A Structural Model for Vanadyl–Histidine Interactions: Structure Determination of [VO(1-vinylimidazole)₄Cl]Cl by a Combination of X-Ray Crystallography and X-Ray Absorption Spectroscopy

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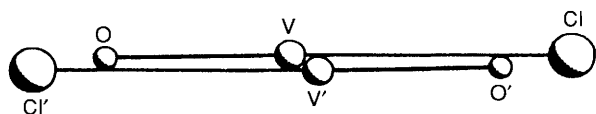[b] Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU, UK

[VO(1-vinylimidazole)₄Cl]Cl is prepared and spectroscopically characterized and structural information obtained from vanadium K-edge EXAFS used to solve a disorder problem encountered in the refinement of the crystal structure; oxovanadium(IV) bound to imidazole groups has relevance to the possible biochemical functions of vanadium.

Vanadium is a trace element, essential for the normal development and growth of plants and animals.[1,2] Vanadium-dependent non-haem bromo/iodoperoxidases (BPO/IPO) have been identified in marine algae, such as *Ascophyllum nodosum*,[1–4] and a terrestrial lichen (*Xanthoria parienta*).[5] The bromoperoxidase from *A. nodosum* is the best characterized of these systems. During turnover, the enzyme operates with the metal exclusively in the +V oxidation state and, in concert with hydrogen peroxide, produces a brominating species tentatively assigned as HOBr.[6] Reduction of the enzyme with sodium dithionite produces an inactive form of BPO containing V^IV. The accessibility of both diamagnetic (V^V) and paramagnetic (V^IV) states of the metal centre has permitted a variety of spectroscopic investigations directed at the elucidation of the nature of the metal site (or sites). For the V^IV state, ESEEM (electron spin echo envelope modulation) data[7] indicate nitrogen coordination and the results of a vanadium K-edge EXAFS study[8] are consistent with the presence of a VO²⁺ centre coordinated to *ca.* two imidazole groups (of histidine residues) together with *ca.* three O-donor ligands. Although imidazole groups are effective ligands and coordination to VO²⁺ has been monitored spectroscopically,[9] no structural studies of vanadium–imidazole complexes appear to have been reported previously. This is unexpected in view of similar patterns of coordination chemistry seen for VO²⁺ and Cu²⁺ and the large number of crystallographically characterized imidazole complexes of copper(II). Herein, we report the synthesis, structural and spectroscopic characterization of [VO(1-vinylimidazole)₄Cl]Cl 1.

1 was readily prepared by reacting [VOCl₂(tmu)₂][10] (tmu = N,N,N',N'-tetramethylurea) with 1-vinylimidazole (1:6) in CH₂Cl₂ solution; the solution changed from turquoise to magenta upon mixing the reagents. The reaction mixture was refluxed for 30 min to ensure complete reaction; crystallization was effected by slow evaporation in air of a portion of this solution. These crystals† proved amenable to investigation by X-ray crystallography. However, refinement of the structure was prevented by the disorder of the O=V–Cl unit across an inversion centre. This disorder places half a V atom on each

Fig. 1 Twofold disorder of the O=V–Cl unit. The positions shown are those obtained in the final refinement after successful resolution of the disorder; initial refinement tended to reduce the separations of the near-coincident sites.
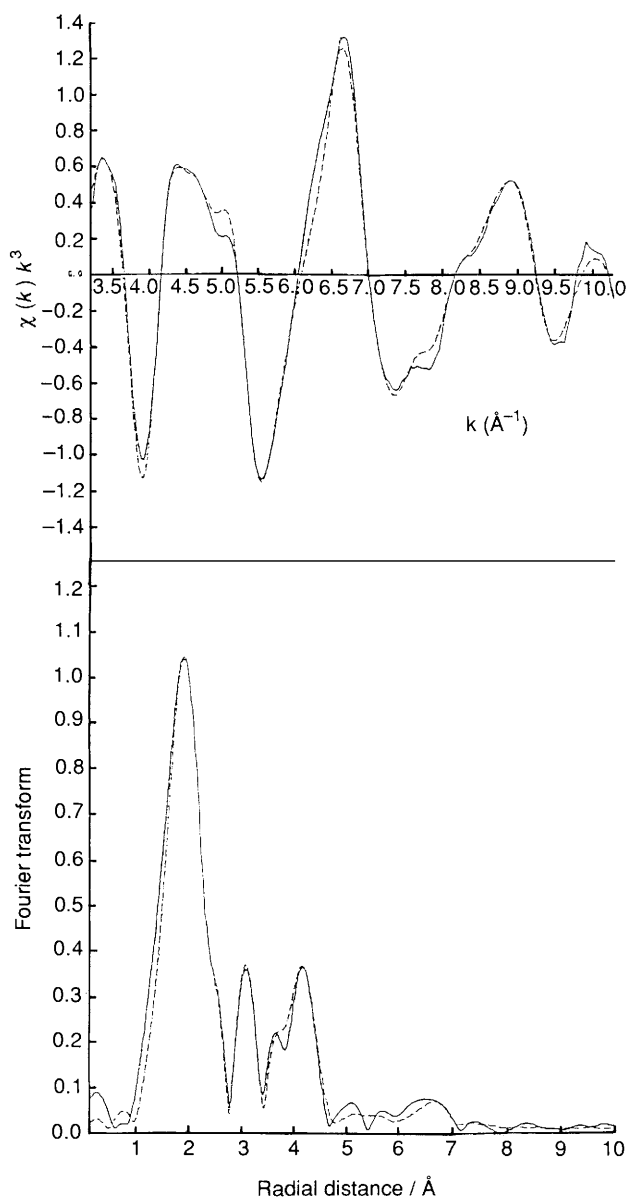
Fig. 2 EXAFS ($\times k^3$) data and Fourier transform for [VOCl(1-vinylimidazole)$_4$]Cl. (———) Experimental data; (– – –) simulation using the parameters given in Table 1.

