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Structure and Bonding of a Novel Mercuracycle Complex Containing B−Hg Bonds at Carborane Vertices

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The known compound 9-CF_3CO_2Hg-1,7-$C_2B_{10}H_{11}$, **3**, was obtained by direct mercuration of 1,7-$C_2B_{10}H_{12}$ (*m*-carborane) with 1 equiv of mercuric oxide in trifluoroacetic acid. Species **3** has now been fully characterized by multinuclear NMR and mass spectroscopy. A byproduct, **4**, $[(1,7\text{-}C_2B_{10}H_{10})_2Hg_4(OH)_2][CF_3CO_2]_2$, obtained from the reaction mixture was found in the solid state to be a cyclic array containing four mercury centers in which four trifluoroacetate anions interact simultaneously with each macrocycle. Two $CF_3CO_2^-$ ions form a pair of hydrogen bonds with the (OH) ligands present in the macrocycle skeleton, and the remaining two trifluoroacetate anions interact with the cycle via moderately strong electrostatic interactions between Hg atoms and the oxygen atoms of the carboxylate groups. Each of the four trifluoroacetate anions is shared by two macrocycles to form a self-assembled 1:2 (mercury cycle to trifluoroacetate ion) polymeric array. Crystallographic data are as follows: triclinic, space group $P\bar{1}$, a = 10.6113(8) Å, b = 11.1127(9) Å, c = 7.2044(5) Å, α = 74.826(2)°, β = 78.473(2)°, γ = 72.591(2)°, V = 775.53 Å^3, Z = 1, ϱ_{calcd} = 2.88 g cm^{-3}, R = 0.049, R_w = 0.058.

Introduction

We recently reported the synthesis and anion complexation studies of "mercuracarborands" such as **1** and **2** (Chart 1).[1] This novel class of macrocycles incorporates carborane cages linked by an equal number of mercury atoms through Hg−C (carborane) bonds in which the Hg atoms serve as Lewis acid centers for binding electron-rich guest species.

As a complement of this study, we prepared unusual mercury-containing carborane derivatives characterized by B−Hg σ-bonds while striving for the synthesis of new types of anion-coordinating ligands as well as investigating their binding properties as compared with those of "mercuracarborands". We are also interested in these B-mercurated carborane derivatives because of the unusual stability of the B−Hg bond toward nucleophilic reagents,[2] a property not shared by their *C*-mercuracarborane analogs. Because of the acidic nature of the hydrogen atoms bound to the cage carbon atoms, the interaction of a *B*-carboranyl derivative of mercury with a base such as *n*-BuLi would result in the formation of the carborane C−Li species,[3] which allows subsequent introduction of functional groups at carbon while the B−Hg bonds remain intact. Among functional groups, conventional crown ether moieties would be quite interesting because heterotopic host molecules[4] constructed in this way would be reasonably expected both to bind a cation within the crown ether and to coordinate an anion by the Lewis acidic mercury centers, as shown in diagram I.

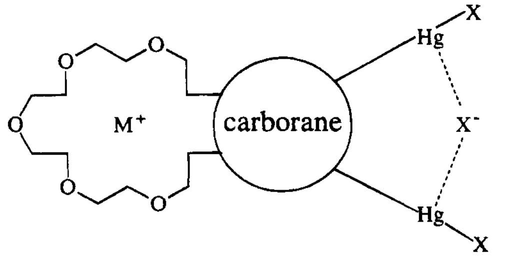

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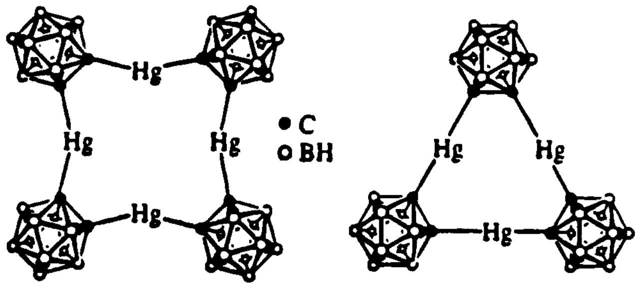
Chart 1



1 **2**

After the discovery of direct mercuration and thallation of carboranes, many B-metalated carborane derivatives were synthesized and their chemistry was extensively explored.[2] Herein we report the synthesis and complete characterization of the known compound 9-CF_3CO_2Hg-1,7-$C_2B_{10}H_{11}$, **3**,[5] and the molecular structure of an unexpected byproduct, **4**.

