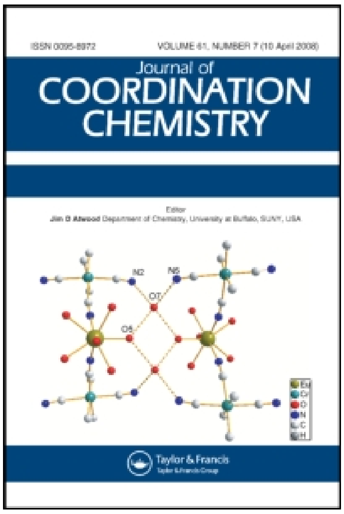

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X-ray characterization of Hnacnac^R and the first vanadium β-diiminate dimer (R = mesityl)

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X-ray characterization of Hnacnac^R and the first vanadium β-diiminate dimer (R = mesityl)

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The synthesis, characterization, and X-ray crystal structure of Hnacnac^R (R = mesityl) **1** as well as the structure of the first vanadium β-diiminate dimer, di-μ-hydroxo-di(nacnac^R)divanadyl(IV) (R = mesityl) **2** are reported. The reported β-diimine, **1**, is prepared through a condensation reaction between 2,4,6-trimethylaniline and 2,4-pentanedione. Compound **1** crystallizes in the $P\bar{1}$ space group with $Z' = 8$; **2** also crystallizes in $P\bar{1}$ with $Z' = 1$. The vanadium(IV) in **2** has the expected distorted square pyramidal geometry. Although the hydroxide hydrogen atoms can be found in the electron difference map, the existence of the bridging hydroxide in **2** was further confirmed through bond distance comparisons and bond valence sum analysis. Compound **1** was characterized by NMR, IR, and X-ray crystallography. (Hnacnac^R (R = mesityl) = 4-(2,4,6-trimethylphenylimino)-2-(2,4,6-trimethylphenylamino)-pent-2-ene; mesityl = 2,4,6-trimethylphenyl).

Keywords: Vanadium; X-ray crystal structure; Bond valence sums; β-diiminates

1. Introduction

Sterically bulky β-diiminates, often commonly referred to as 'nacnac' owing to their structural similarity to acetylacetonate (acac), have been shown to reduce the reactivity of normally very reactive species [1]. Our interest in the β-diiminate ligand arose from its ability to force vanadium(III) into an unusual tetrahedral geometry [2]. We had hoped to use the β-diiminate ligand (Hnacnac^R) to stabilize an abnormal geometry in a tetranuclear vanadium(III) phosph(on)ate cluster [3, 4]. Many variations of nacnac^R, where R is the group attached to the nitrogens, have been reported with an extensive series of metal complexes synthesized using these ligands [5]. Over the past ten years, the nacnac^R ligand has become common in inorganic coordination chemistry mainly due to its steric and electronic tuneability as well as its ability to stabilize complexes that exist in uncommon geometries or have typically unstable ligands [6–12]. This tuneability is seen in the variance of the aryl groups bound to the nitrogen atoms and in the backbone of the nacnac ligand. Demonstrating the nacnac ligand's ability to stabilize compounds in typically unstable geometries, very recently a linear homocatenated hexaindium compound was reported with each indium coordinated to a β-diiminate

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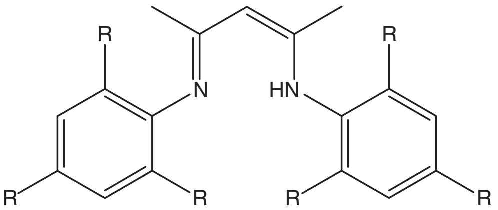
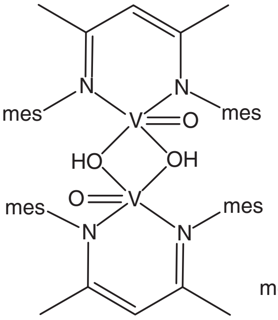


phenyl nacnac (R = H)
mesityl nacnac (R = CH_3), **1**

Scheme 1.



mes = 2,4,6-C_6H_2-Me_3

di-μ-hydroxo-di(nacnac^R)divanadyl(IV) (R = mesityl), **2**

Scheme 2.

(nacnac^R (R = 3,5-dimethylphenyl)) [12]. Here we present the synthesis and X-ray structural characterization of Hnacnac^R (R = mesityl) **1** (4-(2,4,6-trimethylphenylimino)-2-(2,4,6-trimethylphenylamino)pent-2-ene) (mesityl = 2,4,6-trimethylphenyl), as well as the X-ray structural characterization of a vanadium(IV) hydroxide bridged dimer, di-μ-hydroxo-di(nacnac^R)divanadyl(IV) (R = mesityl) **2**. Bond valence sum (BVS) calculations were used to confirm the oxidation state of the vanadium and the bridging hydroxide in **2**.