Table 1 Parameters used to simulate the vanadium K-edge EXAFS of [VOCl(1-vinylimidazole)$_4$]Cl

Atom	N^a	R/Å^b	$2\sigma^2/\text{Å}^2$	Crystallographic values
O	1.0	1.59	0.001^c	1.60(2)
N^d	4.0	2.12	0.006^c	2.05(2)–2.19(2)
C	4.0	3.03	0.012^c	3.05–3.13
C	4.0	3.10	0.012^c	3.04–3.26
N^e	4.0	4.32	0.025^c	4.18–4.29
C	4.0	4.34	0.025^c	4.18–4.35
C^f	4.0	5.39	0.049^c	5.48–5.61
C^f	4.0	6.70	0.031^c	6.17–6.66
Cl	1.0	2.44	0.015^c	2.47(2)

^{a} Coordination numbers were fixed throughout data analysis. ^{b} Vanadium-backscatterer distance. ^{c} Debye–Waller parameter. ^{d} Scattering angles: V–N–C ($\sim$3.07 Å) 126 ± 4° and V–N–C ($\sim$4.33 Å) 166 ± 4°. ^{e} Treated as C in the EXAFS analysis. ^{f} Vinyl carbons, scattering angles: V–N–C (5.39 Å) 136° and V–N–C (6.70 Å) 166°.
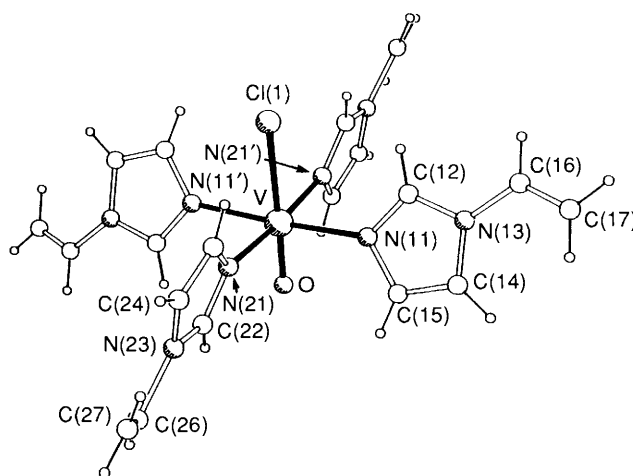
Fig. 3 Structure of the [VOCl(1-vinylimidazole)$_4$]$^+$ ion. Selected dimensions: V–O 1.597(20), V–Cl(1) 2.468(18), V–N(11) 2.138(16), V–N(21) 2.190(16), V–N(11′) 2.114(15), V–N(21′) 2.045(16) Å, O–V–Cl(1) 178.2(9), O–V–N(11) 93.8(7), Cl(1)–V–N(11) 87.0(7), O–V–N(21) 91.7(8), Cl(1)–V–N(21) 86.7(5), N(11)–V–N(21) 86.8(6), O–V–N(11′) 92.7(9), Cl(1)–V–N(11′) 86.4(5), N(11)–V–N(11′) 172.4(8), N(21)–V–N(11′) 88.9(6), O–V–N(21′) 94.9(8), Cl(1)–V–N(21) 86.7(7), N(11′)–V–N(21′) 92.2(6), N(21)–V–N(21′) 173.4(10), N(11′)–V–N(21) 91.3(6)°. Primed atoms are related to the corresponding unprimed atoms by inversion symmetry.

side of the inversion centre, with a V–V′ separation <0.3 Å, and gives near coincidence of O with Cl′ and Cl with O′ (Fig. 1). Any corresponding twofold disorder of the vinyl-imidazole ligands was not resolvable. The close proximity of atom sites in the two O=V–Cl disorder components rendered refinement unstable and it led also to ambiguities in the assignment of individual sites to the two components and hence ambiguities in the bond lengths and angles.

