Crystals of $[As(C_6H_5)_4]_2[B_{11}H_{11}AlCH_3]$ were obtained by slow diffusion of diethyl ether into a concentrated acetonitrile solution. The molecular structure was determined from single-crystal X-ray diffraction data.[4] The structure of $[B_{11}H_{11}AlCH_3]^{2-}$ is that of an icosahedron (Figure 1). All hydrogen atoms bonded to boron atoms were located and refined. The boron–hydrogen distances range from 1.07 (3) to 1.16 (3) Å. Boron–boron distances in the plane of atoms B2–B6 range from 1.815 (5) to 1.856 (5) Å while the remaining boron–boron distances range from 1.760 (5) to 1.788 (5) Å. All the boron–boron distances and boron–hydrogen distances are within the normal range for boron hydrides.[5] Boron–aluminum distances range from 2.131 (4) to 2.140 (4) Å with the boron–aluminum–carbon angles ranging from 131.5 (2) to 134.7 (2)°. The aluminum–carbon distance is 1.942 (4) Å. The aluminum–carbon vector is essentially perpendicular to the plane formed by boron atoms B2–B6, tilting just 2° from perpendicularity.

$Na_2[B_{11}H_{13}]$ was prepared in a "one-pot" procedure from B_5H_9. By the literature procedure,[6] $Na[B_{11}H_{14}]$ (10.53 mmol) was prepared from NaH (287.1 mg, 88% activity, 10.53 mmol of active NaH) and B_5H_9 (2.53 mL, 0 °C, 26.45 mmol) in glyme. In order to ensure complete removal of excess B_5H_9, volatiles were removed from $Na[B_{11}H_{14}]$ for 12 h, under dynamic vacuum, and a yellow "gum" resulted. $Na_2B_{11}H_{13}$ was then prepared from this "gum" by using a modification of the literature preparation of the $[B_{11}H_{13}]^{2-}$ anion.[7] NaH was employed as the deprotonating agent, and glyme was used as the solvent. The product $Na_2[B_{11}H_{13}]$ was obtained in 74% yield based upon the amount of hydride employed in the preparation of $Na[B_{11}H_{14}]$.

The $[B_{11}H_{11}AlCH_3]^{2-}$ dianion is prepared from $Na_2[B_{11}H_{13}]$ and $Al(CH_3)_3$. In the glovebox, a reaction bulb, with a glass tube extending from its bottom and a Kontes stopcock attached to its top, was charged with a magnetic stirbar and $Na_2B_{11}H_{13}$ (253.0 mg, 1.42 mmol). The vessel was evacuated, and $Al(CH_3)_3$ (~3 mL) was condensed onto the $Na_2B_{11}H_{13}$ at −196 °C, followed by glyme (1.52 mmol). [*Caution*! Neat $Al(CH_3)_3$ is spontaneously flammable when in contact with air! Proper precautions must be taken.] The vessel was warmed to room temperature followed by slow warming of the slurry, with stirring, to 105–110 °C. This temperature was maintained for a period of 4 days. Methane gas formed during the reaction was measured (96% of theory). All volatiles were pumped from the reaction vessel, which was then transferred to the glovebox, and the solid reaction residue was rinsed with toluene (~20 mL) into another flask. This flask was attached to an extractor, and the solid was washed three times with toluene to remove any remaining $Al(CH_3)_3$ and glyme. Volatiles were removed, and the vessel taken into the glovebox, where the crude $Na_2[B_{11}H_{11}AlCH_3]$ was scraped from the frit (yield 294.3 mg, 95%; 4% of $Na_2[B_{11}H_{11}]$ formed by the thermal decomposition of $Na_2[B_{11}H_{13}]$ was present as an impurity).

