TSLIF,[20] we tentatively ascribe the precursor of the TSLIF to the tautomer triplet state. For this case, at this stage, whether the rate of $T'_2 \rightarrow T'_1$ internal conversion is exceptionally slow (e.g., several hundred picoseconds) due to the large T'_2–T'_1 energy gap or the rate of $T'_2 \rightarrow S'_1$ intersystem crossing is remarkably fast cannot be determined. Research focused on the study of the dynamics of the triplet state is currently in progress.

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[20] The TSLIF reaches a maximum intensity at a delay time of 50 ns, which is the response time of our TSLIF measurement.

Unprecedented Example of Four Coordination at a Vanadium(II) Center. Synthesis, Structure, and Properties of a Reactive, Nearly Planar V(II) Phenolate Complex, [V(DIPP)$_4${Li(THF)}$_2$] (DIPP = 2,6-Diisopropylphenolate)

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Characterization of the coordination chemistry of divalent vanadium, particularly for nonorganometallic complexes, has lagged well behind that of most of the other first-row transition elements.[1] For example, the first V^{II} porphyrin complex was reported quite recently.[2] Presumably, this situation is a consequence of the tendency for many such complexes to be oxidized to V^{IV} and V^{V} oxo species in the presence of even traces of oxygen and/or water. While a considerable number of V^{II} complexes are known,[1] they are invariably six-coordinate and their reaction chemistry is often dominated by outer-sphere electron-transfer processes.[1,3] As a part of our ongoing effort to obtain very reactive, low-valent, coordinatively unsaturated vanadium complexes, it was discovered that reduction of the four-coordinate V^{III} phenolate species [V(DIPP)$_4${Li(THF)}][4] was not a fruitful pathway to the desired V^{II} analogue.[5] However, by using V^{II} starting materials we were successful in isolating a V^{II}–phenolate complex, [V(DIPP)$_4${Li(THF)}$_2$] (**1**), the subject of this report. This species represents the first example of a four-coordinate V^{II} complex and displays remarkable reactivity properties.

In our initial synthetic procedure, **1** was prepared from [V$_2$Cl$_3$(THF)$_6$](PF$_6$) (**2**), which can be obtained in turn from the corresponding $(Zn_2Cl_6)^{2-}$ salt by metathesis with [(n-Bu)$_4$N](PF$_6$) in THF solution.[6] To 1.51 g (1.92 mmol) of **2** and 3.89 g (21.14 mmol) of Li(DIPP) was added 45 mL of dry hexanes, and the reaction mixture was stirred for 2 days and then filtered. Cooling of the filtrate at −30 °C for 2 days afforded a crop of PF$_2$(DIPP)$_3$.[7] The yellow-green solution was decanted away and cooled for an additional 2 days, after which time a crop of **1** was collected (0.540 g, 30% yield). Crystals suitable for elemental analysis,[8] X-ray crystallography,[9] and magnetic and spectroscopic measurements were obtained by recrystallization from hexanes. Because it was found that the PF$_6^-$ anion was not innocent in the aforementioned reaction, another V^{II} starting material was sought. Recently we have prepared compound **1** from [V(THF)$_4$(CF$_3$SO$_3$)$_2$][10] in 77% yield by a procedure similar to that described above. Judging from UV–vis–near IR spectra, it is difficult to obtain **1** with less than approximately 3% of [V(DIPP)$_4${Li(THF)}] (**3**) present as an impurity.