In an attempt to resolve this disorder, and to provide independent experimental confirmation of the coordination of vanadium, the vanadium K-edge X-ray absorption spectrum of **1** was recorded in transmission mode at *ca.* 80 K on Station

8.1 of the Daresbury Synchrotron Radiation Source operating at 2 GeV and 180 mA. A slitless double crystal Si(111) monochromator was employed, thus minimising harmonic contamination.[12] Crystal glitches[13] limited the data range to approximately 400 eV beyond the edge. Data analysis was accomplished *via* the curved-wave method for EXAFS calculation, with phase shifts derived from *ab initio* calculations,[14] and included multiple-scattering for the imidazole contributions.[15] The EXAFS, its simulation and their Fourier transforms are shown in Fig. 2 and the values obtained are compared with the final distances obtained from X-ray crystallography in Table 1. The V–O, V–N and V–Cl distances obtained from EXAFS were used as restraints in subsequent refinement of the crystal structure and as confirmation of the assignment of the individual half-atom sites to the two disorder components of the O=V–Cl unit. The restraints allowed a successful resolution of the near-coincident sites and, in particular, the introduction of anisotropic thermal parameters for these atoms. In the final cycles of refinement, once the positional and thermal parameters had almost

reached their convergence values, it was possible to release the restraints completely, so that the reported molecular geometry from the crystal structure is then independent of the EXAFS-derived geometry. The bond lengths to vanadium are not significantly different in the two experiments. Such use of the local radial distribution information available from EXAFS may have utility in resolving disorder problems for other crystals and also could be of value in the interpretation and refinement of powder diffraction data.

The structure of the $[VO(1\text{-vinylimidazole})_4Cl]^+$ complex is shown (with only one component of the disorder) in Fig. 3. The cation involves a VO^{2+} centre coordinated by one chloride *trans* to the oxo-group and a plane of four imidazole nitrogens perpendicular to the O=V–Cl axis with the vanadium 0.12 Å out of the plane in the direction of the oxo-group. The rings of the imidazole groups are inclined at 65° and 75° to the N_4 plane. Thus, the gross stereochemistry at the vanadium approximates to axial symmetry. The V=O, mean V–N and V–Cl distances of 1.60(2), 2.05(2)–2.19(2) and 2.47(2) Å are unexceptional, as are the dimensions of the imidazole rings and the vinyl groups. The discrete chloride anion lies on an inversion centre. Because the disordered vanadium atom sites lie slightly off the inversion centre for the cation, the four V–N bond lengths are not related in exact pairs, as would be the case for a vanadium atom exactly on the inversion centre.

The IR spectrum of **1** contains absorptions at 949 and 343 cm^{-1} which are attributed to the V=O and V–N stretching frequencies, respectively. The UV–VIS absorption spectrum of **1** dissolved in absolute ethanol contains λ_{max} at 13 000 and 18 000 cm^{-1} ($\varepsilon = 44$ and 12 cm^{-1} mol^{-1} dm^{-3}, respectively) —attributed to the two lowest energy d–d transitions of this six coordinate complex—together with intense absorptions in the 28 500–40 000 cm^{-1} region which are attributed to π–π^* transitions of the imidazole groups.

The fluid solution ESR spectrum of **1** in MeCN containing an excess of 1-vinylimidazole shows a single species with $\bar{g} = 1.980(\pm0.004)$, $\bar{A} = -92(\pm0.5) \times 10^{-4}$ cm^{-1}. The frozen solution displays an axial-like spectrum, at both X- and Q-band frequencies, with apparent parameters $g_{\parallel} = 1.951$, $g_{\perp} = 1.983$; $A_{\parallel} = -162$, $A_{\perp} = -63 \times 10^{-4}$ cm^{-1}, consistent with the 'VON$_4$Cl' environment. Comparative 'powder' ESEEM spectra of **1** and BPO have been used to establish the presence of N-donor groups in the latter.[16]

The characterization of **1** shows that VO^{2+}, like many other transition metal cations, is capable of coordination by imidazole groups. The environment of VO^{2+} in **1** may be compared with that found for the Type II Cu^{II} centre in Cu/Zn bovine superoxide dismutase.[17] This knowledge and the spectroscopic details reported herein may help illuminate and elucidate the coordination chemistry of vanadium in biological systems.

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