The $N(C_2H_5)_4^+$ and $As(C_6H_5)_4^+$ salts of the $[B_{11}H_{11}AlCH_3]^{2-}$ dianion were obtained by metathesis reactions between tetraethylammonium or tetraphenylarsonium chloride and $Na_2[B_{11}H_{11}AlCH_3]$ in CH_3CN in 68% and 66% yields, respectively. Anal. Calcd for $[As(C_6H_5)_4]_2[B_{11}H_{11}AlCH_3]$: Al, 2.87; As, 15.96; B, 12.67; C, 62.69; H, 5.81. Found: Al, 2.79; As, 16.10; B, 12.45; C, 62.41; H, 5.63.

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Supplementary Material Available: Listings of selected bond distances, selected bond angles, positional parameters, and anisotropic thermal parameters (20 pages); a listing of calculated and observed structure factor amplitudes (42 pages). Ordering information is given on any current masthead page.

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(4) Crystal data for $[As(C_6H_5)_4]_2[B_{11}H_{11}AlCH_3]$: space group $P2_1/n$, $a = 10.2764$ (46) Å, $b = 21.7110$ (75) Å, $c = 21.9454$ (41) Å, $\beta = 98.68$ (2)°, $v = 4840.1$, ρ(calcd) = 1.290 g cm^{-3}, $M_r = 938.76$, $Z = 4$, μ(Mo Kα) = 1.5 cm^{-1}. Diffraction data were collected at −50 °C with an Enraf-Nonius CAD4 diffractometer. Crystallographic computations were carried out on a PDP 11/44 computer using SDP (Structure Determination Package). The structure was solved by a combination of the direct method MULTAN 11/82 and difference Fourier syntheses. Full-matrix least-squares refinements were employed. $R_F = 0.028$ and $R_{wF} = 0.034$ (615 variables refined) for 4186 reflections $[I \geq 3.0\sigma(I)]$ of 6290 independent reflections collected over the range $4° \leq 2\theta \leq 45°$.

(5) Lipscomb, W. N. *Boron Hydrides*; W. A. Benjamin: New York, 1963; Chapter 1.

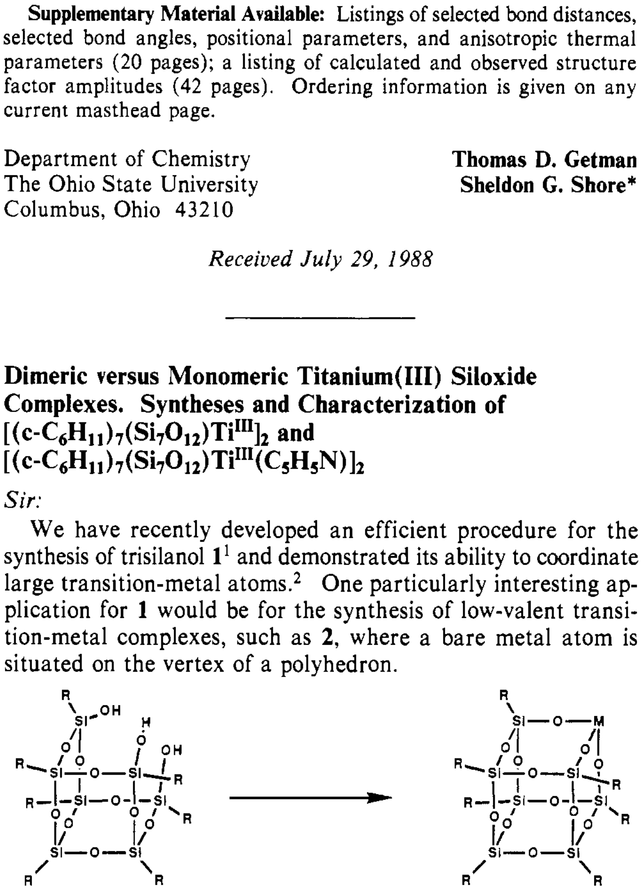
(6) Hosmane, N. S.; Wermer, J. R.; Hong, Z.; Getman, T. D.; Shore, S. G. *Inorg. Chem.* **1987**, *26*, 3638.