Although other transition metal nacnac dimers with bridging hydroxide have been reported with M = Co [13], Cu [14], Zn [15, 16], and Ni [17], **2** represents the first example of a vanadium nacnac dimer.

2. Experimental

2.1. *Materials*

All solvents were of reagent grade and used as received. 2,4,6-trimethylaniline (Acros, 97%) and 2,4-pentanedione (Aldrich, 99 + %) were used as received.

2.2. *Physical measurements*

NMR spectra (^1H, ^{13}C) were collected on a 400 MHz varian spectrometer and were referenced to residual solvent [18]. Microanalyses were conducted by the

Microanalytical Laboratory, School of Chemical Sciences, University of Illinois, Urbana-Champaign, IL USA. Infrared data were collected on a Perkin-Elmer Spectrum 100 FT-IR spectrometer as neat powders on a diamond anvil cell.

2.3. *Synthesis of Hnacnac^R (R = mesityl) (1)*

An amount of 1.00 mL (9.8 mmol) 2,4-pentanedione was added to 40 mL of absolute ethanol and 3.00 mL (21.3 mmol) of 2,4,6-trimethylaniline and 0.80 mL (9.6 mmol) of concentrated hydrochloric acid was added dropwise turning the solution a golden brown. The reaction flask was refluxed for three days; the ethanol was removed *in vacuo* to afford an orange-yellow solid. The solid was dissolved in 20 mL of methylene chloride and washed with saturated aqueous Na_2CO_3 for 2 h until being placed in a seperatory funnel. The organic layer was dried with $MgSO_4$ and reduced *in vacuo* leaving an orange-red oil. The oil was placed on the vacuum line and pumped for thirty minutes after which 10 mL of methanol was added to the oil to precipitate an off-white colored solid. Compound **1** can be recrystallized from ethanol. X-ray quality crystals were formed by sublimation. Yield: 1.3193 grams (3.9442 mmol) (41% based on 2,4 pentanedione): Anal. Calcd for $C_{23}H_{30}N_2$: C, 82.58; H, 9.05; N, 8.38. Found: C, 82.37; H, 9.15; N, 8.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.21 (s, NH, 1H), 6.90 (s, Ar–H, 4H), 4.90 (s, =C–H), 2.30 (s, CH_3, 6H), 2.17 (s, CH_3, 12H), 1.73 (s, CH_3, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 161.2, 141.4, 133.7, 132.0, 128.7, 93.6, 21.1, 20.5, 18.5. m.p.: 90–91°C. IR (cm^{-1}): 2915, 2853, 2729, 1732, 1618, 1548, 1491, 1473, 1427, 1373, 1357, 1339, 1306, 1273, 1251, 1186, 1145, 1024, 1011, 958, 928, 882, 853, 795, 710. This compound has been further characterized using X-ray crystallography.

2.4. *Synthesis of di-μ-hydroxo-di(nacnac^R)divanadyl(IV) (R = mesityl) (2)*

Complex **2** was prepared serendipitously in an attempt to synthesize the previously reported nacnac^{R}dichlorovanadium(III) (R = mesityl) [2]. The addition of Li(nacnac^R) (R = mesityl) to $VCl_3(THF)_3$ [19] occurred quickly in THF and gave a dark brown solution. The THF was removed under reduced pressure leaving a brown solid that was heated at 80°C for 75 min. Hexane (6 mL) was added to the solid upon which some of the solid dissolved affording a brown-green solution. This hexane wash was allowed to sit at 4°C for 3 days upon which dark green X-ray diffraction quality crystals formed. X-ray diffraction data showed that the complex formed was a hydroxide bridged β-diiminate dimer, di-μ-hydroxo-di(nacnac^R)divanadyl(IV) (R = mesityl) (**2**).

