corded on a Nicolet TT-23 instrument operating at 25.14 MHz. All operations were performed under nitrogen.

Tris[(hexamethyldisilyl)amido]chlorozirconium(IV). Sodium (hexamethyldisilyl)amide (2.3 g, 0.013 mol) dissolved in diethyl ether (30 mL) was added to a suspension of zirconium(IV) chloride (1.0 g, 0.0043 mol) in diethyl ether (40 mL). After the mixture was stirred for 24 h, diethyl ether was removed under vacuum and the residue was extracted into pentane (2 × 50 mL) and concentrated to ca. 20 mL. Cooling of the concentrate (−10 °C) afforded white needles in 65% (1.7 g) yield. Anal. Calcd for $C_{18}H_{54}ClN_3Si_6Zr$: C, 35.6; H, 8.90; N, 6.92; Cl, 5.85. Found: C, 35.9; H, 8.93; N, 6.84; Cl, 5.52.

Tris[(hexamethyldisilyl)amido]chlorohafnium(IV). Sodium (hexamethyldisilyl)amide (10.4 g, 0.0590 mol) dissolved in diethyl ether (100 mL) was added to hafnium(IV) chloride (4.40 g, 0.0190 mol) suspended in diethyl ether (75 mL). After the mixture was stirred for 24 h, the diethyl ether was removed under vacuum and the residue was extracted into pentane (3 × 75 mL). Concentration of the filtrate to ca. 50 mL and cooling of the concentrate (−10 °C) yielded white needles in 61% (8.0 g) yield. Anal. Calcd for $C_{18}H_{54}ClHfN_3Si_6$: C, 31.1; H, 7.78; N, 6.05; Cl, 5.11. Found: C, 31.4; H, 7.69; N, 6.40; Cl, 5.25.

Tris[(hexamethyldisilyl)amido]methylzirconium(IV). Methyllithium (0.63 mL of a 0.88 M diethyl ether solution, 0.00056 mol) was added to tris[(hexamethyldisilyl)amido]chlorozirconium (0.34 g, 0.00056 mol) in diethyl ether (30 mL) at 0 °C. The suspension was stirred at 0 °C for 4 h and evaporated to dryness under vacuum, and the residue was extracted with pentane (30 mL). Concentration of the extract to ca. 5 mL and cooling of the concentrate (−10 °C) yielded white needles in 29% (0.10 g) yield. Anal. Calcd for $C_{19}H_{57}N_3Si_6Zr$: C, 38.9; H, 9.72; N, 7.16. Found: C, 39.1; H, 9.74; N, 7.19. The compound yields a $(M - 15)^+$ peak in its mass spectrum.

Tris[(hexamethyldisilyl)amido]methylhafnium(IV). Methyllithium (2.3 mL of a 0.88 M diethyl ether solution, 0.0018 mol) was added to tris[(hexamethyldisilyl)amido]chlorohafnium (1.3 g, 0.0018 mol) in diethyl ether (50 mL) at 0 °C. The mixture was stirred for 12 h at 0 °C and then evaporated to dryness under vacuum. Pentane (40 mL) was added to the residue and it was filtered. The filtrate was concentrated to ca. 10 mL. Cooling of the concentrate (−10 °C) yielded white needles in 89% (1.1 g) yield. Anal. Calcd for $C_{19}H_{57}HfN_3Si_6$: C, 33.8; H, 8.46; N, 6.24. Found: C, 33.7; H, 8.35; N, 6.37. The compound yields a $(M - 15)^+$ ion in its mass spectrum.

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Registry No. $ClZr[N(SiMe_3)_2]_3$, 69897-59-2; $ClHf[N(SiMe_3)_2]_3$, 69897-60-5; $MeZr[N(SiMe_3)_2]_3$, 69897-61-6; $MeHf[N(SiMe_3)_2]_3$, 69927-29-3; zirconium(IV) chloride, 10026-11-6; hafnium(IV) chloride, 13499-05-3; sodium (hexamethyldisilyl)amide, 1070-89-9.

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Correspondence

A Novel Copper(II) Trimer Containing 2′-Deoxyguanosine

Sir:

DNA, the material responsible for the transmission of genetic information, consists of a polymeric network of a special class of nucleic acid bases called deoxyribonucleotides. Metal ions are known to interact with nucleic acids and their constituents,[1-3] and their role in the replication, translation, and transcription of nucleic acids is well documented.[4] Although copper(II) complexes containing guanine residues have been spectroscopically characterized,[5-8] there have been no reports to date of a solid metal ion complex with any deoxyribonucleic acid residue. We wish to report the synthesis and electronic and magnetic properties of the first metal ion complex with one member of this very important class of nucleic-acid bases, $Cu_3(2'\text{-deoxyguanosine})_2(OH)_4 \cdot 4H_2O$. This complex is also the first example of a sugar-coordinated nucleic acid component and of a bent, trinuclear metal ion complex containing a nucleic acid constituent.

