X-Ray absorption fine structure study of the bound state electronic transitions at the vanadium K and L edges in low symmetry, molecular, vanadium-(IV) and -(V) complexes with oxyoxime and oxyoximate ligands ‡

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A combination of vanadium K- and L-edge XAFS has been used to characterise a series of monomeric oxovanadium(IV), monomeric dioxovanadium(V) and dimeric oxovanadium(V) complexes with oxyoxime and oxyoximate ligands. The K- and L-edge spectra confirm the presence of V^V in the dimeric species and the L-edge spectra have been used to discriminate between six-co-ordinate V−N−O−V bridged oxovanadium(V) dimers and seven-co-ordinate phenolate bridged oxovanadium(v) dimers containing η^2-N−O groups.

The bound state electronic transitions in the X-ray absorption fine structure (XAFS) spectra of 3d transition elements at their K- and L-edges have very different intensities because of the dipole selection rules.[1] Thus, at the K-edge, the 1s ⟶ 3d transitions are dipole-forbidden and therefore in general are only seen as weak 'pre-edge' features prior to the onset of the absorption edge and the subsequent extended X-ray absorption fine structure (EXAFS) which can be used to give structural information.[1] In the case of vanadium the intensity of the 1s ⟶ 3d transitions can be significantly enhanced depending upon: (i) the extent of 3d–4p mixing at the vanadium; (ii) the overlap of the vanadium 3d orbitals with ligand 2p orbitals (especially in compounds containing V=O moieties); and (iii) deviations from high symmetry geometries. The position, shape and relative intensity of these pre-edge features are dependent on oxidation state and co-ordination environment, and hence they have been used to investigate vanadoenzymes and synthetic analogues of their active sites,[2,3] as well as an extensive range of vanadium compounds and complexes.[4,5] Although useful information has been obtained using this approach, Weidemann et al.[3] have advised exercising caution against over interpretation of the data.

In contrast to the K-edge, the L-edge spectra are dominated by intense, well structured transitions which arise from dipole-allowed $2p^6 3d^n \longrightarrow 2p^5 3d^{n+1}$ transitions which have about a quarter of the natural linewidths of the corresponding K-edge features;[6] whilst 2p ⟶ 4s transitions are allowed, their transition probabilities are much smaller.[7] The L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) components are split by spin–orbit coupling of the core–hole, and as there is a strong interaction between the 2p core–hole and the valence 3d orbitals, the position of, and structure on,

the $L_{2,3}$ absorptions are very sensitive to *oxidation state*, *spin state*, *ligand field* and *local environment*, as well as being *element specific*.[7] This can be especially powerful for d^0 electronic configurations, and where d–d transitions are obscured by (intense) charge transfer bands in the optical spectra. The technique has found use in the study of minerals, metalloproteins and co-ordination compounds.[8] The application of L-edge spectroscopy to solid state physics and chemistry has also been reviewed.[9] Abbate et al. have shown that vanadium L-edge XAFS is sufficiently sensitive to distinguish between V_2O_5, VO_2 and V_2O_3,[10] and that there are observable differences in the spectrum of VO_2 above and below its first order phase transition at 67 °C.[11] However, in the case of $LiVO_2$ there was very little change in the spectra above and below the phase transition.[12] Polarisation dependent, single crystal vanadium L-edge experiments have been used to study the 2p ⟶ 3d transitions in greater detail in V_2O_5,[13–15] VO_2,[13] V_2O_3[13] and V_6O_{13}.[13,14] Chen et al.[16] have demonstrated a shift in the vanadium L-edge features of vanadium oxide model compounds of 0.68 ± 0.03 eV per oxidation state, and have used this to identify the oxidation state of vanadium carbide on a vanadium (110) surface. A comparison of the experimental and theoretical spectrum of VF_3 has been reported,[17] and vanadium L-edge XAFS has also been used for oxidation state identification and quantification in a range of vanadium-containing minerals.[18,19]

We have recently developed the synthesis and structural characterisation of a series of oxovanadium-(IV) and -(V) complexes containing oxyoxime and oxyoximate ligands.[20–22] Fig. 1(a) shows the formulae of these proligands, which bond to vanadium either as mononegative oxyoxime units by deprotonation of the phenol function or as dinegative oxyoximate ligands when the N-hydroxy group is additionally deprotonated. Fig. 1(b)–(e) shows the various structural types which we have identified using single crystal X-ray diffraction on