2.5. *X-ray structure determinations*

Single X-ray diffraction quality crystals were obtained for **1** through sublimation, and by slow evaporation of hexane for **2**. Intensity data were collected on an Oxford Diffraction Xcalibur3 diffractometer equipped with a CCD area detector. Graphite monochromated Mo-Kα radiation from an Enhance source was used. Data were reduced and corrected for absorption using the CrysAlis Software Suite [20]. Structure solutions were obtained by direct methods and were refined on F^2 with the use of full-matrix least-squares techniques [21]. All non-hydrogen atoms were refined

Table 1. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{23}H_{30}N_2$	$C_{46}H_{60}N_4O_4V_2$
Formula weight	334.49	834.86
Temperature (K)	110(2)	110(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.3203(10)	8.2270(11)
b (Å)	13.5617(16)	10.4781(12)
c (Å)	32.798(7)	13.5987(14)
α (°)	81.218(13)	71.568(10)
β (°)	88.036(13)	78.152(10)
γ (°)	80.597(10)	76.934(2)
V (Å^3)	4041.8(11)	1071.9(2)
Z'	8	1
μ (mm^{-1})	0.064	0.483
Reflections collected	48203	15431
Independent reflections	19350	4408
R_1[a]	0.0488	0.0560
wR_2[b]	0.0998	0.1197

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]\}^{1/2}$; $w_1 = 1/[\sigma^2(F_o^2) + (0.0547P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$; $w_2 = 1/[\sigma^2(F_o^2) + (0.0653P)^2 + 0.9005P]$ where $P = (F_o^2 + 2F_o^2)/3$.

anisotropically and hydrogen atoms were refined with a riding model or in the case of the hydroxide hydrogen were found then fixed. Both compounds solved and refined routinely. The crystallographic results are summarized in table 1. Further details are available in Supporting Information.

3. Results and discussion

3.1. *Syntheses*

The synthesis of **1** represents a modification to a synthetic procedure that has been previously reported for Hnacnac^R (R = 2,6–C_6H_3–$^iPr_2$) [22]. The reaction to produce **1** is condensation between 2,4,6-trimethylaniline and 2,4-pentanedione. The final product is precipitated from the oil through the addition of methanol.

The hydroxide present in **2** most likely originated from trace amounts of water; these bridging hydroxide molecules in **2** indicate the high oxophilicity of vanadium [23]. Numerous unsuccessful attempts were made to perform a direct synthesis for **2**. Single crystals of **2** were isolated in such small amounts that we were, alas, unable to obtain the IR spectrum.

3.2. *X-ray structures*

3.2.1. Hnacnac^R (R = mesityl) (1). Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with four crystallographically unique molecules within the asymmetric unit and two asymmetric units per unit cell ($Z = 2$, $Z' = 8$). The data show that no evidence of a supercell and no evidence of additional symmetry was found using the ADDSYM program of the PLATON suite of programs [24]. A displacement ellipsoid plot of one of the unique molecules in the asymmetric unit of **1** is shown in figure 1. Selected bond

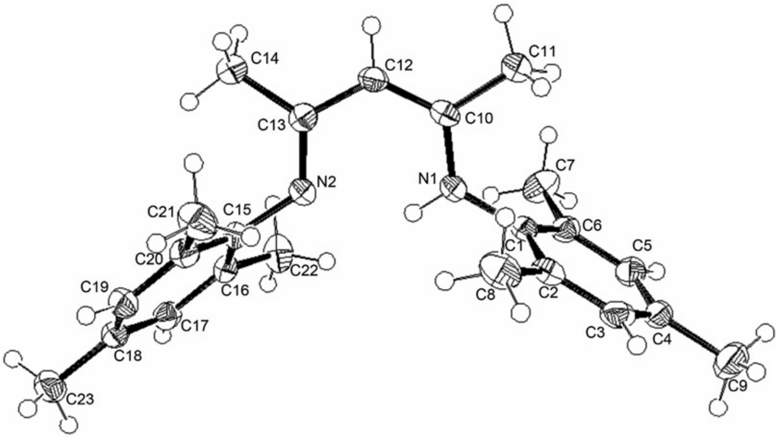


Figure 1. 50% displacement ellipsoid plot of **1**. Four molecules exist in the asymmetric unit; one molecule is shown for clarity.

Table 2. Selected bond distances (Å) angles (°) and torsion angles (°) for one molecule in the asymmetric unit of **1**.[a]

C1–C2	1.389 (2)	C12–C13	1.417 (2)
C1–C6	1.396 (2)	C13–N2	1.315 (2)
C1–N1	1.424 (2)	C13–C14	1.503 (2)
C2–C3	1.388 (2)	C15–C20	1.395 (2)
C2–C8	1.505 (2)	C15–C16	1.397 (2)
C3–C4	1.377 (3)	C15–N2	1.424 (2)
C4–C5	1.379 (3)	C16–C17	1.386 (2)
C4–C9	1.508 (3)	C16–C22	1.499 (2)
C5–C6	1.388 (2)	C17–C18	1.383 (2)
C6–C7	1.502 (3)	C18–C19	1.384 (3)
C10–N1	1.334 (2)	C18–C23	1.510 (2)
C10–C12	1.378 (2)	C19–C20	1.391 (2)
C10–C11	1.498 (2)	C20–C21	1.501 (3)
C10–C12–C13	125.82 (16)	C13–N2–C15	124.14 (14)
C10–N1–C1	125.14 (14)		
N1–C10–C12–C13	4.2 (3)	C10–C12–C13–N2	0.6 (3)

