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Communications

Vanadium(III) Phenolate Complexes. Synthesis, Structure, and Properties of $[\{V(OC_6H_5)_6\}\{Li(DME)\}_3]$ and Two Species Containing the $[V(DIPP)_4]^-$ Anion (DME = 1,2-Dimethoxyethane, DIPP = 2,6-Diisopropylphenolate)

Sir:

In general terms, the coordination chemistry of transition-element aryloxides has enjoyed relatively little attention compared to that of alkoxides.[1] In recent years, however, numerous reports of the synthesis and reaction chemistry of early-transition-metal aryloxide complexes have appeared, particularly for elements Ti[2], Nb,[3] Mo,[4] Ta,[5] and W.[6] In connection with our interest in exploring the coordination chemistry and reactivity of lower valent vanadium,[7] we have initiated a study of the phenolate chemistry of this element in the +2 and +3 oxidation states. One reason for investigating this area is that vanadium and its neighbor in the periodic table, titanium, in their lower oxidation levels, with anionic oxygen donors, display interesting reactivity behavior, such as the capability of dinitrogen fixation.[2e,8] Development of low-valent vanadium chemistry is also desirable from the standpoint of attempting to understand further its biological role in organisms such as tunicates.[9] Herein are reported the first examples of structurally characterized homoleptic four- and six-coordinate vanadium(III) phenolate species, $[\{V(OC_6H_5)_6\}\{Li(DME)\}_3]$ (**1**), $[\{V(DIPP)_4\}\{Li(THF)\}]$ (**2**), and [Li(12-crown-4)]$[V(DIPP)_4]$ (**3**).[10,11]

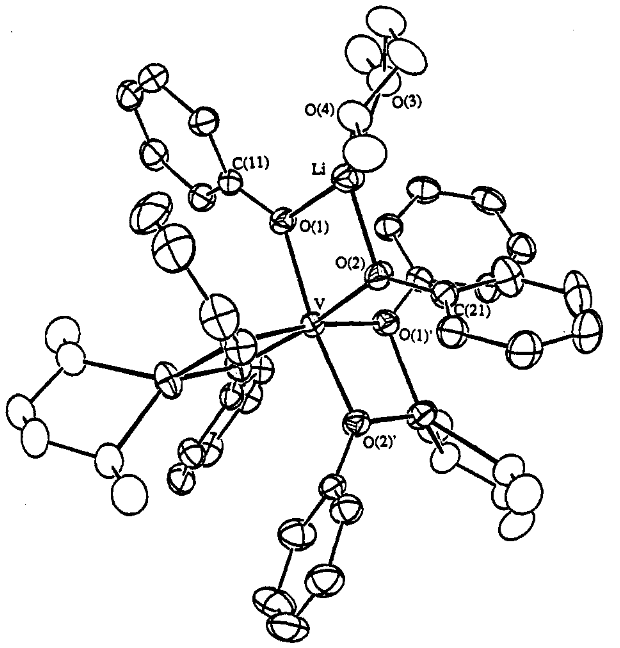

Figure 1. Structure of $[\{V(OC_6H_5)_6\}\{Li(DME)\}_3]$ (**1**) showing the 30% probability thermal ellipsoids and atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: V–O(1), 2.023 (1); V–O(2), 2.007 (1); Li–O(1), 1.902 (3); Li–O(2), 1.878 (3); Li–O(3), 2.054 (3); Li–O(4), 2.038 (3); O(1)–C(11), 1.334 (2); O(2)–C(21), 1.338 (2); O(1)–V–O(1'), 96.46 (4); O(1)–V–O(2), 79.72 (4); O(1)–V–O(2'), 91.29 (4); O(1)–V–O(2''), 171.73 (4); O(2)–V–O(2'), 92.97 (4); V–O(1)–C(11), 141.04 (9); V–O(2)–C(21), 133.58 (9); O(1)–Li–O(2), 86.2 (1); O(3)–Li–O(4), 80.9 (1); O(1)–Li–O(3), 110.4 (1); O(1)–Li–O(4), 142.9 (2); O(2)–Li–O(3), 141.1 (2); O(2)–Li–O(4), 107.3 (1); V–O(1)–Li, 96.38 (9); V–O(2)–Li, 97.68 (9).

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(1) Malhotra, K. C.; Martin, R. L. *J. Organomet. Chem.* **1982**, *239*, 159–187.

