

The paramagnetic anisotropy of (TPP)FeCl in the 77–5 K temperature range is thus in agreement with the deduction from the high-temperature anisotropy data that the ZFS parameter D in this case is 6.0 cm^{-1} . In this respect (TPP)FeCl appears to resemble closely chlorohemin and other structurally similar iron(III) porphyrins.⁸ A very recent Mössbauer study²¹ also gives $D = 7.0 \pm 1.0 \text{ cm}^{-1}$ for (TPP)FeCl.

Registry No. (TPP)FeCl, 16456-81-8.

References and Notes

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- (2) M. Kotani, *Prog. Theor. Phys., Suppl.*, **17**, 41 (1961).
- (3) S. Mitra, *Prog. Inorg. Chem.*, **22**, 309 (1977).
- (4) C. Maricondi, W. Swift, and D. K. Straub, *J. Am. Chem. Soc.*, **91**, 5205 (1969).
- (5) G. N. LaMar, G. R. Eaton, R. H. Holm, and F. A. Walker, *J. Am. Chem. Soc.*, **95**, 63 (1973).
- (6) G. L. Neiheisel, J. L. Imes, and W. P. Pratt, *Phys. Rev. Lett.*, **35**, 101 (1975).
- (7) H. Uenoyama, *Biochim. Biophys. Acta*, **230**, 479 (1971).
- (8) (a) P. L. Richards, W. S. Caughey, H. Eberspaecher, G. Feher, and M. Malley, *J. Chem. Phys.*, **47**, 1187 (1967); (b) G. C. Brackett, P. L. Richards, and W. S. Caughey, *ibid.*, **54**, 4387 (1971).
- (9) D. V. Behere, V. R. Marathe, and S. Mitra, *J. Am. Chem. Soc.*, **99**, 4149 (1977).
- (10) M. Sato, A. S. Rispin, and H. Kon, *Chem. Phys.*, **18**, 211 (1976).
- (11) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).
- (12) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Am. Chem. Soc.*, **89**, 1992 (1967).
- (13) K. S. Krishnan and S. Banerjee, *Phil. Trans. R. Soc. London, Ser. A*, **234**, 265 (1935).
- (14) D. J. Mackey, S. V. Evans, and R. L. Martin, *J. Chem. Soc., Dalton Trans.*, 1515 (1976).
- (15) K. Lonsdale and K. S. Krishnan, *Proc. R. Soc. London, Ser. A*, **516**, 597 (1936).
- (16) M. Gerloch and P. N. Queded, *J. Chem. Soc. A*, 2307 (1971).
- (17) K. S. Murray and R. M. Sheahan, *Aust. J. Chem.*, **28**, 2623 (1975).
- (18) The observation in Figure 1 that the $\mu_{\perp}^2 - \mu_{\parallel}^2$ vs. $1/T$ plot passes through the origin ensures that there is no g anisotropy in (TPP)FeCl.⁸ Hence the assumption $g_{\parallel} = g_{\perp} = 2$ seems reasonable.
- (19) V. R. Marathe and S. Mitra, *Chem. Phys. Lett.*, **19**, 140 (1973).
- (20) V. R. Marathe and S. Mitra, *Indian J. Pure Appl. Phys.*, **14**, 893 (1976).
- (21) D. H. Dolphin, J. R. Sams, T. B. Tsin, and K. L. Wong, *J. Am. Chem. Soc.*, **100**, 1711 (1978).

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Chloro- and Methyltris(hexamethyldisilyl)amido]zirconium(IV) and -hafnium(IV)

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In contrast to the large number of compounds with the (hexamethyldisilyl)amido ligand which have been described for the first-row transition series,^{1,2} only one is known for a second- or third-row transition element, $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Zr}(\text{NMe}_2)_2$.³

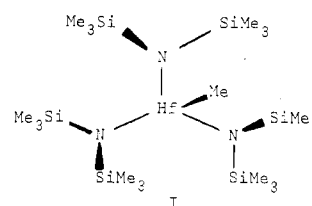
Reaction of lithium or sodium (hexamethyldisilyl)amide

with zirconium or hafnium tetrachloride yields the hydrocarbon-soluble $\text{ClM}[\text{N}(\text{SiMe}_3)_2]_3$. Physical properties are shown in Table I. The chloro amides are surprisingly substitutionally inert. They are air- and water-stable, and they are not hydrolyzed by dilute mineral acid. A suspension of the compounds in dilute nitric acid does not yield a precipitate of silver chloride upon addition of aqueous silver nitrate. The amides do not react with (trimethylsilyl)methyl lithium, lithium tetrahydroborate, nor with sodium (hexamethylsilyl)amide, the last in refluxing toluene.

