

## [Vanadium(salen)benzilate]—A Novel Non-oxo Vanadium(IV) Complex

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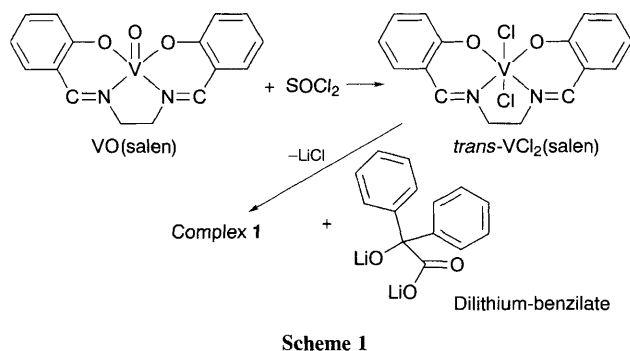
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[Vanadium(salen)benzilate].1.5CH<sub>2</sub>Cl<sub>2</sub>, the preparation, X-ray structure, redox and spectroscopic properties of which are reported, is the first monomeric non-oxo vanadium(IV) complex with concomitant vicinal carboxylate and hydroxylate coordination.

Vanadium attains an important role in various biological processes,<sup>1</sup> a fact which has invoked recent interest in vanadium coordination compounds that exhibit relevance to biogenic systems. While the chemistry of oxovanadium(V) and (IV) is on a well developed level,<sup>2</sup> far less information is available on non-oxo ('bare') complexes.<sup>3</sup> Non-oxo vanadium centres have been reported for amavadin, a low molecular weight V<sup>IV</sup> compound with mixed carboxylate hydroxylamide coordination present in mushrooms of the genus *Amanita*,<sup>4</sup> and for the co-factor in vanadium nitrogenase. The nature of the V centre of the nitrogenases appears to be very similar to that of the Mo site from XAS spectroscopic studies,<sup>5</sup> *i.e.* vanadium is coordinated to  $\mu_3$ -S<sup>2-</sup>, and probably also to histidin-N and the alkoxo and central carboxylate group of homocitrate.<sup>6a</sup> Carboxylate (glutamate or aspartate) and alkoxide (serine) coordination has also been inferred from, *inter alia*, EXAFS data of the active site of vanadate-dependent bromoperoxidase.<sup>6b</sup> We report here on the preparation, structure and redox properties of a model compound for simultaneous, non-bridging carboxylate/alkoxide plus N (enamine) coordination to bare vanadium, *viz.* [V(salen)benzilate] **1**, where salen is the double Schiff base formed from salicylaldehyde and ethylenediamine. A few dimeric oxovanadium complexes with either carboxylate or alkoxide in bridging positions have been described earlier. Examples are the V<sup>IV</sup> complex [(VO)<sub>2</sub>(citrate)<sub>2</sub>]<sup>4-</sup>,<sup>7a</sup> and the V<sup>V</sup> complexes [(VO(O<sub>2</sub>))<sub>2</sub>(citrate)<sub>2</sub>]<sup>2-</sup><sup>7b</sup> and [(VO<sub>2</sub>)<sub>2</sub>(2-oxo-2-ethylbutanoate)<sub>2</sub>]<sup>2-</sup>.<sup>7c</sup> Further, the complex [H<sub>x</sub>VVO<sub>3</sub>(lactate)]<sup>(3-x)-</sup> has been characterized in solution,<sup>8</sup> while hydroxycarboxylic acids with the OH at a secondary or primary carbon are usually oxidatively decarboxylated by V<sup>V</sup>.<sup>9</sup>

For the synthesis of **1** (Scheme 1), we took advantage of the deoxygenation reaction of [VO(salen)] with SOCl<sub>2</sub> to produce [VCl<sub>2</sub>(salen)].<sup>10</sup> Compound **1** was prepared by sequentially adding, in inert gas atmosphere, the Li<sub>2</sub>-salt of benzilic acid (prepared from benzilic acid and butyllithium in hexane) to [VCl<sub>2</sub>(salen)] in CH<sub>2</sub>Cl<sub>2</sub>. Red-brown 1.1.5CH<sub>2</sub>Cl<sub>2</sub> was recovered in 70% yield after about 24 h of reaction time by filtration and slow evaporation of the solvent from the filtrate.† Characteristic IR bands (KBr) were found at 1618 (C=N), 1600 (CO<sub>2</sub><sup>-</sup>), 1284 (Ph-O) and 1151 cm<sup>-1</sup> (C-O). No band typical of the vanadyl group was found as long as the samples were handled under strict exclusion of air.