(2) (a) Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720–4722. (b) Durfee, L. D.; Latesky, S. L.; Rothwell, I. P.; Huffman, J. C.; Folting, K. *Inorg. Chem.* **1985**, *24*, 4569–4573. (c) Svetich, G. W.; Voge, A. A. *Acta Crystallogr.* **1972**, *B28*, 1760–1767. (d) Watenpaugh, K.; Caughlan, C. N. *Inorg. Chem.* **1966**, *5*, 1782–1786. (e) Flamini, A.; Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 454–459.

(3) (a) Coffindaffer, T. W.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1519–1522. (b) Chestnut, R. W.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1988**, *27*, 752–754.

(4) (a) Walborsky, E. C.; Wigley, D. E.; Roland, E.; Dewan, J. C.; Schrock, R. R. *Inorg. Chem.* **1987**, *26*, 1615–1621. (b) Coffindaffer, T. W.; Niccolai, G. P.; Powell, D.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 3572–3583. (c) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1987**, *109*, 5840–5842.

(5) (a) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 2575–2578. (b) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *Polyhedron* **1987**, *6*, 1765–1774. (c) Chamberlain, L. R.; Kerschner, J. L.; Rothwell, A. P.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6471–6478. (d) Chamberlain, L. R.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Dalton Trans.* **1987**, 155–162. (e) Fanwick, P. E.; Oglivy, A. E.; Rothwell, I. P. *Organometallics* **1987**, *6*, 73–80. (f) Wang, R.; Folting, K.; Huffman, J. C.; Chamberlain, L. R.; Rothwell, I. P. *Inorg. Chim. Acta* **1986**, *120*, 81–83.

(6) (a) Davies, J. I.; Gibson, J. F.; Skapski, A. C.; Wilkinson, G.; Wong, W.-K. *Polyhedron* **1982**, *1*, 641–646. (b) Handy, L. B.; Fair, C. K. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 496–500. (c) Listemann, M. L.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 7207–7208.

(7) See for example: Randall, C. R.; Armstrong, W. H. *J. Chem. Soc., Chem. Commun.* **1988**, 986–987.

(8) (a) Van Tamelen, E. F. *Acc. Chem. Res.* **1970**, *3*, 361–367. (b) Shilov, A. E. In *Energy Resources Through Photochemistry and Catalysis*; Grätzel, M.; Ed., Academic: New York, 1983; pp 535–558.

(9) (a) Boas, L. V.; Pessoa, J. C. In *Comprehensive Coordination Chemistry*, Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 3, pp 486–487 and references therein. (b) Frank, P.; Carlson, R. M. K.; Hodgson, K. O. *Inorg. Chem.* **1988**, *27*, 118–122. (c) Brand, S. G.; Hawkins, C. J.; Parry, D. L. *Inorg. Chem.* **1987**, *26*, 627–638.

(10) Abbreviations used: DME, 1,2-dimethoxyethane; DIPP, 2,6-diisopropylphenolate; 12-crown-4, 1,4,7,10-tetraoxacyclododecane; DMP, 2,6-dimethylphenolate; salophen, *N,N'-o*-phenylenebis(salicyladeneaminato) dianion; EPR, electron paramagnetic resonance.

(11) During the final stages of this work, mixed-ligand mononuclear and dinuclear V(III) species were reported: Gambarotta, S.; van Bolhuis, F.; Chiang, M. Y. *Inorg. Chem.* **1987**, *26*, 4303–4305.