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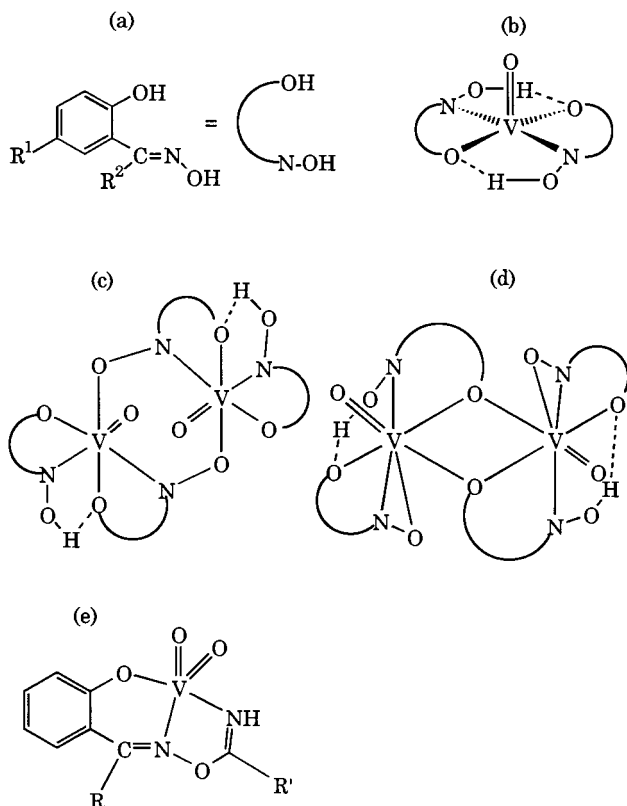
Fig. 1 Representation of the structures of: (a) proligands (R^1 = H, R^2 = H, H_2L^H; R^1 = H, R^2 = Me, H_2L^{Me}; R^1 = H, R^2 = Et, H_2L^{Et}; R^1 = Oct^t, R^2 = H, $H_2L^{Oct^t}$; R^1 = Bu^t, R^2 = H, $H_2L^{Bu^t}$; R^1 = Cl, R^2 = H, H_2L^{Cl}; (b) five-co-ordinate monomeric bis(oxyoxime)oxovanadium(IV) complex: (c) six-co-ordinate oxyoxime-bridged oxovanadium(V) dimer containing μ-N–O units; (d) seven-co-ordinate, phenolate-bridged, oxovanadium(V) dimer, containing η²-N–O units; (e) dioxovanadium(V) monomer, [$VO_2\{C_6H_4(O)C(R)=NOC(R')=NH\}$] (R = Me, R' = Ph; R = H, R' = Me, Ph or 4-$O_2NC_6H_4$)

selected complexes. The monomeric oxovanadium(IV) complexes [Fig. 1(b)] show a typical hydrogen-bonded uninegative form of the ligand in a bis complex. They are stable over a period of months in the solid state, but in chlorinated or hydrocarbon solvents the solutions rapidly darken as the complexes undergo oxidation to dimeric species. The particular structural type formed depends on the substituent in the hydroxyoxime proligand and also the starting material since some of the dimers can be formed without oxidation using [NH_4][VO_3] as the vanadium precursor. In these proposed higher oxidation state dimers the oxovanadium(V) centres are bound by both mononegative oxyoxime and dinegative oxyoximate ligands. The V–N–O–V bridged structure [Fig. 1(c)] has two six-co-ordinate pseudo-octahedral metal centres, whereas the phenolate-bridged structure [Fig. 1(d)] has pseudo-pentagonal bipyramidal seven-co-ordination at each metal, which includes the η²-N–O bonding mode of the oxyoximate ligands. Reaction of the oxovanadium(IV) monomers with nitriles (MeCN, PhCN and 4-$O_2NC_6H_4CN$) led to oxidation to dioxovanadium(V) monomers [Fig. 1(e)] with the formation of a novel organic ligand.[23]