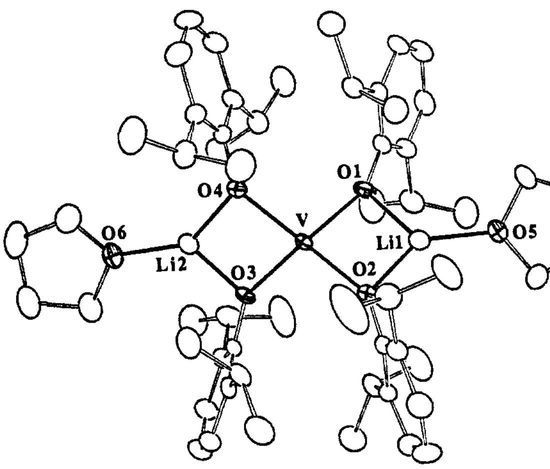

Figure 1. Structure of [V(DIPP)$_4${Li(THF)}$_2$] (**1**) showing the anisotropic thermal ellipsoids and atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (degrees), are as follows: V–O(1), 2.007 (2); V–O(2), 2.034 (3); V–O(3), 2.010 (2); V–O(4), 2.034 (2); Li(1)–O(1), 1.835 (6); Li(1)–O(2), 1.811 (7); Li(1)–O(5), 1.888 (7); Li(2)–O(3), 1.830 (7); Li(2)–O(4), 1.835 (7); Li(2)–O(6), 1.875 (7); O(1)–V–O(2), 79.4 (1); O(1)–V–O(3), 162.9 (1); O(1)–V–O(4), 103.2 (1); O(2)–V–O(3), 104.3 (1); O(2)–V–O(4), 161.9 (1); O(3)–V–O(4), 78.6 (1); V–O(1)–C(11), 145.8 (2); V–O(2)–C(21), 145.7 (2); V–O(3)–C(31), 147.3 (2); V–O(4)–C(41), 140.0 (2).

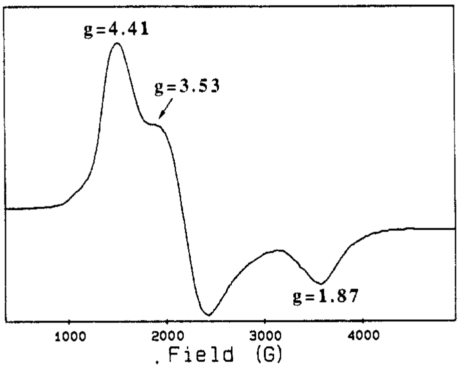

Figure 2. X-band (ν = 9.33 GHz) EPR spectrum of **1** in cyclohexane at 77 K obtained by using the following instrument settings: microwave power, 12.6 mW; field modulation amplitude, 10 G; modulation frequency, 100 kHz.

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[1] Boas, L. V.; Pessoa, J. C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverly, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 3, pp 462–473 and references therein.

[2] (a) Poncet, J.-L.; Barbe, J.-M.; Guilard, R.; Oumous, H.; Lecomte, C.; Protas, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1421–1422. (b) Oumous, H.; Lecomte, C.; Protas, J.; Poncet, J.-L.; Barbe, J.-M.; Guilard, R. *J. Chem. Soc., Dalton Trans.* **1984**, 2677–2682.

[3] Examples of inner sphere reactivity behavior of low-valent vanadium species: (a) (Pinacol cross-coupling reactions) Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 8014–8016. (b) (Dinitrogen coordination) Edema, J. J. H.; Meetsma, A.; Gambarotta, S. *J. Am. Chem. Soc.* **1989**, *111*, 6878–6880. (c) (Dinitrogen fixation) Shilov, A. E. In *Energy Resources Through Photochemistry and Catalysis*; Grätzel, M., Ed., Academic: New York, 1983; pp 535–558.

[4] Abbreviations used: DIPP, 2,6-diisopropylphenolate; 12-crown-4, 1,4,7,10-tetraoxacyclododecane; DMP, 2,6-dimethylphenolate; TMEDA, *N,N,N′,N′*-tetramethylethylenediamine; EPR, electron paramagnetic resonance.

[5] Wilisch, W. C. A.; Scott, M. J.; Armstrong, W. H. *Inorg. Chem.* **1988**, *27*, 4333–4335.

[6] (a) PF$_6^-$ salt: Randall, C. R.; Armstrong, W. H., unpublished results. (b) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 913–917. (c) Canich, J. M.; Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Polyhedron* **1987**, *6*, 1433–1437. (d) Bouma, R. J.; Teuben, J. H.; Beukema, W. R.; Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 2715–2718.

[7] The identity of this product was confirmed by X-ray crystallography.

[8] Elemental analysis for **1**. Calcd for $C_{56}H_{84}O_6Li_2V$: C, 73.26; H, 9.22. Found: C, 72.73; H, 9.34.

[9] Compound **1** crystallizes in the monoclinic space group Pn, with a = 13.103 (3) Å, b = 12.150 (5) Å, c = 17.109 (4) Å, β = 97.63 (2)°, V = 2701 (3) Å^3, Z = 2, and ρ_{calcd} = 1.129 g cm^{-3}. X-ray diffraction data were collected at 183 K by using Mo Kα radiation out to 2θ = 45°, yielding 3163 reflections with $I > 3\sigma(I)$. The structure was solved by direct methods (SHELXS 86) and refined by using 584 parameters to final R (R_w) values of 3.87% (4.69%).