Suitable crystals for an X-ray structure analysis‡ of 1.1.5CH<sub>2</sub>Cl<sub>2</sub> were obtained by slow diffusion of pentane into a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution of the complex. The molecular structure and atomic numbering scheme are depicted in Fig. 1.



The V<sup>IV</sup> ion is in a distorted octahedral environment. One of the phenolate oxygens, the two Schiff base nitrogens and the alkoxide of benzoic acid form the equatorial plane. The remaining phenolate and the carboxylate oxygen, mutually *trans*, complete the coordination sphere. The V–O(phenolic) bond lengths  $d[V-O(1)] = 1.871(6)$  Å and  $d[V-O(2)] = 1.899(4)$  Å compare with V–O(phenolic) bond distances of 1.83–1.80 Å in related Schiff base complexes.<sup>11–14</sup> Similarly, there are no significant differences in the V–N(amine) bond lengths. The V–O(carboxylate) distance of 2.004(4) Å extends the usual range of 1.92–1.98 Å reported for monodentate carboxylates of vanadium.<sup>12,15</sup> Somewhat elongated  $d[V-O(carboxylate)]$  have been reported for coordinated carboxylate additionally involved in hydrogen bonds;<sup>14</sup> no such H-bond interaction has been observed in the case of **1**. On the other hand, the comparatively large  $d[C(17)-O(5)] = 1.233(8)$  Å [O(5) is the non-coordinated carboxylate oxygen] may be a consequence of a relatively close (2.289 Å) contact to the (CH)<sub>8</sub> of the ethylenediamine group of a symmetry-related molecule in the adjacent unit cell.  $d[V-O(alkoxide)] = 1.809(5)$  Å compares to  $d(V-OR)$  in vanadate esters<sup>16</sup> but is longer than the 1.72 Å distance associated with assumed serine coordination in native (V<sup>V</sup>) vanadate-dependent bromoperoxidase.<sup>6</sup>

The X-band EPR spectrum of **1** in MeCN at ambient temperature consists of an eight-line pattern with  $g_{iso} = 2.047$  and  $A_{iso} = 99.05 \times 10^{-4}$  cm<sup>-1</sup>. Cyclic voltammetric studies show that **1** dissolved in MeCN is capable of both, a reversible one-electron oxidation at  $E_{1/2} = +0.92$  V and a reversible one-electron reduction at  $E_{1/2} = -0.338$  V vs. SCE (V<sup>III</sup> is the oxidation state of vanadium in oxidized vanadium nitrogenase).

