

## A VO<sup>3+</sup> Complex Incorporating Aromatic Carboxylate Binding : Synthesis, Structure and Metal Redox

Joydip Chakravarty, Somnath Dutta and Animesh Chakravorty\*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

In the title complex [VOL<sup>1</sup>L<sup>2</sup>] derived from the tridentate 2-hydroxy-2'-carboxy-5-methylazobenzene (H<sub>2</sub>L<sup>1</sup>) and the bidentate quinolin-8-ol (HL<sup>2</sup>) the V–O(carboxylate) and V–N(azo) distances are respectively 1.892(4) and 2.098(5) Å; frozen solution (77 K) EPR parameters of electrogenerated [VOL<sup>1</sup>L<sup>2</sup>]<sup>–</sup> lie close to those of reduced bromoperoxidase (low pH).

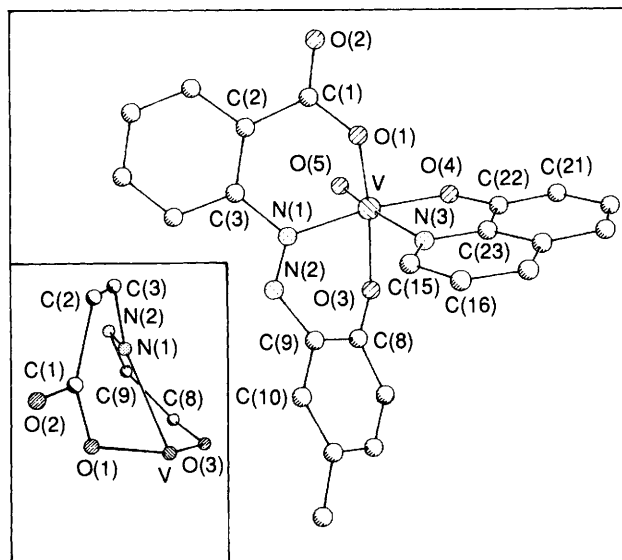
The VO<sup>3+</sup> motif coordinated to O–N donors is relatively uncommon<sup>1</sup> and structurally characterized species incorporating carboxy binding are very rare.<sup>2,3</sup> Such binding is of special interest since it has been implicated<sup>4</sup> within the O–N ligated<sup>5</sup> VO<sup>3+</sup> site of bromoperoxidases.<sup>6</sup> Herein we describe an O–N coordinated VO<sup>3+</sup> complex in which one of the binding sites is an aromatic carboxylate function (the other binding functions are phenolate, azo and pyridine).

A solution of equimolar (1 mmol each) proportions of 2-hydroxy-2'-carboxy-5-methylazobenzene (H<sub>2</sub>L<sup>1</sup>) and bis-(acetylacetonato)oxovanadium(IV) was heated to reflux (3 h) in methanol (20 cm<sup>3</sup>). The solvent was removed and the residue was washed with dichloromethane; quinolin-8-ol (1 mmol) (HL<sup>2</sup>) and methanol (20 cm<sup>3</sup>) were then added. The solution was heated in air on a steam-bath affording the diamagnetic nonelectrolytic complex [VOL<sup>1</sup>L<sup>2</sup>] as a black solid (yield, 90%; satisfactory elemental analysis obtained;  $\nu_{\text{VO}}$  970 cm<sup>–1</sup>).

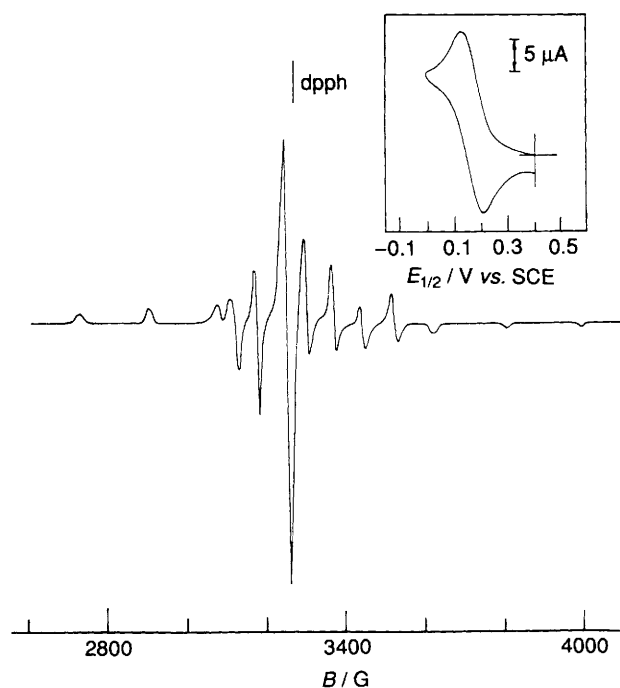
The X-ray structure† of [VOL<sup>1</sup>L<sup>2</sup>].2MeOH is shown in Fig.