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Synthesis of four-coordinate and six-coordinate vanadium(III) phenolate complexes was accomplished by using either vanadium(II) or vanadium(III) starting materials. Initially, compound **1** was prepared by allowing a slurry of 0.1 g (0.38 mmol) of "$VCl_2·2THF$",[12] obtained by $LiAlH_4$ reduction of $VCl_3·3THF$, to react with 0.39 g (2.27 mmol) of LiOPh·THF with stirring in 40 mL of DME for 30 min. Isolation of pure, X-ray quality green crystals[14,15] of **1** (50% yield) was achieved by diffusing hexanes into the reaction mixture after concentration to 15 mL. Subsequently, the six-coordinate species was synthesized in a straightforward manner directly from $VCl_3·3THF$ and LiOPh in DME.[16] In order to decrease the number of phenolate ligands at the vanadium center, with the goal being to allow for coordination of small molecules, a more sterically hindered ligand was examined, 2,6-diisopropylphenolate (DIPP). In this case, 1.00 g (5.43 mmol) of LiDIPP was added to a slurry of 0.50 g (1.34 mmol) of $VCl_3·3THF$ in 20 mL of hexanes. After the reaction mixture was stirred for 12 h, the green hexanes solution was filtered, concentrated, and cooled to −20 °C. This procedure afforded 0.96 g of **2**·THF (79% yield) as fine green needles.[17] X-ray quality crystals of **2**[18] were obtained from a supersaturated hexanes solution at room temperature. Precipitation of $V(DIPP)_4^-$ as the Li(12-crown-4)$^+$ salt (**3**) was achieved by addition of 12-crown-4 to a hexanes solution of **2**. Crystals of **3** suitable for X-ray diffraction studies[19] were isolated from THF/cyclohexane. With the synthetic procedures described above, $[V(DMP)_4]^-$ was also obtained (DMP = 2,6-dimethylphenolate). As was the case for **1**, the four-coordinate complexes were also obtained from V(II) starting materials. For example, **3** can be isolated in approximately 40% yield as a deep blue solid by allowing $[V_2Cl_3(THF)_6]^+$ salts[20] to react with Li(DIPP) in hexanes, followed by filtration and addition of 12-crown-4. Attempts to identify the oxidizing agent in the aforementioned reactions that employ V(II) are under way. While disproportionation has been observed in other V(II)–phenolate systems,[11] there is no evidence for this process in the synthesis of **1** from "$VCl_2·2THF$", for example.

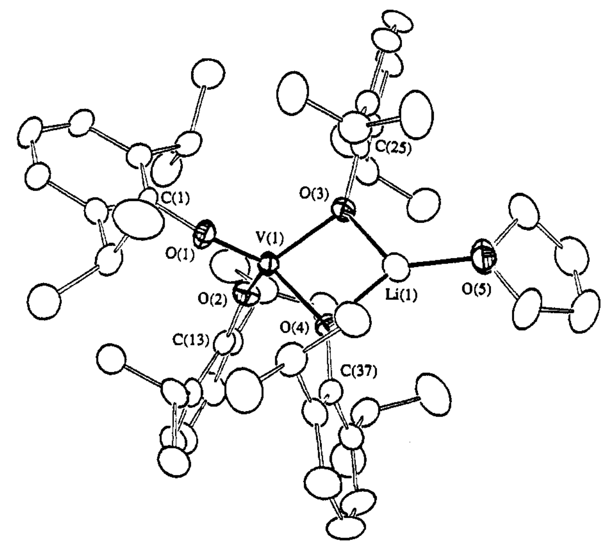

Figure 2. ORTEP drawing of one of the two crystallographically distinct vanadium complexes in the structure of $[\{V(DIPP)_4\}\{Li(THF)\}]$ (**2**) showing 50% probability thermal ellipsoids and atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: V(1)–O(1), 1.839 (2); V(1)–O(2), 1.820 (2); V(1)–O(3), 1.931 (2); V(1)–O(4), 1.956 (3); O_{Ar}–C, 1.353 (4)–1.374 (5); Li(1)–O(3), 1.846 (7); Li(1)–O(4), 1.841 (7); Li(1)–O(5), 1.822 (7); O(1)–V(1)–O(2), 118.5 (1); O(1)–V(1)–O(3), 113.8 (1); O(1)–V(1)–O(4), 110.5 (1); O(2)–V(1)–O(3), 114.6 (1); O(2)–V(1)–O(4), 112.0 (1); O(3)–V(1)–O(4), 81.6 (1); O(3)–Li(1)–O(4), 87.0 (3); O(3)–Li–O(5), 127.4 (4); O(4)–Li–O(5), 145.3 (4); V(1)–O(3)–Li(1), 96.0 (2); V(1)–O(4)–Li(1), 95.3 (2); V(1)–O(1)–C(1), 138.3 (2); V(1)–O(2)–C(13), 146.3 (2); V(1)–O(3)–C(25), 139.0 (3); V(1)–O(4)–C(37), 140.1 (2).

