

Preparation and Characterization of the First Vanadium Ynolate Complex

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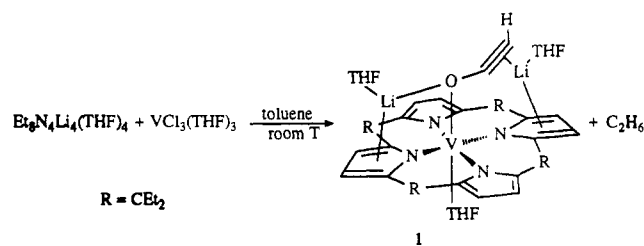
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Ynolate anion ligands (also known as ketenyl) have received only limited attention over the past few years,¹ despite the fact that they are extremely useful synthetic reagents.² A possible reason for this paucity lies in the difficulty of the synthetic methodology currently employed, which involves the coupling of alkylidyne and carbonyl ligands via either nucleophile-induced or photoinduced reactions.³ Furthermore, research in this area essentially has revolved only around low-valent carbophilic Mo and W complexes.^{1,4} In all these cases, the ynolate moiety is bonded to the transition metal by the carbon donor atom, which acts as either an η^1 (two-electron donor) or an η^2 (four-electron donor) ligand. Therefore, in view of the promising reactivity,² a significantly different chemistry might be expected for the coordinated ynolate anion when the anchoring is through oxygen, as, for example, in the case of an oxophilic transition metal such as vanadium.

It has recently been reported that photogenerated ynolates can be trapped by electrophiles,⁵ and it has also been postulated that the formation of aluminum-saturated ynolates may be brought about by electrophilic induction of the alkylidyne-carbonyl coupling.⁶ On the other hand, alkylidene-carbonyl coupling is normally induced by the addition of a strong nucleophile to the metal center.⁴ In view of these findings, the use of transition metalate complexes containing both a hard acidic and an electron-rich oxophilic metal, such as a low-valent early transition metal, should provide a different approach to the stabilization and investigation of ynolate complexes.

Following our interest in the preparation of transition-metal compounds of polyaza ligands,⁷ we attempted the preparation of a vanadium(III) complex of the octaethylporphyrinogen ligand.⁸ However, the reaction of $\text{VCl}_3(\text{THF})_3$ with the tetralithium salt of the octaethylporphyrinogen macrocyclic ligand $[\text{Et}_8\text{N}_4\text{Li}_4(\text{THF})_4]$,⁹ carried out in toluene at room temperature,¹⁰ proceeded

Scheme I



further than expected to form the vanadium ynolate complex $(\text{Et}_8\text{N}_4)\text{VLi}_2(\text{O}-\text{C}\equiv\text{CH})$ (**1**) (Scheme I). Although serendipitous, the reaction is synthetically useful, since it can be carried out on a very large scale. The reaction is instantaneous, as indicated by the rapid color change from red to deep orange observed upon mixing. The paramagnetic **1** [$\mu_{\text{eff}} = 2.76 \mu_{\text{B}}$] was isolated in excellent yield as deep orange prisms after evaporation to dryness and recrystallization from toluene-hexane. Significant amounts of ethane are formed during the reaction, as demonstrated by both the NMR spectrum carried out on the reaction volatiles and the GC analysis of the reaction mixture. No ethylene or hydrogen was detected. A sharp and intense resonance in the IR spectrum at 1607 cm^{-1} might be ascribed to either a $\text{C}=\text{C}$ double bond or to a considerably stretched carbonyl group. Another intense and sharp band at 584 cm^{-1} suggests the presence in the complex of a $\text{V}-\text{O}$ bond. The characteristic resonances of coordinated THF are also present at 1058 and 851 cm^{-1} .