(7) Aftandilian, V. D.; Miller, H. C.; Parshall, G. W.; Muetterties, E. L. *Inorg. Chem.* **1962**, *1*, 734.

Dimeric versus Monomeric Titanium(III) Siloxide Complexes. Syntheses and Characterization of $[(c\text{-}C_6H_{11})_7(Si_7O_{12})Ti^{III}]_2$ and $[(c\text{-}C_6H_{11})_7(Si_7O_{12})Ti^{III}(C_5H_5N)]_2$

Sir:

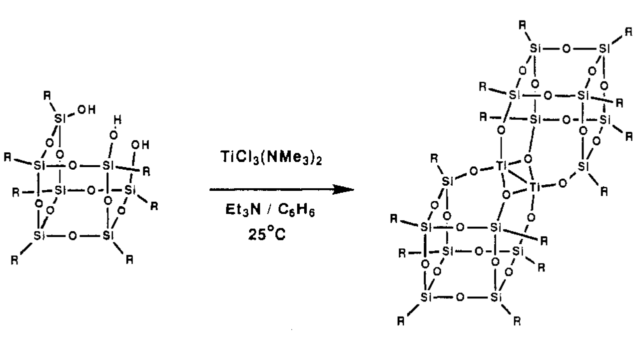
We have recently developed an efficient procedure for the synthesis of trisilanol **1**[1] and demonstrated its ability to coordinate large transition-metal atoms.[2] One particularly interesting application for **1** would be for the synthesis of low-valent transition-metal complexes, such as **2**, where a bare metal atom is situated on the vertex of a polyhedron.



1 **2**

This paper reports our efforts to synthesize Ti(III) complexes derived from **1**. Despite the unique steric and geometric requirements of **1** as a ligand, which present the best opportunity yet for the synthesis of pyramidalized ML_3 complexes, mononuclear complexes are not observed. Instead, siloxy-bridged dinuclear complexes are the thermodynamically preferred products.

The room-temperature reaction of **1** with $Ti[N(SiMe_3)_2]_3$[4] or $TiCl_3(NMe_3)_2$[4] in C_6H_6/Et_3N affords high yields of blue dinuclear complex **3**.[5]



1 **3**

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(1) Feher, F. J.; Newman, D. A.; Walzer, J. F.; manuscript in preparation.

(2) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3850–2.

(3) (a) Horvath, B.; Strutz, J.; Geyer-Lippmann, J.; Horvath, E. G. *Z. Anorg. Allg. Chem.* **1981**, *483*, 205–18 and references cited therein. (b) Nishimura, M.; Asakura, K.; Iwasawa, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1660–1.

(4) Bradley, D. C.; Copperthwaite, R. G. *Inorg. Synth.* **1978**, *18*, 112–20.

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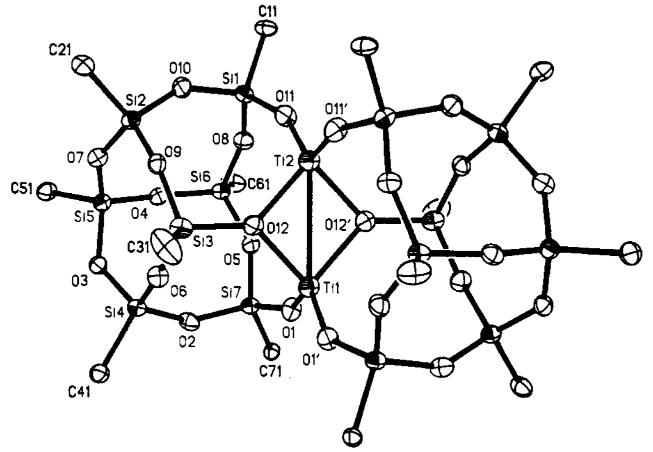


