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# Structural and Spectroscopic Characterization of a Novel Vanadium(V)−Amide Complex

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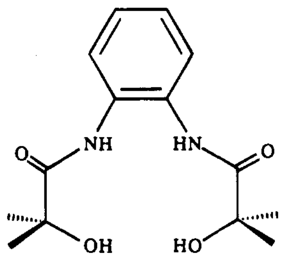
The interaction of vanadium with proteins is of current interest due to the discovery of several vanado enzymes[1] and the insulin mimetic effect of vanadate.[2,3] Vanadate has long been recognized as an inhibitor (or, in limited cases, activator) of phosphate metabolism.[4] Additionally, there are several examples of the ability of vanadate to catalyze photocleavage of the peptide backbone in phosphate binding proteins.[5] Amide complexes of copper[6] and cobalt[7] each undergo photodecomposition of the ligand via ligand-to-metal charge transfer. Given these precedents for the involvement of amide ligands in peptide photocleavage and the ubiquitous presence of the amide group in proteins, we have examined the vanadium coordination chemistry of this functional group. To date, the structures for four vanadium(IV)−amide complexes[8,9] and one vanadium(III)−amide complex[8b] have been reported. Herein we report the synthesis and molecular structure of the first vanadium(V)−amide complex in which the deprotonated amide nitrogens are directly coordinated to the metal.

The ligand 1,2-bis(2-hydroxy-2-methylpropanamido)benzene, **1**, was prepared according to Collins *et al.*[10] The ligand **1** and similar "redox innocent" ligands have been used extensively by Collins and co-workers to prepare stable, high-valent metal complexes.[11] The corresponding potassium salt of the vanadium(V) complex, **2**, was prepared by refluxing an equimolar solution of **1** and $V^{IV}O(ACAC)_2$ in acetonitrile/ethanol for ca. 8 h in the presence of air and 4 equiv of KOH. The cloudy brown solution was filtered, and the solvent was removed under vacuum. The residue was redissolved in acetone, the insoluble salts were removed by filtration, and the filtrate was evaporated under vacuum. The resulting brown residue was recrystallized from acetone−chloroform (1:4) at −20 °C to obtain a 47% yield of analytically pure product.[12] X-ray diffraction quality crystals of **2** were obtained by slow diffusion of toluene into an acetone solution of **2**. During the period of crystal formation, demetalation of the ligand occurs as is evidenced by co-crystallization of the free-base ligand; *vida infra.* Other products from this process have not been determined.



**1**

The molecular structure of the anion **2** is presented in Figure 1, and important parametrical data are provided in the figure caption.[13] The first coordination sphere consists of an oxo donor (1.598(3) Å), two alkoxide oxygen donors (1.800(3), 1.799(3) Å) and two deprotonated amide-nitrogen donors (2.008(3), 2.006(3) Å). The overall geometry is best described as a distorted square pyramid based on idealized polytopal forms.[14] The angle between the basal planes containing O4, N1, and N2 and O4, O3, and N1 is 5.3°. The vanadium sits 0.58 Å out of the best plane defined by O3, O4, N1, and N2. The vanadium−amide distances are longer than expected considering the range for the five vanadium(III or IV)−amide structures previously reported (range = 1.970(2)−2.026(6) Å; mean = 1.996 Å).[8,9] The planarity of the amide moiety confirms the deprotonated nature of the amide nitrogen atom. Kabanos and co-workers have recently reported the structure of a six-coordinate vanadium(V)−amide complex in which the amide oxygen, and not

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(12) Elemental analysis for **2** is as follows. Calcd for $KVC_{14}H_{16}N_2O_5$: C, 35.91; H, 3.42 N, 5.58; V, 10.2; K, 7.8. Found: C, 35.60; H, 3.44; N, 5.52; V, 10.2. $^1H$ NMR in $d_6$-acetone, δ (ppm): mult., 8.05, m; 6.76, m; 1.71, s; 1.40, s. Strong FT-IR bands ($cm^{-1}$): 1622, 1574, 1476, 1375, 1354, 1161, 974, 905, 762, 688, 636, 577.

(13) X-ray parameters for **2·1·**0.5acetone: $C_{29.5}H_{39}N_4O_{10.5}KV$, 691.40 g/mol, *C*2/*c* (No. 15); $a = 15.867(4)$ Å, $b = 14.603(4)$ Å, $c = 29.605(9)$ Å, $\beta = 104.00(2)°$; $V = 6656(3)$ Å$^3$; $Z = 8$; $\varrho_{calc} = 1.412$ g/cm$^3$, $\varrho_{obs} = 1.37$ g/cm$^3$; $\lambda$(Mo Kα) = 0.710 73 Å; crystal dimensions, 0.20 × 0.24 × 0.40 mm; largest residual +0.34/−0.31 e/Å$^3$. The intensities of 4354 unique reflections ($3 < 2\theta < 45$) were measured at ambient temperature on a Siemens R3m/μ diffractometer. The structure was solved by Patterson and difference Fourier techniques using the SHELXTL program package. The structure was refined using the block diagonal least squares method. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the free ligand, including those on O2a, O4a, N1a, and N2a, were located on the difference map and refined isotropically. Other hydrogen atoms were placed in fixed positions and refined isotropically. For 3204 data with $F_o \geq 6\sigma(F)$, the final $R = 0.0574$ and $R_w = 0.0433$. $R = \Sigma(|F_o - F_c|)/(\Sigma|F_o|)$; $R_w = [\Sigma(w|F_o - F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

