1)° is far more distorted than the other cis angles subtended by a single ligand, which lie in the range 85–97°. A larger Mn–Mn separation (of approximately 3.5 Å) would relieve the strain in this portion of the molecule but lead to an unacceptably short O(1)---O(1') separation in the dimer. The actual O(1)---O(1') separation of 2.736 (7) Å is approximately twice that of the van der Waals radius of oxygen (2.80 Å)[22,23] and probably represents a lower limit for the O---O separation in dimers of this type. Some of the steric strain in this portion of the molecule would be reduced by the insertion of a methylene unit between O(1) and N(3), since that would convert the present five-membered ring into a six-membered ring; in the Schiff base complex [Mn(SALPS)]$_2$,[10] where the analogous unit does form a six-membered ring, the O–Mn–N angle is widened to an average value of 81.4°, and in a related Mn(III) dimer with alkoxy bridges, the angle is opened to 93.66 (8)°.[24]

The Mn–O(1) bond lengths in the bridging unit are asymmetric, but the values of 2.096 (3) and 2.156 (4) Å are in the range expected for a binuclear manganese(II) complex.[28] As anticipated, these bond lengths are about 0.20 Å longer than those observed in aryloxy- and alkoxo-bridged binuclear manganese(III) complexes[9,24,25] and approximately 0.30 Å longer than those in mixed-valence Mn(III)/Mn(IV) systems.[3,4,6,8,26] The bridging Mn$_2$O$_2$ unit is rigorously planar, with a Mn–O(1)–Mn' angle of 99.9 (1)°. This value is similar to that[9] of 99.8 (1)° in the phenoxo-bridged Mn(III) dimer [Mn(sal)py]$_2$$^{2-}$, larger than those in alkoxo-bridged Mn(III) dimers,[24,25] and slightly smaller than those of 100.5 (2) and 101.3 (1)° in the Mn(II) dimers [Mn$_2$Cl$_4$(O-C$_6$H$_4$CH$_3$)$_2$]$^{2-}$ and [Mn(SALPS)]$_2$, respectively.[10,11]

The THF ligand is tightly bound to the metal, and the Mn–O(1s) bond length is 2.300 (4) Å. This distance can be compared to those in a variety of recent reports, in which the M–O bond length ranges from 2.124 to 2.380 Å.[27-31]

The geometry of the perchlorate anion is close to that of a regular tetrahedron, although one angle appears to deviate from the ideal value by more than 6σ. The Cl–O bond lengths fall in the range 1.328 (7)–1.361 (5) Å, with an average length of 1.341 (14) Å, consistent with earlier observations.[32]

(B) Spectroscopic Properties. The room-temperature EPR spectrum of the solid complex **1** is the same as that obtained in a frozen CH$_3$CN solution at 77 K. Only a broad band is seen, which is centered at $g = 1.910$. The signal is evidently broadened as a result of the antiferromagnetic coupling (vide infra). At liquid-helium temperature, the spectrum remains very broad although some structure is observable.

The electronic spectrum shows only the ligand $\pi-\pi^*$ transitions between 200 and 300 nm. One band at 215 nm ($\epsilon = 4.63 \times 10^4$ M^{-1} cm^{-1}) corresponds to the pyrazole $\pi-\pi^*$ transition, and the other at 290 nm ($\epsilon = 8.73 \times 10^3$ M^{-1} cm^{-1}) is assigned to the benzene $\pi-\pi^*$ absorption.

(C) Magnetic Properties. No maximum in the susceptibility data is observed in the temperature range 1.5–300 K. The plot of effective magnetic moment as a function of temperature, however, shows a gentle decrease from the room-temperature value of 5.83 μ_B (very close to the spin-only value of 5.92 μ_B for a high-spin d^5 ion) to 5.20 μ_B at 22 K. At lower temperatures, μ_{eff} declines rapidly to a value of 2.3 μ_B at 1.5 K. This behavior clearly indicates some antiferromagnetic interaction between two high-spin d^5 metal ions. The temperature at which the magnetic susceptibility for such a complex should maximize is given by the expression

$$-2J = 0.241(T_{max})$$

where $2J$ is defined by the simple Van Vleck Hamiltonian

$$\mathcal{H} = -2JS_1S_2$$

and the energies of the triplet, quintet, septet, nonet, and undecet are $-2J$, $-6J$, $-12J$, $-20J$, and $-30J$, respectively. As a result, the observation that T_{max} is less than 1.5 K leads to the conclusion that $-2J$ is smaller than 0.36 cm^{-1}.

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Kinetic Study of the Rhodium(I)-Catalyzed Decarbonylation of Phenylacetyl Chloride

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We have been engaged in investigations of the mechanisms of decarbonylations of acid chlorides catalyzed by Rh(I) complexes.[1] We have established that the product-forming step is the rate-determining step in these decarbonylation reactions and that the rate of the formation of decarbonylation products depends greatly on the structure of the acid chloride.[2,3] As part of our investigation

(1) For a recent review of this decarbonylation chemistry, see: Doughty, D. H.; Pignolet, L. H. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 343–375.

(2) (a) Kampmeier, J. A.; Harris, S. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1981,** *103,* 1478–1485. (b) Kampmeier, J. A.; Rodehorst, R. M.; Philip, J. B., Jr. *Ibid.* **1981,** *103,* 1847–1849.

(3) (a) Kampmeier, J. A.; Mahalingam, S. *Organometallics* **1984,** *3,* 489–491. (b) Kampmeier, J. A.; Mahalingam, S.; Liu, T.-Z. *Ibid.* **1986,** *5,* 823–825.