Figure 1. Perspective ORTEP plot of **3** showing 20% thermal ellipsoids. For clarity only the carbon atoms attached to silicon have been drawn. Selected interatomic distances (Å) and angles (deg) are as follows: Ti1–Ti2, 2.917 (6); Ti1–O12, 2.000 (11); Ti1–O1, 1.820 (10); Ti2–O11, 1.817 (10); Ti2–O12, 1.979 (11); Si1–O11, 1.615 (10); Si3–O12, 1.649 (12); Si7–O1, 1.616 (10); O12–Ti1–O12′, 85.1 (6); O12–Ti2–O12′, 86.3 (7); O1–Ti1–O1′, 124.1 (7); O1–Ti1–O12, 111.1 (4); O1–Ti1–Ti2, 118.0 (4); O11–Ti2–O11′, 123.1 (7); O11–Ti2–O12, 107.5 (4); O11–Ti2–Ti1, 118.5 (4); Ti1–O1–Si7, 147.9 (7); Ti1–O12–Ti2, 94.3 (5); Ti1–O12–Si3, 133.5 (7); Ti2–O11–Si1, 156.6 (8); Ti2–O12–Si3, 131.6 (6).

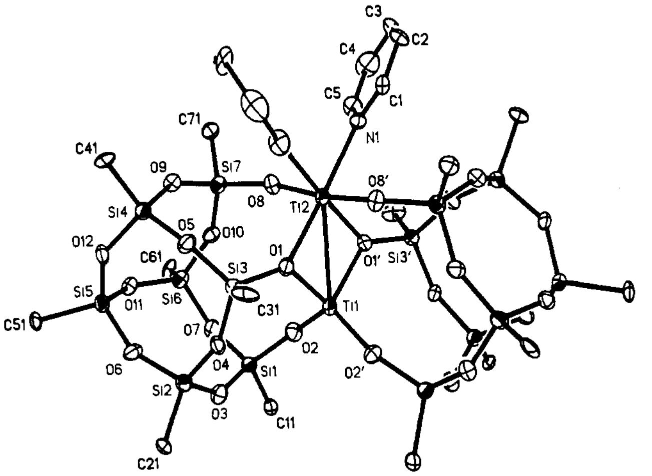
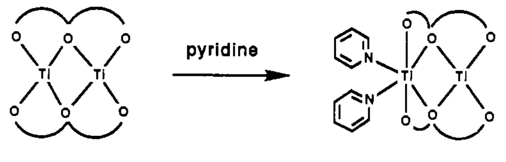


Figure 2. Perspective ORTEP plot of **4** showing 20% thermal ellipsoids. For clarity only the carbon atoms attached to silicon have been drawn. Selected interatomic distances (Å) and angles (deg) are as follows: Ti1–Ti2, 2.901 (4); Ti1–O1, 1.990 (7); Ti1–O2, 1.829 (9); Ti2–N1, 2.247 (9); Ti2–O1, 2.070 (7); Ti2–O8, 1.916 (9); Si1–O2, 1.615 (9); Si3–O1, 1.631 (7); Si7–O8, 1.600 (9); O1–Ti1–O1′, 91.0 (4); O1–Ti2–O1′, 86.6 (4); O1–Ti1–O2, 113.2 (3); O2–Ti1–O2′, 115.5 (5); O1–Ti1–Ti2, 45.5 (2); O1–Ti2–O8, 92.5 (3); O1–Ti2–N1, 176.7 (3); O1–Ti2–Ti1, 43.3 (2); O8–Ti2–N1, 87.3 (4); O8–Ti2–O8′, 172.8 (5); O8–Ti2–Ti1, 93.6 (2); N1–Ti2–N1′, 79.9 (5); Ti1–O1–Si3, 128.8 (4); Ti2–O1–Si3, 139.0 (4); Ti1–O2–Si1, 151.2 (5); Ti2–O8–Si7, 156.3 (4).

Complex **3** is extremely air-sensitive, is insoluble in most solvents with which is does not react, and exhibits weak paramagnetism (vide infra). Unambiguous structural characterization was therefore accomplished by single-crystal X-ray crystallography.[6] An ORTEP diagram of **3** is shown in Figure 1.