The chemical connectivity of **1** as well as its formulation has been demonstrated by an X-ray crystal structure.¹¹ The molecule comprises a vanadium atom placed in the center of a rather regular octahedron (Figure 1). The equatorial plane is defined by the four nitrogen atoms of the macrocycle [av $\text{V}-\text{N} = 2.079(3) \text{ \AA}$, $\text{N}1-\text{V}1-\text{N}3 = 178.8(1)^\circ$, $\text{N}1-\text{V}1-\text{N}5 = 90.0(1)^\circ$], while the two apical positions are occupied by the oxygen atom of the ynoate moiety [$\text{V}1-\text{O}4 = 2.009(2) \text{ \AA}$] and the oxygen atom of a coordinated molecule of THF [$\text{V}1-\text{O}3 = 2.112(2) \text{ \AA}$, $\text{O}3-\text{V}1-\text{O}4 = 176.18(8)^\circ$]. The plane of the macrocyclic ligand is considerably puckered. The two lithium cations are placed on the same side of the ligand and are perpendicular with respect to each of two *trans*-positioned pyrrole rings. Each lithium forms identical bonding distances with the four carbon and nitrogen ring atoms, thus suggesting a rather regular η^5 -bonding mode [ranging from $\text{Li}2-\text{C}2 = 2.293(7) \text{ \AA}$ to $\text{Li}2-\text{N}1 = 2.357(6) \text{ \AA}$]. Each alkali cation bears also one molecule of THF [$\text{Li}-\text{O}2 =$

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(10) Preparation of **1**. A suspension of $\text{VCl}_3(\text{THF})_3$ (5.89 g, 15.76 mmol) in toluene (300 mL) was treated with octaethylporphyrinogen tetralithium salt⁸ (14.21 g, 17 mmol) at ambient temperature. The color changed almost immediately when the $\text{VCl}_3(\text{THF})_3$ went into solution. Stirring was continued overnight at room temperature. The mixture was then heated at 60°C for 2 h. Following filtration to remove LiCl , the maroon-orange filtrate was concentrated to dryness, and hexane (150 mL) added to the residue. The orange microcrystalline product obtained upon the solution standing at room temperature was isolated and dried in vacuo (8.1 g, 60%). Recrystallization from hexane or toluene-hexane mixtures afforded orange prisms suitable for X-ray crystallography. Satisfactory combustion analysis data have been obtained. IR [Nujol, KBR, cm^{-1}]: 1607, 1309, 1262, 1164, 1058, 973, 923, 890, 851, 848, 761, 677, 584, 417. $\mu_{\text{eff}} = 2.7 \mu_{\text{B}}$.

(11) Crystal data for **1**: $\text{C}_{50}\text{H}_{73}\text{N}_4\text{O}_3\text{Li}_2\text{V}$, $\text{FW} = 858.97$, orange prism, triclinic, $P1$, $a = 11.984(4) \text{ \AA}$, $b = 17.142(5) \text{ \AA}$, $c = 11.680(2) \text{ \AA}$, $\alpha = 99.19(2)^\circ$, $\beta = 103.05(2)^\circ$, $\gamma = 89.79(2)^\circ$, $Z = 2$, $V = 2306(2) \text{ \AA}^3$, $D_c = 1.237$, $\mu = 2.53$, $T = -151^\circ \text{C}$. The structure was solved by direction methods, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located but not refined due to the unfavorable observation-to-parameters ratio. Of the 7704 reflections collected in the range $6.0 < 2\theta < 50^\circ$, 7276 were unique. Refinement converged at $R = 0.052$ ($R_w = 0.065$) for 5819 reflections and 560 parameters. All calculations were performed with use of a TEXSAN crystallographic software package on a VAX workstation. The identification and sequencing of the ynolate carbon and oxygen atoms have been determined on the basis of the satisfactory refinement of the thermal parameters. Other possibilities including $\text{V}-\text{O}=\text{C}=\text{O}-\text{Li}$, $\text{V}-\text{N}_2\text{O}-\text{Li}$, $\text{V}-\text{ON}_2-\text{Li}$, $\text{V}-\text{C}(\text{H})=\text{C}=\text{O}-\text{Li}$ were taken into consideration and discarded on the basis of worse convergence and unreasonable thermal parameters.

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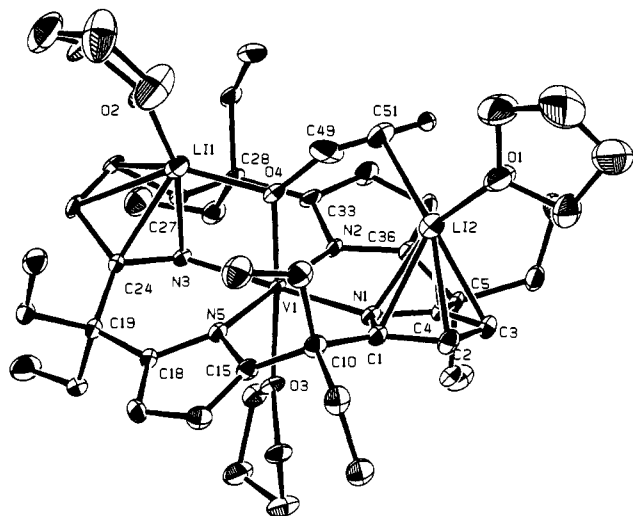