Results and Discussion

The known compound 9-CF_3CO_2Hg-1,7-$C_2B_{10}H_{11}$, **3**, was obtained by direct mercuration of 1,7-$C_2B_{10}H_{12}$ (*m*-carborane) with 1 equiv of mercuric oxide in trifluoroacetic acid[5] and was characterized by multinuclear NMR and mass spectroscopy.[6] The two characteristic quartets (chemical shifts 120.7 and 161.1 ppm, respectively) of a trifluoroacetate were revealed by ^{13}C

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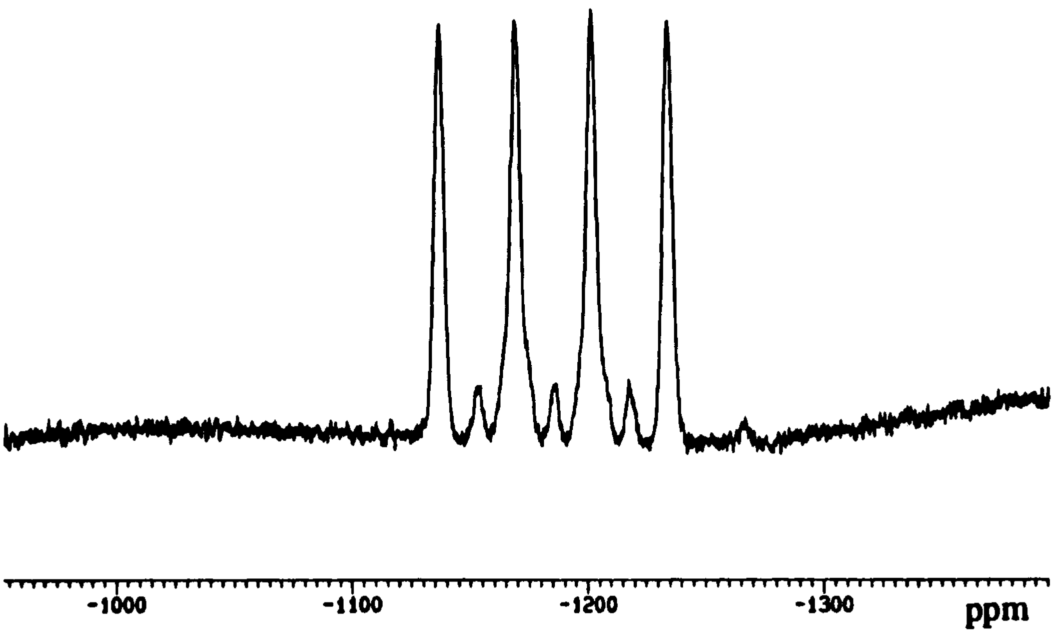

Figure 1. ^{199}Hg NMR spectrum of **3** which demonstrates the coupling of the ^{199}Hg nucleus to both ^{11}B and ^{10}B nuclei (quartet, $J_{^{199}\text{Hg}-^{11}\text{B}} = 2900$ Hz; heptet, $J_{^{199}\text{Hg}-^{10}\text{B}} = 960$ Hz).

NMR data. The ^{11}B NMR spectrum indicates that the carborane cage is monosubstituted. The ^{199}Hg NMR spectrum shows distinct spin-coupling of the ^{199}Hg nucleus with both the ^{11}B (80.4%, $S = ^3/_2$) and ^{10}B (19.6%, $S = 3$) nuclei,[7] thus confirming the existence of a Hg−B bond in this compound (Figure 1). The apparent absence of four of the expected heptet signals is due to their overlap with the quartet, as shown by the broadening of the two central quartet signals. Similar multiplets of ^{1}H resonance which result from coupling with ^{11}B and ^{10}B nuclei have been reported previously.[8] However, such data are rarely useful in providing structural information on boranes and carboranes because the signals are usually either too broad or too complex for interpretation.