The two titanium atoms in **3** are separated by 2.917 (6) Å and are situated on a crystallographic 2-fold rotational axis that relates the two chelating ligands. The coordination geometries about both titanium atoms are approximately equally distorted tetrahedrons, although the bridging siloxy group is slightly closer to one titanium atom (2.000 (11) vs 1.979 (11) Å). The distances and angles around the silicon and oxygen atoms of the ligand framework differ significantly from those of the free ligand[1] but are within the typical ranges observed for cyclic and polyhedral siloxanes and silicates.[2,7]

Despite indications of steric congestion around the central Ti_2O_2 core as suggested by both the ORTEP diagrams and molecular models, the titanium atoms in **3** are capable of coordinating additional ligands. For example, the reaction of **3** with pyridine affords dimer **4**, in virtually quantitative yield.[8]



3

4

This interesting molecule is strongly pleochroic: depending on the viewing angle, light transmitted through the crystal appears either very pale blue or varying shades of burgundy. Since it is also weakly paramagnetic (vide infra), characterization was accomplished by a single-crystal X-ray diffraction study.[6] An ORTEP diagram of **4** is shown in Figure 2.

The two titanium atoms in **4** are separated by 2.901 (4) Å and are situated on a crystallographic 2-fold rotational axis that relates the two pairs of trisilanol and pyridine ligands. The coordination geometry around Ti(1) is distorted tetrahedral, while the geometry around Ti(2) is approximately octahedral. Predictably, the oxygen atoms bridging the two titanium atoms are somewhat closer (0.08 Å) to Ti(1), the metal center possessing the lower coordination number. As in **3**, the distances and angles around the ligand framework very considerably but are within the expected ranges.[2,7] Trisilanol **1** therefore appears to be quite flexible and capable of accommodating many different coordination geometries.

Although the intermetallic distances in both **3** (2.917 Å) and **4** (2.901 Å) are comparable to the Ti–Ti distance in α-Ti metal (2.8956 Å),[9] both compounds are weakly paramagnetic and exhibit visible absorbances in the range characteristic of isolated Ti^{3+} ions.[5,8] This behavior is usually observed for strongly antiferromagnetically coupled bimetallic complexes, where the metal centers are too far apart to form stable bonds.[10] The close

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(5) In a typical experiment performed in a glovebox under nitrogen, solid $TiCl_3(NMe_3)_2$ (122 mg, 0.448 mM) was added to solution of trisilanol **1** (434 mg, 0.446 mM) in 15 mL of benzene containing 10% (v/v) Et_3N. After the mixture was stirred for 30 min at 25 °C, the solvent was removed in vacuo (30 °C, 10^{-4} Torr). The blue residue was extracted with pentane, and the solution was filtered and allowed to stand for 2 days at −30 °C. Large dark blue crystals of **3** precipitated (320 mg, 71% based on **1**). Anal. Calcd (found) for $C_{84}H_{154}O_{24}Si_{14}Ti_2$: C, 49.53 (49.03); H, 7.26 (7.74). ^1H NMR (500.11 MHz, C_6D_6, 25 °C): δ 2.409 (m, 9 H), 2.319 (m, 10 H), 1.887 (m, 51 H), 1.360 (m, 70 H), 1.046 (m, 7 H), 0.859 (m, 7 H). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 25 °C): δ 27–29 (complex cluster, CH_2), 24.350, 24.177, 23.975, 23.833, 23.532 (s, 2:2:1:1; CH). UV–vis (C_6H_6, 25 °C): λ_{max} 759 nm (ϵ_{max} 145). Mp: 272 °C dec.

(6) See the supplementary material for details regarding the X-ray crystal structures of **3** and **4**.

(7) (a) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984; pp 982–1043. (b) Liebau, F. *Structural Chemistry of Silicates*; Springer-Verlag: New York, 1985.