The complex was obtained by addition (in small increments) of a basic solution of 2′-deoxyguanosine (2′-dGH), prepared by adding 20 drops of a 10% NaOH solution to 20 mL of water at 70 °C containing 0.501 g (2 mmol) of 2′-dGH, to 4 mL of a 0.25 M $CuAc_2 \cdot H_2O$ solution at the same temperature with constant swirling. A green mixture resulted after addition of ca. one-half of the ligand solution. The final mixture (pH 10) was chilled in an ice bath and filtered, and the precipitate was oven-dried at 85 °C. Anal. Calcd for $Cu_3(2'\text{-dG})_2(OH)_4 \cdot 4H_2O$ ($Cu_3C_{20}H_{36}N_{10}O_{16}$): C, 27.83; H, 4.20; N, 16.23. Found: C, 27.79; H, 3.52; N, 15.92. The dark green complex decomposes between 142 and 147 °C. The electron paramagnetic resonance (EPR) spectra were obtained with a Varian HFE-12 spectrometer at room and liquid nitrogen (77 K) temperatures by using X-band frequencies, the variable temperature bulk magnetic susceptibility measurements (12–300 K) with a Faraday balance setup previously described,[9,10] the electronic spectrum (8–25 $cm^{-1} \times 10^3$) by using a Nujol mull with a Beckman DK-2A spectrometer, and the infrared spectra (0.66–4.0 $cm^{-1} \times 10^3$) by using KBr pellets with a Perkin-Elmer Model 21 spectrometer. All measurements were made on polycrystalline material; IR spectra with pellets and mulls (Nujol and fluorolube) were comparable.

The electronic spectrum exhibits a broad, structureless absorption at 14.3 $cm^{-1} \times 10^3$ which can be ascribed to the ${}^2E \leftarrow {}^2B_{1g}$ transition of copper(II) in a distorted octahedral ligand field. Similar absorption maxima have been observed[8] in a series of axially coordinated bis(8X-guanosine)copper(II) complexes. The EPR spectra contained resonances originating in the $S = {}^1/_2$ (doublet) and ${}^3/_2$ (quartet) spin states, the latter being considerably weaker in intensity. A typical axial spectrum for copper(II)[11] with g values (${}^{63,65}Cu$ hyperfine) of 2.26 (175 G) and 2.03 (13 G) in addition to spin transitions originating in the quartet spin state at 1300, 3800, and 4860 G was observed at room temperature. No evidence of additional resonances was obtained at 77 K.

The bulk magnetic susceptibility is shown in Figure 1 where ○ and × represent the experimental points for the inverse corrected molar susceptibility and magnetic moment per copper(II) ion, respectively. The lines represent a theoretical best fit to a bent, exchange-coupled copper(II) trimer[12] and yield the parameters $g = 2.00$, $2J_{12} = -58$ cm^{-1}, and $2J_{22'} = -52$ cm^{-1}, where the subscripts 1 and 2 refer to central and terminal copper(II) ions, respectively. Other magnetic models were tried in an attempt to fit the experimental data but gave poor fits in all cases. The data indicate antiferromagnetic coupling of relatively low intensity, with similar coupling between terminal copper(II) ions and central and terminal copper(II) ions. The room-temperature magnetic moment (1.51 μ_B) suggests a substantial population of the quartet spin state by the three electrons in the Cu_3 core. Support for this

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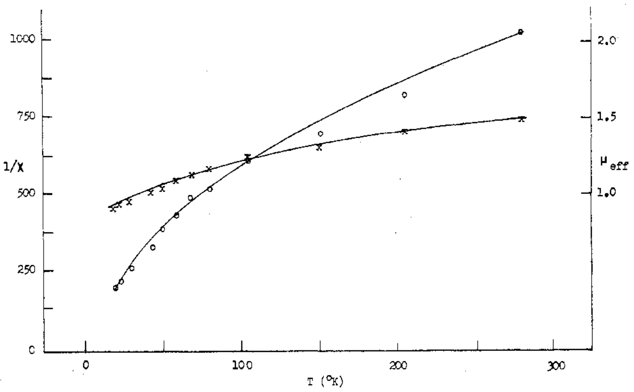

Figure 1. Magnetic susceptibility data for $Cu_3(2'\text{-}dG)_2(OH)_4 \cdot 4H_2O$. ○ and × are experimental points for the inverse corrected molar susceptibility and magnetic moment, respectively, and the lines are theoretical best fits to a bent trimer model.