[a]See the supplementary material for all bonds and angles for all molecules.

distances and angles for **1** are listed in table 2. The hydrogen atoms were refined using a riding model. The N–H hydrogens were fixed to the nitrogen with the longer C–N bond. The three dimensional packing of **1** is dominated by π–π stacking where the methyl groups of the mesityl units are pseudo-eclipsed. The average distance between the mesityl rings is 4.7361(21) Å. Figure 2 shows the stacking of the aromatic rings. The X-ray structure for **1** was also collected at room temperature on an Enraf-Nonius CAD-4 diffractometer; no significant changes in the unit cell were observed.

3.2.2. Di-μ-hydroxo-di(nacnac^{R})divanadyl(IV) (R = mesityl) (2). Compound **2** crystallizes in the triclinic spacegroup $P\bar{1}$,with one molecule in the unit cell and one half of a molecule in the asymmetric unit ($Z = 2$, $Z' = 1$). The inversion center in this molecule resides between the two vanadium atoms. Selected bond distances and angles for **2** are listed in table 3. The vanadyl, V=O, bond length in **2** (1.594(2) Å) is typical of

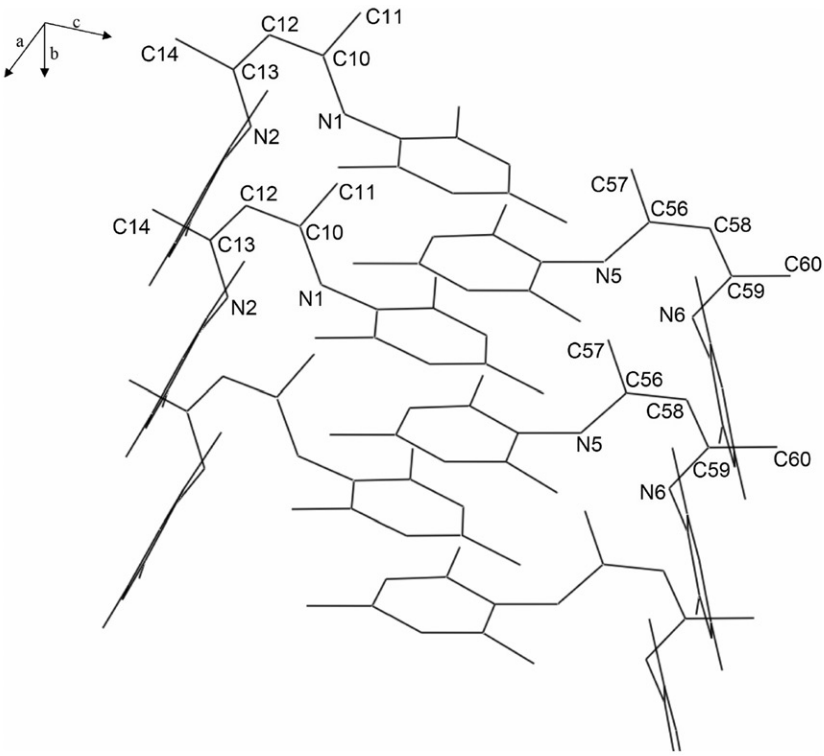


Figure 2. π–π stacking in **1** viewed approximately along ($\bar{1}$ 1 0).

Table 3. Selected bond distances (Å) angles (°) and torsion angles (°) for **2**.[a]

O1–V1	1.594 (2)	N1–V1	2.043 (3)
O2–V1	1.983 (2)	N2–V1	2.052 (3)
O2–V1A[b]	1.979 (2)		
O1–V1–O2	110.19 (11)	O1–V1–N2	104.64 (11)
O1–V1–N1	104.54 (11)	O2–V1–N2	144.68 (10)
O2–V1–N1	89.18 (10)	N1–V1–N2	87.69 (11)
O1–V1–O2A[b]	110.13 (11)	O2–V1–O2A[b]	110.13 (11)
O2A[b]–V1–N1	144.80 (10)	O2A[b]–V1–N2	89.38 (10)
C12–C10–N1–V1	−22.3 (4)	C10–N1–V1–N2	37.9 (2)
C12–C13–N2–V1	13.3 (4)	C1–N1–V1–N2	−148.6 (2)
C10–N1–V1–O2	−177.2 (2)		

[a] See the supplementary material for complete details.
[b] Symmetry code $-x$, $-y$, $-z$.

complexes of this type [25–39]. A displacement ellipsoid plot for **2** is shown in figure 3. Compound **2** represents the first di(nacnac^R) vanadium dimer, but structural comparisons can be made to other bridged divanadyl molecules to support the hydroxide bridged vanadium(IV) dimer over the oxo bridged vanadium(V) dimer.