(8) In a typical experiment performed in a glovebox under nitrogen, **3** (200 mg, 0.098 mM) in a small test tube was dissolved in 8 mL of benzene containing a couple of drops of Et_3N. This tube was lowered into a larger test tube containing 10 mL of 20% (v/v) pyridine in benzene. After the large tube was stoppered and allowed to stand for 3–5 days, large crystals of **4** precipitated. Anal. Calcd (found after benzene removal in vacuo) for $C_{94}H_{164}N_2O_{24}Si_{14}Ti_2$: C, 51.44 (51.33); H, 7.53 (7.87). ^1H NMR (500.11 MHz, C_6D_6, 25 °C): δ 8.977 (m, 2 H), 6.990 (m, 4 H), 6.870 (m, 4 H), 2.137 (m, 21 H), 1.620 (m, 61 H), 1.260 (m, 55 H), 0.901 (m, 3 H), 0.865 (m, 14 H). $^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6, 25 °C): δ 26.6–29.0 (complex cluster), 25.497, 24.631, 24.547, 23.895, 23.732 (s, approximately 2:1:1:2:1; CH). UV–vis (C_6H_6, 25 °C); λ_{max}, nm (ϵ_{max}): 280 (2150), 486 (2530) 708 (219). Mp: 217 °C dec.

(9) Weast, R. C. *Handbook of Chemistry and Physics*, 57th ed.; CRC: Cleveland, OH, 1976; p F-216.

intermetallic distances in both **3** and **4** are, however, inconsistent with such an explanation; therefore, the magnetic properties of these dimers were examined in detail to determine the nature of the metal-metal interaction.

Molar susceptibilities for **3** and **4** were measured between 6 and 300 K on a SQUID susceptometer. Above 100 K the observed magnetism is predominantly due to temperature-independent paramagnetism (TIP), resulting from orbital mixing of the spin-singlet ground states with low-lying (paramagnetic) excited states.[11] Below approximately 50 K the sample magnetization is dominated by traces (<0.25%) of paramagnetic impurities. The experimental data can be accurately simulated by assuming 99.78% purity and a TIP of 8.8×10^{-5} cgsu/mol of Ti for **3** and 99.75% purity and a TIP of 1.68×10^{-4} cgsu/mol of Ti for **4**.[12] EPR spectroscopy establishes that both compounds have normal metal-metal bonds, rather than spin-coupled diradical ground states: except for a small impurity peak at $g = 1.972$, characteristic of magnetically dilute Ti^{3+} ions,[13] the EPR spectra of both **3** and **4** are featureless at both 298 and 77 K.[14]

The mechanism by which **3** is formed, and whether or not it involves the intermediacy of monomeric complexes such as **2** (M = Ti), is not yet known. What is clear, however, is that the formation of dimeric complexes, such as **3**, is greatly preferred over pyramidalized monomers, such as **2**, for the trisilanol ligand used here. The use of smaller transition-metal ions (e.g., V(III), Cr(III), or Fe(III)), which can adopt less pyramidalized coordination geometries with **1**, should favor the formation of **2** and is currently being explored.

Acknowledgment. We thank Professor Christopher Reed (University of Southern California) for his assistance with the magnetic studies and Professor T. Don Tilley (University of California, San Diego) for providing access to an EPR spectrometer. These studies were supported by the National Science Foundation (Grant CHE-8703016) and an NSF-Presidential Young Investigator Award (CHE-8657262). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Funds for the purchase of the X-ray diffraction equipment were made available from NSF Grant CHE-85-14495.

Supplementary Material Available: An index for the supplementary material, X-ray crystal data for **3** and **4** including experimental procedures, tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles and magnetic data for **1**, **3**, and **4** including experimental procedures, tables of SQUID data, a detailed description of the simulation procedure, and plots of experimental and simulated data (33 pages); listings of calculated and observed structure factors (36 pages). Ordering information is given on any current masthead page.