† Crystal data for [VOL<sup>1</sup>L<sup>2</sup>].2MeOH (the crystal was sealed in a capillary containing the mother liquor in absence of which loss of solvent and crystallinity occurred rapidly): C<sub>25</sub>H<sub>24</sub>N<sub>3</sub>O<sub>7</sub>V, *M* = 529.4, triclinic, space group *P* $\bar{1}$ , *Z* = 2, *a* = 8.104(3), *b* = 12.217(4), *c* = 12.573(5) Å,  $\alpha$  = 100.62(3),  $\beta$  = 92.26(3),  $\gamma$  = 105.81(3)°, *V* = 1176(1) Å<sup>3</sup>, *T* = 295 K, *D*<sub>c</sub> = 1.495 g cm<sup>–3</sup>,  $\mu(\text{Mo-K}\alpha)$  = 4.76 cm<sup>–1</sup>, crystal dimension 0.32 × 0.43 × 0.56 mm<sup>3</sup>. Data were collected in the range 3.0 ≤ 2θ ≤ 50° by the ω-scan method on a Nicolet R3m/V four-circle diffractometer. Lorentz-polarization corrections were applied. Out of 4250 unique reflections, 2605 with *I* > 3.0σ(*I*) were used for structure solution (direct methods). All non-hydrogen atoms were refined anisotropically. No. of variables 325. Hydrogen atoms were included at calculated positions (*U* = 0.08 Å<sup>2</sup>). The structure refined to *R* = 6.69% and *R*<sub>w</sub> = 6.69%. The highest difference Fourier peak was 0.76 e Å<sup>–3</sup>. All calculations were done using the SHELXTL-PLUS program<sup>7</sup> package. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

1 and selected bond parameters are listed in the legend. The MeOH molecules (not shown) are not linked to the metal complex in any way. The metal atom is shifted towards O(5) by 0.30 Å away from the plane of O(1), N(1), O(3) and O(4).



**Fig. 1** Perspective view of [VOL<sup>1</sup>L<sup>2</sup>].2MeOH. The nonplanarity of the VL<sup>1</sup> chelate rings is shown in the inset. Pertinent distances (Å) and angles (°): V–O(1), 1.892(4); V–O(3), 1.895(5); V–O(4), 1.841(4); V–O(5), 1.579(4); V–N(1), 2.098(5); V–N(3), 2.387(4); O(1)–C(1), 1.303(8); O(2)–C(1), 1.218(10); O(3)–C(8), 1.298(8); O(4)–C(22), 1.350(6); O(1)–V–O(3), 158.2(2); O(1)–V–O(4), 95.5(2); O(3)–V–O(4), 95.3(2); O(1)–V–O(5), 99.1(2); O(3)–V–O(5), 97.7(2); O(4)–V–O(5), 99.9(2); O(1)–V–N(1), 81.7(2); O(3)–V–N(1), 81.8(2); O(4)–V–N(1), 160.4(2); O(5)–V–N(1), 99.6(2); O(1)–V–N(3), 79.7(2); O(3)–V–N(3), 84.5(2); O(4)–V–N(3), 76.3(2); O(5)–V–N(3), 175.8(2); N(1)–V–N(3), 84.2(2).



**Fig. 2** X-Band EPR spectra of electrogenerated  $[\text{VOL}^1\text{L}^2]^-$  in dichloromethane at 77 K; dpph = diphenylpicrylhydrazyl. Cyclic voltammogram of  $[\text{VOL}^1\text{L}^2]$  in dichloromethane ( $0.1 \text{ mol dm}^{-3} \text{ Et}_4\text{NClO}_4$ ) at 298 K is shown in the inset.