The crystal structure of **1** is shown in Figure 1. This compound joins $[W(OC_6H_5)_6]^-$[6a] and $[Nb(O\text{-}3,5\text{-}Me_2C_6H_3)_6]^-$[3a] as rare examples of structurally characterized, homoleptic six-coordinate phenolate complexes. The vanadium atom lies on a crystallographic 3-fold axis. Distortion from octahedral symmetry is induced by the presence of three bridging lithium atoms between pairs of phenolate ligands. For example, the bite angle O(1)–V–O(2) is 79.7°, somewhat smaller than the bite angle of catecholate in $V(cat)_3^{3-}$ (average 81.3°).[21] The V–O bond distances are about 0.1 Å longer than those found in the V(III) Schiff base complex [V(salophen)(Cl)(THF)],[22] presumably owing to the bridging interaction to Li$^+$. A lengthening of this magnitude due to Li$^+$ coordination is also observed within the structure of $[\{W(OC_6H_5)_6\}\{Li(THF)_2\}]$.[6a]

Compounds **2** and **3** are only the second and third examples of structurally characterized mononuclear four-coordinate V(III) species to our knowledge.[23] The distorted tetrahedral structure of **2** is depicted in Figure 2. There are two independent complexes in the asymmetric unit of the crystal lattice, one of which is shown. The presence of the lithium atom restricts one of the O–V–O

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(12) Handlíř, K.; Holečk, J.; Klikorka, J. *Z. Chem.* **1979**, *19*, 265–266.

(13) Manzer, S. E. *Inorg. Synth.* **1982**, *21*, 135–140.

(14) X-ray analysis of **1**: The complex $[\{V(OC_6H_5)_6\}\{Li(DME)\}_3]$ crystallizes in the rhombohedral system, space group $R\bar{3}$, with $a = 13.524$ (2) Å, $\alpha = 96.71$ (1)°, $V = 2418.3$ (11) Å^3, $Z = 2$, $\rho_{calcd} = 1.237$ g cm^{-3}, and $\rho_{obsd} = 1.27$ g cm^{-3}. With use of 2238 reflections ($I > 3\sigma(I)$) collected at 298 K with Mo Kα ($\lambda = 0.71073$ Å) radiation out to $2\theta = 55°$ on a single-crystal X-ray diffractometer, the structure was solved by using Patterson and difference Fourier methods and refined to final R (R_w) values of 3.4% (4.4%).

(15) Characterization of **1**: Anal. Calcd for $C_{48}H_{60}Li_3O_{12}V$: C, 64.01; H, 6.71. Found: C, 63.71; H, 6.95. Electronic spectrum in DME: λ 280 nm (ϵ 24 000 cm^{-1} M^{-1}) 348 (sh, 1350), 640 (34). Magnetism: 2.90 μ_B (THF-d_8, Evans method).

(16) For example, to a suspension of 1.00 g (2.68 mmol) of $VCl_3·3THF$ in 30 mL of THF was added with stirring 1.60 g of solid LiOPh (16.0 mmol). The reaction mixture became green and homogeneous instantaneously and was stirred for 2 days. Removal of solvent afforded a green-brown solid, which was dissolved in 15 mL of DME and cooled to −27 °C. This procedure gave 1.88 g (78.0% yield) of **1** as a microcrystalline green solid.

(17) Characterization of **2**·THF: Anal. Calcd for $C_{56}H_{84}LiO_6V$: C, 73.82; H, 9.29. Found: C, 73.78; H, 9.06. Electronic spectrum in hexanes: λ 256 nm (ϵ 24 000 cm^{-1} M^{-1}), 315 (sh), 370 (sh), 506 (129), 638 (717), 805 (340), 924 (344), 1040 (sh), 1090 (sh), 1200 (sh). Magnetism: 2.75 μ_B (toluene-d_8, Evans method).

(18) X-ray analysis of **2**: The compound $[\{V(DIPP)_4\}\{Li(THF)\}]$ crystallizes in the monoclinic system, space group $P2_1$, with $a = 13.899$ (4) Å, $b = 17.672$ (3) Å, $c = 20.342$ (3) Å, $\beta = 94.56$ (2), $V = 4980$ (3) Å^3, $Z = 4$, and $\rho_{calcd} = 1.215$ g cm^{-3}. Data were collected at 148 K with Mo Kα radiation out to $2\theta = 45°$. With the use of 5762 reflections ($I > 3\sigma(I)$) the structure was solved by Patterson and difference Fourier methods and refined to current R (R_w) values of 4.07% (5.05%).