[10] The novel V^{II} starting material, [V(THF)$_4$(CF$_3$SO$_3$)$_2$], was prepared by reduction of V(CF$_3$SO$_3$)$_3$[11] using metallic zinc. Full details of the synthesis and structure will be reported elsewhere.

[11] A modified literature procedure was employed for V(CF$_3$SO$_3$)$_3$: Singh, S.; Amita; Gill, M. S.; Verma, R. D. *J. Fluorine Chem.* **1985**, *27*, 133–142.

0002-7863/90/1512-2429$02.50/0

The crystal structure of **1** is presented in Figure 1. The average V-O bond distance of 2.021 Å in **1** is 0.08 Å longer than the corresponding distance in the V^{III} analogue, **3**.[5] In contrast to the distorted tetrahedral geometry of **3** and the nearly perfect tetrahedral coordination sphere that results when Li$^+$ is taken away from **3** with 12-crown-4, the geometry of **1** approaches a square-planar configuration. From inspection of orbital diagrams for planar vs tetrahedral ML$_4$ species as presented by Albright et al.,[12] it follows that on electronic grounds the geometrical preference of a four-coordinate d^3 complex is for the square-planar configuration.[13] Distortion from idealized square-planar geometry is due in part to the relatively small bite angle of the [Li(DIPP)$_2$]$^-$ bidentate ligands (79.0°). Furthermore, it is likely that the sterically bulky ligands are responsible for the nonzero (27.2°) dihedral angle between the O(1)VO(2) and O(3)VO(4) coordination planes. For comparison, the corresponding dihedral angle in W(DIPP)$_4$ is 17.5°.[14] With the less bulky DMP ligand, more rigorously square planar complexes of W^{IV} [14] and Cr^{II} [15] have been obtained. Steric crowding in **1** forces the aromatic rings to be nearly perpendicular to the VO$_4$ plane, as is also the case with W(DIPP)$_4$[14] and [Cr(DMP)$_4${Na(TMEDA)}$_2$].[15] In the structure of W(DIPP)$_4$,[14] a relatively large average W-O-C angle (156°) has been taken to be indicative of π donation to the metal. The average V-O-C angle of 145° in **1** is substantially smaller than the corresponding value for W(DIPP)$_4$.[14]

The physical properties of bulk samples of **1** are consistent with a d^3 electronic configuration. Taking into account a V^{III} impurity, the solid-state magnetic moment of **1** is 3.83 μ_B, as expected for an $S = {}^3/_2$ ion. As mentioned above, the green V^{III} impurity often obtained in preparations of **1** has been identified as **3** by UV-vis-near IR spectroscopy.[5] Pure samples of **1** are light yellow-green, and a hexane solution has an absorption maximum at 435 nm (ϵ = 168 M^{-1} cm^{-1}), which presumably corresponds to a d-d transition. While the V^{III} complex **3** has no readily detectable EPR signals at 77 K at X-band frequencies, its V^{II} counterpart **1** displays a rhombic EPR spectrum (Figure 2) characteristic of $S = {}^3/_2$ species. The g values given in Figure 2 are consistent with a rhombicity parameter (E/D) of approximately 0.07.[16]

Although upon inspection of Figure 1 one may conclude that substrate molecules should have access to the vanadium center, space-filling molecular models make it clear that the metal atom is very effectively shielded from attack. The same structural effect was noted for W(DIPP)$_4$.[14] In contrast to the relative stability of W(DIPP)$_4$, which was ascribed to this steric shielding, **1** is quite reactive toward a variety of substrates. For example, **1** will react at room temperature with CO, CO$_2$, acetylenes, epoxides, ketones, aldehydes, and alcohols. Ligand redistribution and redox chemistry are observed in the reaction with excess CO, such that the principle products obtained are **3** and [V(CO)$_6$]$^-$. Compound **1** behaves as an oxygen atom acceptor in its reaction with cyclohexene oxide to form cyclohexene along with a dimeric V^{IV} complex.[17] The greater reactivity of [V(DIPP)$_4${Li(THF)}$_2$] compared to W(DIPP)$_4$ is attributed to principally two factors: (1) the greater reducing power of the V^{II} complex and (2) the relative ease of loss of Li(DIPP) from **1** compared to the loss of DIPP$^-$ from W(DIPP)$_4$.

In conclusion, the first example of a four-coordinate V^{II} complex has been isolated. Attainment of a rigorously square planar geometry as predicted for a four-coordinate d^3 ion is prevented by coordination to the Li$^+$ ions and the sterically bulky phenolate ligands. Compound **1** displays reactivity toward molecules with a variety of functional groups. Products from the reaction of **1** with CO and with cyclohexene oxide have been identified. Further definition of several other of the aforementioned reactions is in progress.