The  $\text{VL}^2$  fragment, O(5) and N(1) form a good plane but the six-membered  $\text{VL}^1$  rings are highly nonplanar (Fig. 1). The  $\text{V}=\text{O}$  length,  $1.579(4) \text{ \AA}$ , is normal<sup>1-3</sup> and the long bond *trans* to it is formed with N(3) of  $\text{L}^2$ . The  $\text{V}-\text{O}(\text{phenolato})$  length in the  $\text{VL}^1$  fragment is *ca.*  $0.05 \text{ \AA}$  longer than that in the  $\text{VL}^2$  fragment and correspondingly the  $\text{C}-\text{O}(\text{phenolato})$  length is significantly shorter in  $\text{VL}^1$ . In native bromoperoxidases the  $\text{V}=\text{O}$ ,  $\text{V}-\text{O}$  and  $\text{V}-\text{N}/\text{O}$  lengths are  $1.61$ ,  $1.72$  and  $2.11 \text{ \AA}$  respectively (EXAFS data).<sup>5</sup> The agreement with  $[\text{VOL}^1\text{L}^2]\cdot 2\text{MeOH}$  is not particularly striking since  $\text{L}^1$  and  $\text{L}^2$  are not expected to reproduce the details of enzyme ligand environment.

To our knowledge  $[\text{VOL}^1\text{L}^2]\cdot 2\text{MeOH}$  is the only structurally characterized  $\text{VO}^{3+}$  complex incorporating aromatic carboxylate coordination. The  $\text{V}-\text{O}(\text{carboxylate})$  distance,  $1.892(4) \text{ \AA}$ , is shorter than the corresponding distances ( $1.95$ – $2.08 \text{ \AA}$ , excluding *trans* labilised bonds) in the two structurally known  $\text{VO}^{3+}$  carboxylate (both aliphatic) complexes.<sup>2,3</sup> The present complex is also novel in being the only example of azo binding to  $\text{VO}^{3+}$ .

A characteristic feature of the  $\text{VO}^{3+}$  centre in bromoperoxidases is that it is reducible to form an EPR-active  $\text{VO}^{2+}$  centre.<sup>8,9</sup> The reduced state  $[\text{V}^{\text{IV}}\text{OL}^1\text{L}^2]^-$  of our complex can be generated quantitatively in dichloromethane solution by

coulometric reduction at  $-0.10 \text{ V}$  vs. saturated calomel electrode (SCE) and upon reoxidation at  $+0.40 \text{ V}$  the parent complex is fully regenerated.

The solution magnetic moment of electrogenerated  $[\text{VOL}^1\text{L}^2]^-$  is  $1.74 \mu_{\text{B}}$  and its glassy state EPR spectrum (77 K) is axial with  $g_{\parallel} 1.949$ ;  $g_{\perp} 1.982$ ;  $A_{\parallel} 165.2 \times 10^{-4} \text{ cm}^{-1}$ ;  $A_{\perp} 58.8 \times 10^{-4} \text{ cm}^{-1}$  (Fig. 2). These values are curiously close to those in reduced bromoperoxidase (citrate buffer, low pH)<sup>9</sup>:  $g_{\parallel} 1.950$ ;  $g_{\perp} 1.980$ ;  $A_{\parallel} 167.5 \times 10^{-4} \text{ cm}^{-1}$ ;  $A_{\perp} 55.1 \times 10^{-4} \text{ cm}^{-1}$ .

The  $[\text{VOL}^1\text{L}^2]^-$ – $[\text{VOL}^1\text{L}^2]$  couple (Fig. 2) is observable by cyclic voltammetry, the  $E_{\frac{1}{2}}$  value being  $0.17 \text{ V}$ . Electrogenerated solutions of  $[\text{VOL}^1\text{L}^2]^-$  are readily oxidized to  $[\text{VOL}^1\text{L}^2]$  by oxygen (or air). This explains the formation of  $[\text{VOL}^1\text{L}^2]$  from  $\text{VO}^{2+}$  precursors during chemical synthesis, *vide supra*.

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