The ^{199}Hg nucleus has a spin quantum number of $I = ^1/_2$ and a relatively low natural abundance (16.9%).[9] Mercury-199 NMR spectroscopy has been employed in studying the interactions of organomercurials with a variety of bases and ligands.[10] The interactions between mercury(II) chloride and membranes as well as other ligands have also been revealed by ^{199}Hg NMR studies.[11] Recently, we utilized this technique as a probe in studies of the anion coordination chemistry of "mercuracarborand" hosts in solution.[1] As far as we know, the present work is the first reported example of spin-coupling of ^{199}Hg with the ^{11}B (quartet, $J_{^{199}\text{Hg}-^{11}\text{B}} = 2900$ Hz) and ^{10}B nuclei (heptet, $J_{^{199}\text{Hg}-^{10}\text{B}} = 960$ Hz), thereby providing a unique confirmation of the existence of a B−Hg bond.

Surprisingly, a crystal which grew from an ethereal solution of **3** was found to be composed of a compound having the structure shown in Figure 2. Table 1 summarizes the crystallographic data obtained for this species, **4**. Selected bond lengths and angles are given in Table 2. We believe that this is the first structurally characterized complex having two σ-bonds between nontransition metals and the boron vertices of a carborane cage.[12]

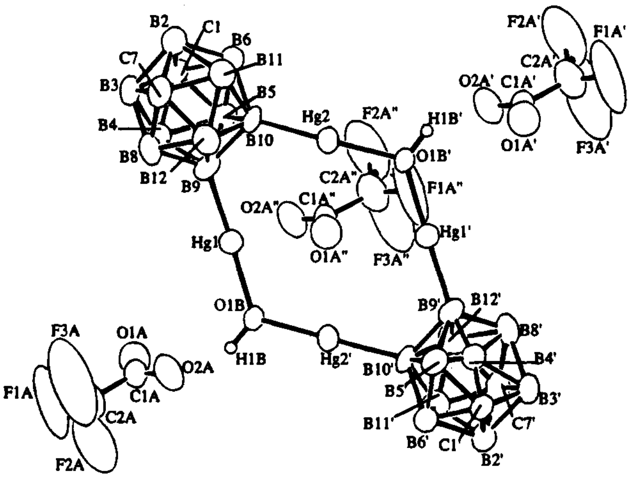

Figure 2. ORTEP representation of **4** including two additional trifluoroacetate anions related by inversion plus translation.

The complex consists of two inversion-related 1,7-carborane cages linked by two Hg−(OH)−Hg segments through four B−Hg bonds. A pair of moderately strong O−H···O hydrogen bonds link the hydroxyl hydrogen atoms to two trifluoroacetate ions (O2A···O1B = 2.65(1) Å, O2A···H1B(1.82) Å and O1B−H1B···O2A = 144(14)°). The mercury cycle also interacts with another pair of trifluoroacetate ions through electrostatic interactions between Hg and the non-hydrogen-bonded oxygen atoms of the trifluoroacetate ion with distances of O1A″···Hg1 = 2.772(10) Å and O1A″···Hg2′ = 2.967(10) Å. These values are significantly shorter than the sum of the van der Waals radii of Hg (1.73 Å)[13] and O (1.40 Å).[14]

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Table 1. Crystallographic Data for **4**

formula	$C_8H_{22}B_{20}O_6F_6Hg_4$	ϱ(calcd), g cm^{-3}	2.88
fw	1349.1	radiation (Mo Kα) λ, Å	0.7107
crystal system	triclinic	abs coeff (μ), cm^{-1}	198
space group	$P\bar{1}$	abs factors (intensity)	1.72−1.00
crystal dimens, mm	0.33 × 0.10 × 0.10	F(000), e	640
crystal color	clear and colorless	temp, K	300
crystal habit	rectangular rods	diffractometer	Huber (Crystal Logic)
a, Å	10.6113(8)	scan mode; speed, deg/min	$\theta-2\theta$; 4.5
b, Å	11.1127(9)	2θ range, deg	1−60
c, Å	7.2044(5)	no. of data collcd, no. of unique data used	4524, 2930 ($I > 3\sigma(I)$)
α, deg	74.826(2)	no. of params refined	203
β, deg	78.473(2)	max resid density, e/Å^3	0.7 (0.98 Å from Hg)
γ, deg	72.591(2)	R	0.049
Z	1	R_w	0.058
V, Å^3	775.53	GOF	1.720