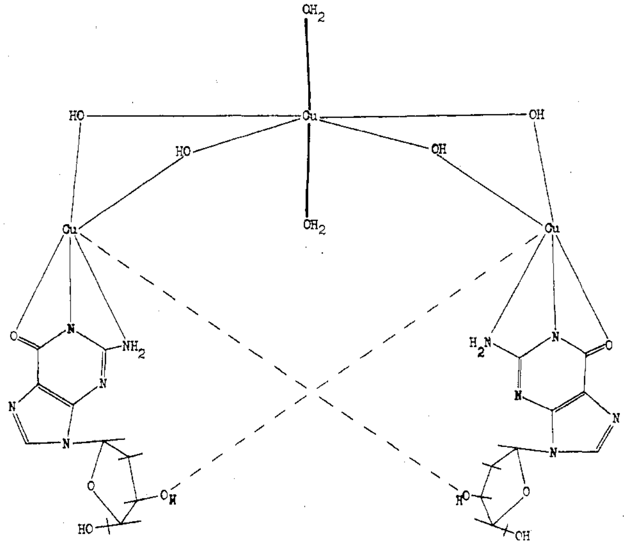

Figure 2. Schematic of the proposed structure for the $Cu_3(2'\text{-}dG)_2(OH)_4 \cdot 4H_2O$ complex.

is seen in the half-field and full-field EPR absorptions (vide supra).

A comparison of the infrared spectra of free and coordinated ligands shows substantial differences. A high-frequency shoulder at 3550 cm^{-1} in the complex supports OH bridging. This assignment is corroborated by the presence of a weak absorption at 957 cm^{-1} in the complex that is not present in the free ligand.[13] The C(6)═O stretch at 1727 cm^{-1} in the free ligand is lost upon complexation and points to C(6)O coordination. The reduction in intensity of δ(N(1)H) at 1525 cm^{-1}, corroborated by the reduction of ring stretches at 1656 and 1637 cm^{-1}, suggests N(1) involvement. The participation by C(2)NH$_2$ is evidenced by the loss of δ(NH$_2$) at 1689 cm^{-1} and ν(NH$_2$) (asymmetric and symmetric) at 3420 and 3333 cm^{-1}, respectively, in the complex. The 2′-deoxyribose oxygen is presumed to be involved in coordination to the metal to some extent as the intensities of both the degenerate 2′-deoxyribose stretches at 1075 and 1031 cm^{-1} and the symmetric 2′-deoxyribose stretches at 833 and 865 cm^{-1} are lost. However, hydrogen bonding to water molecules in the lattice may be contributing to the diminution of the intensities of these stretching modes. These data, together with the results of the electronic, EPR, and variable temperature magnetic susceptibility measurements, suggest a structure as shown in Figure 2. Attempts to grow single crystals suitable for X-ray study have proved unsuccessful.

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Registry No. $Cu_3(2'\text{-}dG)_2(OH)_4$, 69686-91-5.

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Additions and Corrections

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C. A. Tolman,* A. D. English,* S. D. Ittel, and J. P. Jesson: Preparation, Structure, and Reactions of Triphenyl Phosphite Complexes of Iron, Ruthenium, and Osmium.

Page 2375. We are indebted to Dr. A. Foust, University of Bergen, Bergen, Norway, for pointing out that in the caption to Figure 1, the signs of the coupling constants should read $J_{AC} = \mp325$, $J_{AD} = \pm74$ in place of the present $J_{AC} = \pm325$, $J_{AD} = \mp74$.—C. A. Tolman

Gary J. Long: A Mössbauer, Magnetic, and Electronic Structural Study of Two Iron Squarate Complexes.

Page 2706. Reference 7 should read as follows: R. West and H. Y. Niu, *J. Am. Chem. Soc.*, **85**, 2589 (1963); H. Y. Niu, Doctoral Dissertation, University of Wisconsin, 1962, p 99; S. M. Condren, Doctoral Dissertation, University of Missouri—Rolla, 1971, p 51.—Gary J. Long

1979, Volume 18

I. S. Jaworiwsky, J. R. Long, L. Barton, and S. G. Shore*: Directive Effects in Bridge Cleavage Reactions of Methyl-Substituted Boron Hydrides. 1. Preparation and Nuclear Magnetic Resonance Spectra of 3-$CH_3B_6H_{11}$, 3-$CH_3B_6H_{10}$, and 1-$CH_3B_4H_9$.

Page 56. The title of this paper should read as follows: Directive Effects in Bridge Cleavage Reactions of Methyl-Substituted Boron Hydrides. 1. Preparation and Nuclear Magnetic Resonance Spectra of 3-$CH_3B_6H_{11}$, *3-*$CH_3B_5H_{10}$, and 1-$CH_3B_4H_9$.—S. G. Shore