Both amides do, however, react with methyl lithium, yielding $\text{MeM}[\text{N}(\text{SiMe}_3)_2]_3$. These alkyl amides are also stable toward molecular oxygen and water. They are recovered unchanged from methanol, tetrafluoroboric acid, or carbon dioxide. However, they are hydrolyzed by dilute hydrochloric acid, yielding $\text{ClM}[\text{N}(\text{SiMe}_3)_2]_3$.

The surprising lack of reactivity toward a variety of reagents is doubtless due to kinetic stability. The sterically voluminous silylamide ligands effectively prevent potential reactants from getting close enough to the metal atom for reaction to occur. Only the sterically small nucleophile methyl lithium is able to react with the chloro amides.

X-ray crystallographic studies on tris(silylamides), $\text{M}[\text{N}(\text{SiMe}_3)_2]_3$, show them to have a propeller conformation (D_3) in the solid state.⁴ The only tetravalent silylamide which has been examined crystallographically is $\text{BH}_4\text{Th}[\text{N}(\text{SiMe}_3)_2]_3$.⁵ The Me_3Si groups also exist in the propeller conformation in which all three $(\text{Me}_3\text{Si})_2\text{N}$ groups are twisted in the same sense with respect to a reference plane defined by the three nitrogen atoms bonded to the thorium atom. The compound is chiral and may exist in two enantiomeric forms which differ in their sense of twist.⁶ The low-temperature-limiting ^1H NMR spectrum should show two equal-area resonances due to the trimethylsilyl groups. However, only a single resonance due to this group was observed at -65°C for the tetrahydroborate or methylthorium derivatives. In contrast, the methylhafnium compound, $\text{MeHf}[\text{N}(\text{SiMe}_3)_2]_3$, shows two equal-area resonances at δ 0.66 and 0.56 at -40°C due to the trimethylsilyl groups which coalesce due to a single resonance at ca. -25°C . This is consistent with two enantiomeric forms, one form being shown in I. The failure to resolve the line shapes for the



thorium compounds is presumably related to the larger ionic radius of thorium relative to that of hafnium.

Experimental Section

Analyses were by the microanalytical laboratory of this department. The proton nuclear magnetic resonance spectra were recorded on a modified Bruker WH-1180 machine operating at 180 MHz. Proton-decoupled carbon nuclear magnetic resonance spectra were re-

Table I. Physical Properties of $\text{XM}[\text{N}(\text{SiMe}_3)_2]_3$

compd	mp, $^\circ\text{C}$	^1H NMR ^a		$^{13}\text{C}\{^1\text{H}\}$ NMR ^b		infrared ^c	
		Me-M	$(\text{Me}_3\text{Si})_2\text{N-M}$	Me-M	$(\text{Me}_3\text{Si})_2\text{N-M}$	M-Cl	M-N
$\text{ClZr}[\text{N}(\text{SiMe}_3)_2]_3$	182–183		0.67		6.15	348 s	408 s, 400 s
$\text{ClHf}[\text{N}(\text{SiMe}_3)_2]_3$	180–181		0.62		6.38	338 s	404 s, 388 m
$\text{MeZr}[\text{N}(\text{SiMe}_3)_2]_3$	176–177	1.18	0.62	31.4	6.16		404 s, 390 s
$\text{MeHf}[\text{N}(\text{SiMe}_3)_2]_3$	188–190	1.01	0.61	65.4	6.32		400 s, 395 m

^a Benzene solution relative to Me_4Si (δ units) at 37°C . ^b Benzene solution relative to Me_4Si (δ units) at 37°C . ^c Nujol mull.

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). Methyl lithium (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). Methyl lithium (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.

References and Notes

- (1) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273.
- (2) Harris, D. H.; Lappert, M. F. *J. Organomet. Chem. Libr.* **1976**, *2*, 13.
- (3) Chandra, G.; Lappert, M. F. *J. Chem. Soc. A* **1968**, 1940.
- (4) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1.
- (5) Turner, H. W.; Andersen, R. A.; Templeton, D. H.; Zalkin, A., submitted for publication in *Inorg. Chem.*
- (6) Cf.: Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 2165.

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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 measure-

ments (12–300 K) with a Faraday balance setup previously described,^{9,10} the electronic spectrum ($8\text{--}25\text{ cm}^{-1} \times 10^3$) by using a Nujol mull with a Beckman DK-2A spectrometer, and the infrared spectra ($0.66\text{--}4.0\text{ cm}^{-1} \times 10^3$) 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 $14.3\text{ cm}^{-1} \times 10^3$ 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 observed⁸ 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 \circ and \times 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) trimer¹² and yield the parameters $g = 2.00$, $2J_{12} = -58\text{ cm}^{-1}$, and $2J_{22'} = -52\text{ cm}^{-1}$, 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