[a] $R = \Sigma||F_o| - |F_c||/|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. GOF $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)^{1/2}$, where $w = 1/(\sigma^2|F_o|)$.

Table 2. Selected Bond Lengths and Angles for **4**

Lengths (Å)			
Hg1−B9	2.097(15)	Hg2−B10	2.101(13)
Hg1−O1B	2.087(9)	Hg2−O1B′	2.067(8)
Hg1−Hg2	3.5943(7)	Hg1−Hg2′	3.8565(6)
Hg1−Hg1′	5.2712(7)	Hg2−Hg2′	5.2724(7)
C1A−O1A	1.23(2)	C1A−O2A	1.25(2)
O1B−H1B	1.0(2)	O1B−O2A	2.65(1)
O2A−H1B	1.8(2)		
Angles (deg)			
Hg1−O1B−Hg2′	119.8(4)	O1B−Hg1−B9	175.8(5)
O1B′−Hg2−B10	178.9(4)	Hg1−B9−B10	119.5(9)
Hg2−B10−B9	119.5(9)	O1A−C1A−O2A	132.0(14)
O1B−H1B−O2A	144(14)		

The structure of **4** is in agreement with that of common Hg(II) complexes;[15] mercury forms two essentially collinear primary bonds, and it retains appreciable Lewis acidity in the plane perpendicular to these primary bonds, allowing secondary bonding interactions through the use of empty *p* orbitals.[16] Thus O−Hg−B angles about the Hg atom are nearly linear (O1B−Hg1−B9 175.8(5)° and O1B′−Hg2−B10 = 178.9(4)°), and the O−Hg−B angles involving the trifluoroacetate oxygen atoms are 104.5(5)°, (O1A″−Hg1−B9) and 105.9(6)° (O1A″−Hg2−B10). Other angles in the cycle are all nearly 120°, Hg1−O1B−Hg2′ = 119.8(4)°, Hg1−B9−B10 = 119.5 (9)°, and Hg2−B10−B9 = 119.9 (9)°.

Three $CF_3CO_2^-$ ions are shown in Figure 2. $CF_3CO_2^-$ is related to $(CF_3CO_2^-)'$ by inversion and to $(CF_3CO_2^-)''$ by translation. The fourth $CF_3CO_2^-$, which is not illustrated, would be the one interacting with Hg1′ and Hg2 and inversion-related to $(CF_3CO_2^-)''$. Each of the four trifluoroacetate ions interacts with the macrocyclic host through either hydrogen bonding or Hg-O interactions using only one of its two oxygen atoms and with a second cycle using the remaining oxygen. In other words, each trifluoroacetate ion is shared by two mercury cycles and a self-assembled polymeric 1:2 (mercury cycle to trifluoroacetate ion) complex with two trifluoroacetate anions in the crystalline solid is formed as shown in Figure 3 .

Although we do not yet know the factors that govern the formation of compound **4**, it is probably formed during acidic hydrolysis of a small amount of 9,10-bis((trifluoroacetoxy)-mercurio)-*m*-carborane, which is a possible mercuration reaction byproduct, followed by subsequent condensation. Water is the most likely source of the OH ligand.