Figure 1. ORTEP drawing of **1** showing the labeling scheme. Selected values of bond distances (Å) and angles (deg): V1–N1 = 2.110(3), V1–N2 = 2.041(3), V1–N3 = 2.101(3), V1–N5 = 2.065(3), V1–O4 = 2.009(2), V1–O3 = 2.112(2), Li1–O4 = 1.925(6), O4–C49 = 1.301(5), C49–C51 = 1.102(9), Li2–C51 = 2.363(9), Li2–C49 = 2.652(9), Li1–O2 = 1.920(6), Li2–O1 = 1.943(6), Li1–N3 = 2.272(6), Li1–C24 = 2.324(6), Li1–C25 = 2.379(6), Li1–C26 = 2.364(7), Li1–C27 = 2.311(7), Li2–N1 = 2.357(6), Li2–C1 = 2.339(7), Li2–C2 = 2.293(7), Li2–C3 = 2.294(6), Li2–C4 = 2.330(7), O4–V1–O3 = 176.18(8), V1–O4–C49 = 127.8(3), O4–C49–C51 = 148.3(8), N5–V1–N2 = 176.7(1), N1–V1–N3 = 178.8(1), V1–O4–Li1 = 99.7(2), O1–Li2–C51 = 103.2(3).

1.920(6) Å, Li2–O1 = 1.943(6) Å]. The first lithium atom shares the oxygen of the ynoate [Li–O4 = 1.925(6) Å] with vanadium, while the second forms short contacts with both the terminal [Li2–C51 = 2.363(9) Å] and the central carbon atom [Li2–C49 = 2.648(9) Å]. These features, together with the perpendicular positioning of the alkali cation with respect to the C–C multiple bond, suggest that the alkali cation might interact with the π -electrons of the ynoate. Furthermore, the terminal carbon atom has been found disordered over two positions with 50% occupancy. In the second position (C50), the terminal carbon atom forms a nonbonding distance with lithium [Li2–C50 = 2.547(9) Å] which is rather similar to the distance formed by lithium with the central carbon atom of the ynoate unit. The

disorder of the terminal C atom over the two positions suggests that the ynoate anion might rapidly exchange in solution between the σ - and π -coordination coordination mode. The severe bending of the the Li2–O1 vector with respect to the Li2-centroid axis indicates that the interaction of the ynoate moiety with the lithium atom is real. Both the C–C and the C–O distances are substantially shorter than normal [C49–C51 = 1.102(9) Å, C49–O4 = 1.301(5) Å]. In particular, the C–C distance, even shorter than that in free acetylene and coordinated acetylide,¹² is rather difficult to rationalize in terms of coordination to the alkali cation and in view of the considerably low stretching frequency.

This novel method of formation of the ynoate moiety is probably an example of a cooperative interaction between different metals on the same substrate. The fragment is undoubtedly formed by the cleavage of coordinated THF, promoted by the d^2 vanadium and assisted by the two acidic lithium cations lying on the periphery of the macrocycle. This hypothesis is supported by the unprecedented formation of ethane and by the fact that the cleavage of THF into ketene and ethane does not require any redox process. We therefore speculate that initially there is the formation of an $(Et_3N_4)VLiCl(THF)$ species, which cleaves THF with the evolution of ethane. The hydrogen transfer is probably performed by the vanadium atom, assisted by the lithium atom which, firmly coordinating the oxygen of THF, thus labilizes the O–C bond. The subsequent elimination of chlorine from the *trans* position and a proton from the residual coordinated ketene, affords the final product.

We are currently investigating the chemical reactivity of **1**.

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Supplementary Material Available: Details of crystal data collection, tables listing atomic positional parameters, anisotropic thermal parameters, complete bond distances and angles for **1** (40 pages); listing of observed and calculated structure factors for **1** (40 pages). Ordering information is given on any current masthead page.

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