(19) X-ray structure and characterization of **3**: Disorder in the crystal lattice prevented an accurate solution of the structure of the cation; however, the anion structural parameters were well-behaved during the refinement. The [Li(12-crown-4)]$^+$ salt crystallizes in the tetragonal system, space group $I\bar{4}$, with $a = 16.514$ (4) Å, $c = 13.037$ (4) Å, $V = 3556$ (3) Å^3, $Z = 2$, and $\rho_{calcd} = 1.016$ g cm^{-3}. Data were collected at 158 K with Mo Kα radiation out to $2\theta = 45°$, yielding 1137 reflections with $I > 3\sigma(I)$. The structure was solved by Patterson and difference Fourier methods and refined to current R (R_w) values of 8.19% (9.88%). The vanadium complex has crystallographically imposed S_4 symmetry. Selected bond distances (Å) and angles (deg): V(1)–O(1), 1.865 (3); O(1)–C(1), 1.353 (5); O(1)–V(1)–O(1′), 108.6 (2); O(1)–V(1)–O(1″), 109.92 (9); V(1)–O(1)–C(1), 141.9 (3). Elemental analysis was performed on the DME solvate of **3**: Anal. Calcd for $C_{60}H_{94}LiO_{10}V$ (**3**·DME): C, 69.74; H, 9.17. Found: C, 69.67; H, 8.96. Electronic spectrum in THF: λ 300 nm (sh), 350 (sh), 505 (sh), 560 (sh), 642 (ϵ 328 cm^{-1} M^{-1}), 958 (383), 1015 (sh), 1070 (sh). Magnetism: 2.72 μ_B (THF-d_8, Evans method).

(20) (a) Canich, J. M.; Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Polyhedron* **1987**, *6*, 1433–1437. (b) Bouma, R. J.; Teuben, J. H.; Beukema, W. R.; Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 2715–2718.

(21) Cooper, S. R.; Koh, Y. B.; Raymond, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 5092–5102.

(22) Mazzanti, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 2308–2314.

(23) Structure of $[V(mesityl)_3(THF)]$: Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1984**, 886–887.

angles to be substantially smaller than 109.5° (O–V–O, 81.6 and 83.2°). With two of the phenolate oxygen atoms drawn back in the bridging interaction to Li, the angle between the remaining two V–O bonds opens up to 118.5 and 114.4° for the two independent complexes. Another consequence of the bridging interaction to Li^+ is that the V–O bonds involved in the bridges are approximately 0.1 Å longer than the terminal ones. The distorted tetrahedral structure of **2** relaxes to a nearly perfect tetrahedral geometry in **3**[19] when the lithium cation is separated from the anion by treatment with 12-crown-4. Whereas there are no particularly short V···H interactions in **3**, complex **2** has some rather small V···H separations (minimum 2.39 Å), indicative of agostic interactions.

Solution magnetic susceptibility data for compounds **1** (2.90 μ_B), **2** (2.75 μ_B), and **3** (2.72 μ_B) are consistent with a d^2 electronic configuration. The solution electronic absorption spectra of **2**[17] and **3**[19] are characteristic of tetrahedral V(III), reminiscent of that reported for VCl_4^- in $CsAlCl_4$.[24] Similar spectra have been reported for $[V(mes)_3(R)]^-$ (mes = mesityl; R = phenyl, *o*-tolyl, Me, CPh_3, mes).[25] A dramatic color change from green to blue occurs upon dissolving **2** in coordinating solvents such as THF, presumably as a result of solvating the lithium ion and thereby removing it from direct contact with the $V(DIPP)_4^-$ unit. The light green color of **1** is consistent with other examples of six-coordinate V(III) species.[26] While under certain conditions EPR spectra have been observed for octahedral[27a] and tetrahedral[27b] V(III) species, solutions of the novel phenolate complexes are EPR-silent at room temperature and 77 K at X-band frequency.

Cyclic voltammetry of compounds **2** and **3** display two quasi-reversible waves tentatively assigned to V^{III}/V^{IV} and V^{IV}/V^V redox couples, as well as irreversible waves corresponding to phenolate oxidation.[28] Reduction to V(II) apparently is not accessible under these conditions, within the solvent window. On the other hand, chemical reduction of **2** with a Na/Hg amalgam proceeds slowly and gives rise to a hexane-soluble product, which possesses an EPR spectrum consistent with an $S = {}^3/_2$ species. Confirmation of this latter product as a vanadium(II) phenolate complex awaits further investigation.