Experimental Section

A. Reagents and Physical Measurements. Mercuric oxide (Aldrich) and trifluoroacetic acid (Aldrich) were used as received. Infrared spectra (Nujol) were recorded with a Nicolet Model 205 FT-IR spectrometer. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AM 360 spectrometer, and the ^{11}B and ^{199}Hg NMR spectra were obtained on an ARX 500 spectrometer. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to residual ^1H and ^{13}C present in deuteriated solvents. Chemical shift values for ^{11}B spectra were referenced to external $BF_3{\cdot}Et_2O$ (0.0 ppm with negative value upfield). The ^{199}Hg NMR spectrum was recorded at 25 °C and 89.4 MHz by using broad-band decoupling. External 1.0 M PhHgCl/DMSO-d_6 solution was used as the reference at −1187 ppm relative to neat Me_2Hg.[17]

B. Synthesis. Synthesis of **3** was carried out according to the previously described procedure.[5] A solution of *m*-carborane, 1,7-$C_2B_{10}H_{12}$ (1.44 g, 10 mmol), and HgO (2.17 g, 10 mmol) in 30 mL of trifluoroacetic acid was refluxed for 10 h. Trifluoroacetic acid was then distilled off. The sticky, grayish residue was triturated with water, and the solid obtained was filtered off, washed with water, and recrystallized from heptane as shining flakes. Yield: 80%. Mp: 118−120 °C. ^1H NMR (200 MHz, $(CD_3)_2CO$, 25 °C): δ 0.5−4.7 (carborane B−H), 3.85 (s, carborane C−H). ^{13}C NMR (90 MHz, $(CD_3)_2CO$, 25 °C): δ 59.4 (s, carborane), 120.7 (q, $\mathit{C}F_3CO_2$), 161.1 (q, $CF_3\mathit{C}O_2$). ^{11}B NMR (160 MHz, $(CH_3)_2CO$, $BF_3{\cdot}Et_2O$ external, decoupled, 25 °C): δ −4.87 (d, 2B), −8.53 (overlap of a singlet (1B) and a doublet (1B)), −11.34 (d, 4B), -13.5 (d, 1B), −14.9 (d, 1B). ^{199}Hg NMR (89.4 MHz, $(CD_3)_2CO$, 25 °C): δ −1186 (q, $J_{^{199}Hg-^{11}B}$ = 2900 Hz; heptet, $J_{^{199}Hg-^{10}B}$ = 960 Hz. IR (Nujol): ν 2600 (carborane B−H), 1687 cm^{-1} (C=O). EIMS (65 eV): *m/z* 143 (**3** − 9-CF_3CO_2Hg, 100), 343 (**3** − CF_3CO_2, 60). The reaction product is always contaminated with a small amount of 9,10-bis((trifluoroacetoxy)mercurio)-*m*-carborane. During workup of the reaction mixtures, acidic hydrolysis of this dimercurated carborane derivative, followed by subsequent condensation, would probably result in the formation of the cyclic compound **4**, and water might be the source of the OH ligand. A similar situation can be found in ref 18.

C. X-ray Data Collection and Processing. A colorless crystal of **4**, obtained from a diethyl ether solution, was mounted

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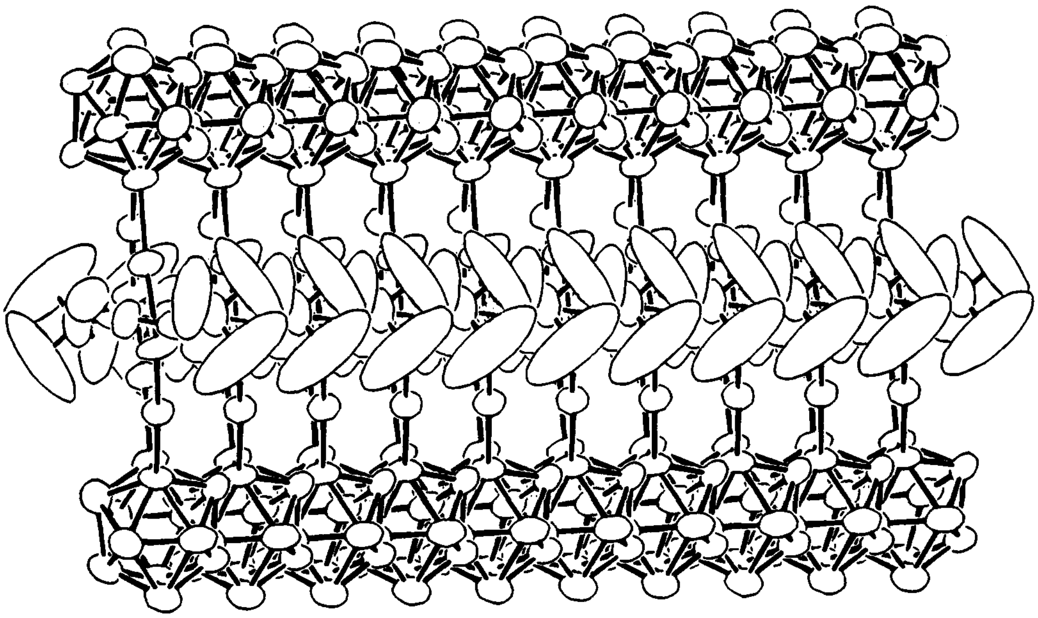