The hydrogens in the hydroxide bridges in **2** were first found in the electron difference map and their thermal parameters were then fixed. The average V–OH distance in **2** is 1.981(3) Å. Using data from the Cambridge Structural Database (CSD) [40], the average $(V{=}O)_2(\mu\text{–}OH)_2$ distance is 1.992 ± 0.087 Å, the average $(V{=}O)_2(\mu\text{–}O)_2$ is

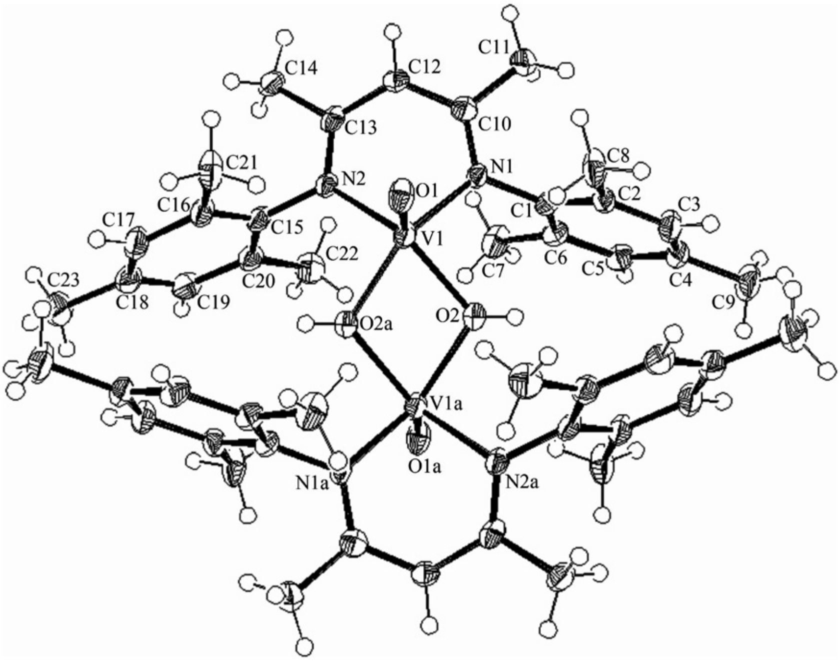


Figure 3. 50% displacement ellipsoid plot of **2**.

2.259 ± 0.26, and the average $(V{=}O)_2(\mu\text{–}OR)_2$ distance is 2.02 ± 0.07. Although the standard deviations in these averages are large, they still support the assignment of a bridging hydroxide in 2.

The coordination environment around each vanadium(IV) in **2** can be described as distorted square pyramidal with each vanadium sitting 0.5968(11) Å above the N/N/O/O plane defined by the nitrogen atoms in the chelating nacnac ligand and the bridging hydroxides.

3.3. *Bond valence sum calculations*

In addition to the comparisons with the known structures in the CSD, the formation of **2** is also suggested through bond valence sum (BVS) calculations [41, 42]. The V^{IV} oxidation state as well as the presence of a bridging hydroxide rather than an oxide were confirmed by these BVS calculations. The values used for the calculations were obtained from the bond lengths in table 3 and published R_o values [43–45]. The results of these calculations show the BVS value for V^{IV} is 3.9, whereas the same calculations using R_o values for V^{III} and V^{V} are 3.6 and 4.2, respectively. The BVS values for V^{III} and V^{V} are significantly different from the expected values of three and five, respectively. Additionally, the calculated BVS for O2 as a bridging oxide is 1.2 which is considerably smaller than the expected BVS of two for an oxygen atom; this indicates a hydrogen is 'missing' from the bridging oxygen. The use of BVS in this fashion is well understood. For example, protonation levels of O^{2-}, MeO^{-}, and MeOH in Mn/Ln tetramers (Ln = Y, Yb) have also been confirmed using

BVS analysis [46]. BVS analysis has been used to successfully determine V^{IV} from V^{V} in extended structures such as V_4O_7 [47], as well as in discrete vanadium clusters [48–50].

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 646995 and 646996 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CBS 1EZ, UK, Fax +44 1223 366 033, Email: deposit@ccdc.ac.uk or on the web at http://www.ccdc.cam.ac.uk. More detailed BVS data as well as characterization of **1** are also available in the supplementary material.

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