Note Added in Proof. Rhenium(IV) phenoxides have been reported recently: Gardiner, I. M.; Bruck, M. A.; Wexler, P. A.; Wigley, D. A. *Inorg. Chem.* **1989**, *28*, 3688-3695. This work was supported by University of California, Berkeley Biomedical Research Grant No. 88-4 and 89-6 and by National Science Foundation Grant No. CHE-8857455.

Acknowledgment. W.C.A.W. was the recipient of an Earle C. Anthony Fellowship at the University of California, Berkeley. This work was supported by University of California, Berkeley Biomedical Research Grant No. 88-4 and 89-6 and by National Science Foundation Grant No. CHE-8857455.

Supplementary Material Available: A fully labeled ORTEP drawing and tables of positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, interatomic distances, and interatomic angles for compound **1** (8 pages). Ordering information is given on any current masthead page.

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[12] Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; John Wiley and Sons: New York, 1985; p 304.

[13] A distorted tetrahedral Cr^{III} complex, [Cr{OCH(CMe$_3$)$_2$}$_4${Li(THF)}], has been reported. However, in this case the bulky alkoxide ligand may prevent planar coordination on steric grounds. Bochmann, M.; Wilkinson, G.; Young, G. B.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1863-1871.

[14] (a) Listemann, M. L.; Schrock, R. R.; Dewan, J. C.; Kolodziej, R. M. *Inorg. Chem.* **1988**, *27*, 264-271. (b) Listemann, M. L.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 7207-7208.

[15] Edema, J. J. H.; Gambarotta, S.; van Bolhuis, F.; Spek, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 2142-2147.

[16] (a) Munck, E.; Rhodes, H.; Orme-Johnson, W. H.; Davis, L. C.; Brill, W. J.; Shah, V. K. *Biochim. Biophys. Acta* **1975**, *400*, 32-53. (b) Huynh, B. H.; Kent, T. A. In *Advances in Mössbauer Spectroscopy*; Thisar, B. V., Iyengar, P. K., Srivasta, J. K., Bhargava, S. C., Eds.; Elsevier: New York, 1983; pp 490-560.

[17] The purple dimeric V^{IV} complex [V$_2$O$_2$(μ-OH)$_2$(DIPP)$_4${Li(THF)$_2$}$_2$] was crystallized from the reaction mixture and characterized by X-ray crystallography. A complex with the same core structure was reported by Wieghardt and co-workers.[18]

[18] Wieghardt, K.; Bossek, U.; Volckmar, K.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 1387-1389.

Isolation and X-ray Structure of a Dinuclear Copper-Nitrosyl Complex

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We have recently described three types of copper-dioxygen complexes, {Cu$_2$-O$_2$}$^{n+}$ (n = 1 or 2), which are formed reversibly by the addition of O$_2$ to either mono- or dinuclear copper(I) complexes (**1**-**3**, Scheme I, PY = 2-pyridyl) at -80 °C in solution.[1] These {Cu$_2$-O$_2$}$^{n+}$ species are best described as peroxo dicopper(II) complexes which are formed through the formal oxidative addition of O$_2$ to **1**-**3**.[2] However, they have substantially different spectroscopic properties and reactivity characteristics.[3] In order to better understand the nature of this oxidative process and to explore the chemistry of the copper(I) precursor compounds, we are studying reactions of **1**-**3** (Scheme I) with a variety of elec-

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[1] (a) Tyeklár, Z.; Karlin, K. D. *Acc. Chem. Res.* **1989**, *22*, 241-248 and references cited therein. (b) Jacobson, R. R.; Tyeklár, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 3690-3692. (c) Karlin, K. D.; Haka, M. S.; Cruse, R. W.; Meyer, G. J.; Farooq, A.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 1196-1207. (d) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Farooq, A.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 2668-2679.

[2] This assignment is based on a variety of criteria obtained from a combination of resonance Raman, X-ray absorption, and UV-vis spectroscopic studies.[1]

[3] For example, the dioxygen complex derived from **2** is relatively unreactive toward stoichiometric amounts of protic acids, whereas those species derived from **1** and **3** react with H$^+$, liberating hydrogen peroxide in high yield. See: Tyeklár, Z.; Paul, P. P.; Jacobson, R. R.; Farooq, A.; Karlin, K. D.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 388-389.

0002-7863/90/1512-2430$02.50/0