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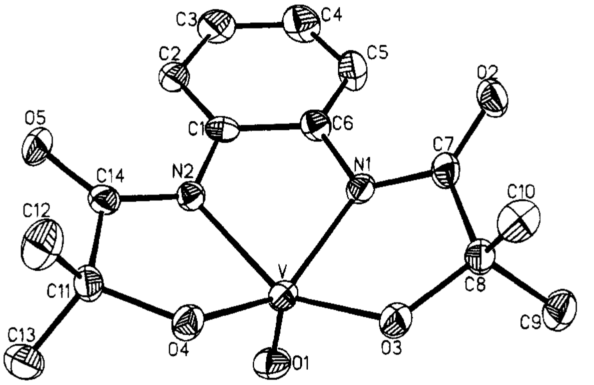

**Figure 1.** Perspective view of the anion of **2** showing 30% probability ellipsoids. Important bond lengths (Å) are as follows: V–O1, 1.598(3); V–O3, 1.800(3); V–O4, 1.799(3); V–N1, 2.006(3); V–N2, 2.008(3); N1–C7, 1.364(5); N2–C14, 1.330(6); C7–O2, 1.229(5); C14–O5, 1.250(5). Important bond angles (degrees) are as follows: O1–V–O3, 110.8(1); O1–V–O4, 109.6(2); O1–V–N1, 108.0(2); O1–V–N2, 102.4(1); O3–V–O4, 102.5(1); O3–V–N2, 143.4(1); O3–V–N1, 79.6(1); O4–V–N2, 79.5(1); O4–V–N1, 138.5(1); N2–V–N1, 75.9(1).

the amide nitrogen, is coordinated to the metal ion in the position trans to the oxo ligand.[15] The anion **2** is strictly five-coordinate.

The vanadium–alkoxide distances are slightly longer than most other vanadium(V)–alkoxide structures reported in the literature.[16] It should be noted that the $V-O_{alkoxide}$ distances are approximately 0.1 Å shorter than analogous distances in vanadium(V)–phenolate complexes. Crystals of **2** consisted of the anionic complex, a potassium cation, a molecule of acetone (located on the 2-fold axis), and one molecule of the free ligand, **1**. The molecular structure of **1** is presented as Figure 2. The interatomic distances in the free ligand are similar to those in the metal complex and do not support any specific electron distribution in the metal–amide structural unit. The potassium cation has weak interactions with the alkoxide oxygens of the anion, the carbonyl oxygens of the free ligand, and an oxo ligand of a second anion. A packing diagram for the unit cell and a diagram of the potassium coordination sphere are provided in the supplementary material. The presence of only one cation is consistent with the vanadium(V) formulation of **2**. We believe that the molecular structure of the anion **2** in the bulk material (for which the elemental analysis was obtained) is the same as that determined by X-ray crystallography. The FAB(–) mass spectra of both the X-ray sample and the analytically pure sample have peaks at *m/z* = 343 amu ($M^-$ for the anion) and 382 amu ($M^-$ for the anion–potassium ion pair). The proposed vanadium(V) oxidation level is also supported by magnetic resonance studies. Complex **2** is ESR silent and NMR active with a single $^{51}V$ resonance at –455 ppm relative to external $V^VOCl_3$ for both the X-ray sample and the analytically pure sample. This shift is consistent with the coordination environment observed in the crystal structure.[17]

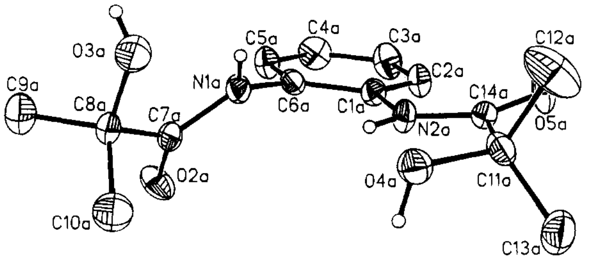

**Figure 2.** Perspective view of the free ligand of **2** showing 30% probability ellipsoids. Important bond lengths (Å) are as follows: C7a–O2a, 1.220(5); C7a–N1a, 1.355(6); C14a–O5a, 1.220(5); C14a–N2a, 1.338(6).

The brown color of acetonitrile solutions of **2** derives from an electronic transition at 368 nm ($\epsilon$ = 4400 $M^{-1}$ $cm^{-1}$). Additional electronic transitions are at 306 nm ($\epsilon$ = 7800 $M^{-1}$ $cm^{-1}$, sh), 296 nm ($\epsilon$ = 9700 $M^{-1}$ $cm^{1}$, sh), and 236 nm ($\epsilon$ = 42000 $M^{-1}$ $cm^{-1}$). The band at 368 nm is tentatively assigned as a ligand-to-metal charge-transfer transition. Similar transitions have been noted for $Co^{III}$ complexes of **1**. Photodecomposition of **1**–$Co^{III}$ yields free **1**, $Co^{II}$, acetone, a cyclic urea (from the phenylenediamine fragment), and 2-hydroxy-2-methylpropionic acid.[7] We are currently examining the photostability of **2** and plan to determine the relationship between any observed photochemistry in **2** and the known vanadium-catalyzed photodecomposition of myosin and dynein.[5]

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**Supplementary Material Available:** For **2**, Tables 1–5 listing fractional atomic coordinates and thermal parameters for non-hydrogen atoms, fractional atomic coordinates and thermal parameters for hydrogen atoms, complete bond distances, complete bond angles, and anisotropic thermal parameters, and Figures S1 and S2, showing the coordination environment of the potassium cation and a packing diagram for the unit cell (7 pages). Ordering information given on any current masthead page.

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