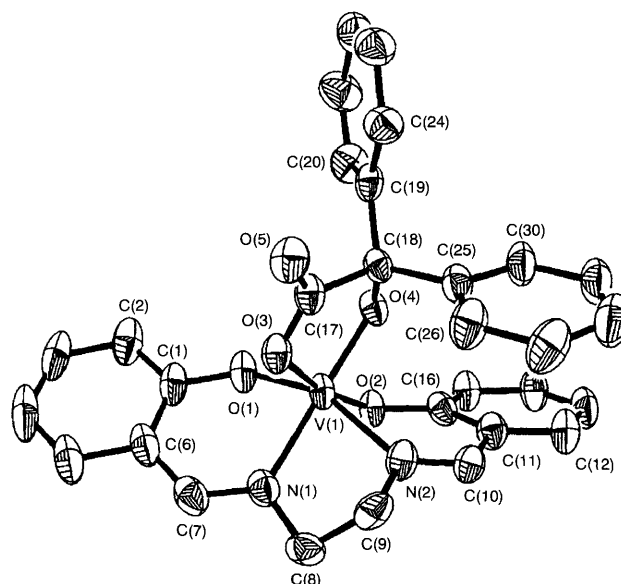


Fig. 1 ORTEP view (50% probability ellipsoids) of [V(salen)benzilate] **1**. Selected bond lengths (Å) and angles (°): V(1)–O(1) 1.871(6), V(1)–O(2) 1.899(4), V(1)–O(3) 2.004(4), V(1)–O(4) 1.809(5), V(1)–N(1) 2.102(8), V(1)–N(2) 2.057(7); O(1)–V(1)–N(1) 85.6(3), O(1)–V(1)–O(2) 87.2(2), O(3)–V(1)–O(4) 79.7(2), O(2)–V(1)–N(2) 85.7(2), N(1)–V(1)–N(2) 75.6(3); O(4)–V(1)–N(1) 156.5(2), O(4)–V(1)–O(1) 108.8(3), O(2)–V(1)–O(3) 168.5(3), O(1)–V(1)–N(2) 155.9(3).

Chemical oxidation of **1** is readily accomplished using  $\text{Ag}[\text{BF}_4]$  to yield the non-oxo  $\text{V}^{\text{V}}$  complex  $[\text{V}(\text{salen})\text{benzilate}][\text{BF}_4]$  **2**. Compound **2** was isolated from the  $\text{CH}_2\text{Cl}_2$  solution after filtration from  $\text{Ag}$  and excess  $\text{Ag}[\text{BF}_4]$  by slow removal of the solvent *in vacuo*.† The  $^{51}\text{V}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  gave a signal at  $\delta -596$  (relative to  $\text{VOCl}_3$ ) with a width at half-height  $W_{1/2} = 95$  Hz. The chemical shift is in accord with the  $\text{N}_2\text{O}_2\text{O}'\text{O}''$  ligand donor set in a somewhat strained octahedral environment.<sup>17</sup>

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## Footnotes

† Satisfactory microanalyses were obtained for  $1 \cdot 1.5\text{CH}_2\text{Cl}_2$  and for **2**.

‡ Crystal data for  $1 \cdot 1.5\text{CH}_2\text{Cl}_2$ ,  $\text{C}_{30}\text{H}_{24}\text{O}_5\text{V} \cdot 1.5\text{CH}_2\text{Cl}_2$ ,  $M = 673.82$ , triclinic space group  $P\bar{1}$ ,  $a = 9.813(2)$ ,  $b = 10.557(2)$ ,  $c = 16.155(4)$  Å,  $\alpha = 103.46(2)$ ,  $\beta = 93.09(2)$ ,  $\gamma = 110.82(2)^\circ$ ,  $Z = 2$ ,  $V = 1504.1(6)$  Å<sup>3</sup>,  $D_c = 1.488$  g cm<sup>-3</sup>,  $\mu = 55.8$  cm<sup>-1</sup>, an absorption correction was applied. Data were collected at 173 K on an Enraf Nonius CAD4 diffractometer (Cu-K $\alpha$  radiation,  $\lambda = 1.54178$  Å, graphite monochromator), in the  $2\theta$  scan mode,  $\theta = 18.45$ – $76.68^\circ$ . Measured reflections 4495; refined parameters 424. The solution of the structure (SHELX 86) and refinement (SHELXL 93) converged to a conventional [*i.e.* based upon 4304 reflections with  $F_o > 4\sigma(F_o)$ ]  $R1 = 0.1062$  and  $wR2 = 0.2610$ . Non-hydrogen atoms were refined anisotropically, hydrogen atoms were calculated into ideal positions and included in the final FMLS refinement. Goodness of fit = 1.042. The relatively high final  $R$  values are a consequence of the disadvantageous crystal form ( $0.07 \times 0.46 \times 0.93$  mm<sup>3</sup>) and disorder problems with  $\text{CH}_2\text{Cl}_2$  of solvation. The disorder of the 3  $\text{CH}_2\text{Cl}_2$  molecules per unit cell extends to the carbons and the chlorines, which were treated with occupancy factors of 1/2. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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