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(10) (a) Fieselman, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2078-84. (b) Fieselman, B. F.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2074-7. (c) Jungst, R.; Setkutowski, D.; Davis, J.; Luly, M.; Stucky, G. D. *Inorg. Chem.* **1977**, *16*, 1645-55. (d) VanderWal, H. R.; Overzet, F.; VanOven, H. O.; DeBoer, J. L.; Liefde Meijer, H. F.; Jellinek, F. *J. Organomet. Chem.* **1975**, *92*, 329-40. (e) Floriani, C.; Fachinetti, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1954-7. (f) Coutts, R. S. P.; Martin, R. L.; Wailes, P. C. *Aust. J. Chem.* **1973**, *26*, 2101-4. (g) Coutts, R. S. P.; Martin, R. L.; Wailes, P. C. *Aust. J. Chem.* **1972**, *25*, 1401-9.

(11) Carlin, R. L.; van Duyneveldt, A. J. *Magnetic Properties of Transition Metal Compounds*; Springer: New York, 1977.

(12) See the supplementary material for full details regarding the simulation procedure.

(13) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance: Elementary Theory and Practical Applications*; McGraw-Hill: New York, 1972; p 318.

(14) Cf.: Coutts, R. S. P.; Martin, R. L.; Wailes, P. C. *Aust. J. Chem.* **1973**, *26*, 941-50.

Articles

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Thermodynamics of Aqueous EDTA Systems: Apparent and Partial Molar Heat Capacities and Volumes of Aqueous Cadmium, Mercury, and Lead EDTA Complexes

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Apparent molar heat capacities and volumes have been measured for $Na_2CdEDTA$(aq), $Na_2HgEDTA$(aq), and $Na_2PbEDTA$(aq). Standard-state partial molar heat capacities $\bar{C}_{p,2}^\circ$ and volumes $\bar{V}_2^\circ$ have been calculated along with the partial molar properties at 0.1 *m* ionic strength that are needed for various thermodynamic calculations. Equilibrium constants for the exchange reactions of Cd^{2+}(aq), Hg^{2+}(aq), and Pb^{2+}(aq) with Ca^{2+}(aq) have been calculated to 250 °C.

Introduction

As part of our research on the thermodynamics of reactions involving aqueous complexes of EDTA (ethylenediaminetetraacetate), we have measured heat capacities and densities of aqueous solutions of $Na_2CdEDTA$, $Na_2HgEDTA$, and $Na_2PbEDTA$.

Aqueous solutions of EDTA are used as sequestering agents in industrial applications that include cleaning boilers, softening boiler and process water, treating oil wells to remove scale minerals, and decontaminating nuclear reactor systems. There are also medicinal uses of EDTA that include treating Alzheimer's disease by complexation of aluminum,[1] treating ulcers,[2] treating periarthritis and similar ailments,[3] and using as agents for increased contrast in NMR body imaging.[4] Specific to the salts studied in this paper is the use of EDTA to remove cadmium, mercury, and lead[5] from the body. EDTA treatment of metal poisoning may introduce risks,[6] but its wide versatility in the complexation

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(1) Yaeger, L. L. *Rejuvenation* **1983**, *11*, 76.

(2) Puscas, I.; Voicu, L.; Breazu, D.; Pop, I.; Ciupe, I.; Terec, L.; Butan, M. R.; Orban, I. Rom. Patent 65968, 1980; Rom. Patent Appl. 90346, 1977.

(3) Guazzotti, L.; PCT Int. Patent Appl. 8601719, 1986; Patent Appl. 85/EP467, 1985.

(4) Runge, V. M.; Foster, M. A.; Clanton, J. A.; Jones, M. M.; Lukehart, C. M.; Hutchison, J. M. S.; Mallard, J. R.; Smith, F. W.; Partain, C. L.; James, A. E., Jr. *Radiology (Easton, Pa.)* **1984**, *152*, 123.

(5) Boscolo, P.; Porcelli, G.; Minini, E.; Finelli, V. N. *Med. Lav.* **1983**, *74*, 370.