In conclusion, three novel vanadium(III) phenolate complexes have been prepared and characterized by X-ray crystallography, magnetic, spectroscopic, and electrochemical methods. These compounds represent the first examples of mononuclear homoleptic four- and six-coordinate vanadium(III) phenolate species. Accessibility of a lower oxidation level in the case of **2** has been demonstrated. Further investigations into reactivity of **1–3** and their reduced analogs are under way.

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Registry No. **1**, 117226-81-0; **2**, 117226-83-2; **3**, 117226-84-3; $VCl_3 \cdot 3THF$, 19559-06-9; $[V_2Cl_3(THF)_6]^+$, 89172-47-4.

Supplementary Material Available: For **1–3**, fully labeled ORTEP drawings and tables of positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, interatomic distances, and interatomic angles (38 pages). Ordering information is given on any current masthead page.

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(24) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984; p 400.

(25) (a) Seidel, W.; Kreisel, G. *Z. Anorg. Allg. Chem.* **1976**, *426*, 150–154. (b) Kreisel, G.; Scholz, P.; Seidel, W. *Z. Anorg. Allg. Chem.* **1980**, *460*, 51–55.

(26) For example, $V(cat)_3^{3-}$ is a similar light green color. See ref 21.

(27) (a) Foner, S.; Low, W. *Phys. Rev.* **1960**, *120*, 1585–1588. (b) Ham, F. S.; Ludwig, G. W. In *Paramagnetic Resonance*, Lowe, W., Ed.; Academic: New York, 1963; Vol. 1, p 163.

(28) Cyclic voltammetry: Potentials (V) were measured vs. Ag/Ag^+, q-r = quasi-reversible, irrev = irreversible. **1** (CH_3CN, 0.1 M Et_4NClO_4): +1.56 (q-r), +0.87 (q-r), –0.77 (irrev). **2** (CH_2Cl_2, 0.1 M Bu_4NPF_6): +1.67 (q-r), +0.28 (q-r), +1.22 (irrev). **3** (CH_3CN, 0.1 M Et_4NClO_4): +1.64 (q-r), +0.52 (q-r), +1.08 (irrev).

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Articles

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Formation and Molecular Structure of the Novel Six-Coordinate Aminoalane Complex $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$

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Reaction of $[(CH_3)_3Si]_3Al \cdot O(C_2H_5)_2$ and NH_3 in a 1:2 ratio results in the formation of $\{[(CH_3)_3Si]_2Al(NH_2)_2\}_3Al$. The compound was characterized by elemental analysis, mass, infrared, and NMR spectroscopic data, and a single-crystal X-ray diffraction analysis. The compound crystallizes in the monoclinic space group *C*2/*c* with a = 13.981 (2) Å, b = 14.064 (2) Å, c = 23.025 (2) Å, β = 106.2 (1)°, Z = 4, V = 4347 (1) Å^3, and ρ = 0.98 g cm^{-3}. Least-squares refinement gave R_F = 9.56% and R_{wF} = 7.37% on 2504 reflections with $F \geq 3\sigma(F)$. The molecular structure shows a central six-coordinate, pseudooctahedral Al atom bonded to three bidentate aminosilyl aluminum ligands, $\{[(CH_3)_3Si]_2Al(NH_2)_2^-\}$. The average central $Al-N(H)_2$ distance is 2.020 (5) Å, and the average $Al-N(H)_2$ distance in the ligand units is 1.932 (5) Å. Pyrolysis of this molecular species provides a mixture of AlN and SiC.

Introduction

The reactions of trialkylaluminum compounds and NH_3 have been studied by Wiberg,[1] and more recently, the reactions of $(CH_3)_3Al$ and $(C_2H_5)_3Al$ have been reinvestigated by Interrante and co-workers[2] and by Tebbe and Bolt.[3] The 1:1 stoichiometric

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(1) Wiberg, E., work discussed by: Bahr, G. *FIAT Review of German Science 1939–1946*; Dieterichsche Verlagsbuchhandlung: Wiesbaden, BRD, 1948; Inorganic Chemistry, Part II.

(2) Interrante, L. V.; Carpenter, L. E.; Whitmarsh, C.; Lee, W.; Garbauskas, M.; Slack, G. A. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 359.

(3) Baker, R. T.; Bolt, J. D.; Chowdhry, U.; Klabunde, U.; Reddy, G. S.; Roe, C.; Staley, R. H.; Tebbe, F. N.; Vega, A. J. *Mater. Res. Soc. Symp. Proc.*, in press.