Figure 3. Lattice orientation of **4** showing the presence of polymeric chains in the solid state.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **4**

	x	y	z	U_{eq}[a]
Hg1	376(5)	1248(5)	1367(7)	54(1)
Hg2	1910(5)	637(5)	6060(6)	48(1)
O1B	−1226(9)	510(10)	1415(11)	62(3)
B2	4391(18)	3389(15)	1518(22)	61(4)
B3	3658(18)	3652(16)	−652(20)	64(4)
B4	3142(15)	2288(16)	−640(20)	55(4)
B5	3561(14)	1116(14)	1537(21)	52(3)
B6	4279(16)	1841(15)	2883(23)	63(4)
B8	1985(16)	3645(15)	49(20)	59(4)
B9	1883(15)	2115(16)	1353(21)	58(4)
B10	2587(15)	1835(14)	3517(18)	50(3)
B11	3106(17)	3183(15)	3484(22)	59(4)
B12	1643(18)	3363(15)	2539(24)	62(4)
C1	4518(12)	2181(12)	414(17)	51(3)
C7	2803(15)	4207(12)	1290(19)	61(3)
C1A	−1903(16)	1889(14)	−3334(20)	64(4)
C2A	−2646(17)	2957(16)	−4785(24)	76(4)
F1A	−2227(16)	3012(15)	−6553(16)	199(6)
F2A	−3775(18)	3013(29)	−4673(29)	378(14)
F3A	−2760(43)	3982(13)	−4597(33)	298(25)
O1A	−980(10)	1086(10)	−4010(16)	77(3)
O2A	−2403(12)	1957(12)	−1633(16)	94(4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

on a fiber with epoxy cement and placed on a Huber diffractometer constructed by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 51 accurately centered reflections ($7.9 < 2\theta < 22.1°$). Data were collected at 27 °C in the $\theta - 2\theta$ scan mode. Of the 4524 unique reflections measured, 2930 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for absorption and secondary extinction. Programs used in this work include locally modified versions of crystallographic programs listed in ref 19.

Atoms were located by use of heavy-atom methods. All calculations were performed on a VAX 3100 computer in the J. D. McCullough X-ray Crystallography Laboratory. All non-hydrogen atoms were refined with anisotropic parameters. Positions of hydrogens on the carborane ligand were located and included in the structure factor calculation but not refined. The hydroxyl hydrogen atom was located, and positional parameters were refined. H atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Scattering factors for H were obtained from ref 20 and for other atoms were taken from ref 21. Anomalous dispersion terms were included for the scattering of Hg. The largest peak on a final difference electron density map was 0.7 e $Å^{-3}$. The cycle is centrosymmetric. Final positional and thermal parameters for non-hydrogen atoms are given in Table 3.

Acknowledgment is made to the NSF (Grant No. CHE-93-14037) for support of this work. We thank Dr. J. M. Strouse for assistance with the ^{199}Hg NMR experiments.

Supplementary Material Available: Tables of positional and thermal parameters, bond lengths and angles, and crystallographic data and an ORTEP view of **4** (5 pages). Ordering information is given on any current masthead page.

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