The assignment of (formal) metal oxidation state in the dimeric compounds can be non-trivial as the magnetic distinction between vanadium-(IV) and -(V) is no longer present if there is strong antiferromagnetic coupling between the oxovanadium(IV) centres. The identification of the dimeric species [Fig. 1(c) and (d)] as oxovanadium(V) followed from a consideration of the bond lengths in the structurally characterised compounds[20,21] in conjunction with Bond Valence Sum Analysis,[24] together with the observation and position of [51]V NMR resonances.[21] Whilst the EPR signal characteristic of monomeric vanadium(IV) complexes was absent from the

spectra of the dimeric complexes, this could be due to the presence of vanadium(V) *or* the spin pairing of the single unpaired electron of two vanadium(IV) centres in the dimers.

Therefore, the present study explored the use of vanadium K- and L-edge XAFS spectroscopy to probe the oxidation state of the vanadium centres in several monomeric and dimeric oxyoxime and oxyoximate complexes of vanadium-(IV) and -(V). This work also assesses the applicability of bound state transitions at these edges to the discrimination of co-ordination environment.

Experimental

Sample preparation

Vanadium(V) oxide and [NH_4][VO_3] were obtained from Aldrich and used as received. The complexes [$VO(acac)_2$],[21] [$VO(acac)_2(py)$],[25] [$VO(salen)$],[21] K_3[$VO(O_2)_2(C_2O_4)$][26] and [$VO_2\{C_6H_4(O)C(R)=NOC(R')=NH\}$][23] (R = Me, R' = Ph; R = H, R' = Me, Ph or 4-$O_2NC_6H_4$) [Fig. 1(e)] were synthesized using previously published methods.§ The synthesis and characterisation of the hydroxyoxime proligands [Fig. 1(a)] will be published elsewhere.[20,21,27] The synthesis of the oxovanadium(IV) oxyoxime complexes [$VO(HL^R)_2$] (R = H, Me, Et, Bu^t or Cl) [Fig. 1(b)] from vanadyl sulfate and the appropriate proligand, and the oxovanadium(V) oxyoxime oxyoximate complexes [$\{VO(HL^R)L^R\}_2$] [R = H, Me, Et or Oct^t (Oct^t = $Me_3CCH_2CMe_2$)] [Fig. 1(c) and (d)] from either oxidation of the vanadium(IV) complex in chlorocarbon or hydrocarbon solvents or the addition of the proligand to [NH_4][VO_3], will be published in detail elsewhere, together with the spectroscopic and crystallographic data.[20,21,27] The numbering scheme for the compounds is given in Table 1.

K-edge X-ray absorption spectroscopy

The vanadium K-edge X-ray absorption data were collected on station 4.2[28] at the Daresbury Laboratory Synchrotron Radiation Source (SRS) operating at 2 GeV with circulating currents of 220–240 mA. The samples were investigated as a slurry in hexane (reagent grade), evaporated onto vanadium-free stainless steel holders and mounted in an ultra-high vacuum chamber. Total electron yield detection was used for all experiments and the spectra were calibrated using the maximum intensity position of the V_2O_5 1s ⟶ 3d pre-edge transition at 5470.60 eV.[5] The accuracy of the measurement of the *absolute* energy is estimated to be ±0.5 eV, and that of the *relative* energy to be ±0.25 eV.

L-edge X-ray absorption spectroscopy

The vanadium L-edge data were obtained on station 5U.1[29] of the undulator beamline at the SRS operating at 2 GeV with circulating currents of 150–250 mA. The general features of the experimental set-up employed have been described in detail elsewhere.[8] The samples were prepared either as slurries of graphite (99.999%; Goodfellows, Cambridge) with CH_2Cl_2 or EtOH and left to evaporate on aluminium plates or as powders on conductive epoxy resin on aluminium plates. The aluminium plates were mounted in an ultra-high vacuum chamber with a base pressure of *ca.* 10^{-7} mbar. Data were collected as total electron yield using drain current methods which gives an estimated sampling depth of *ca.* 30–50 Å. The spectra were normalised to the intensity of the L_3 feature and were calibrated using oxygen K-edge features in the I_0 channel, these having been referenced to the vanadium L_3 peak maximum of V_2O_5 at 516.9 eV, based on the reported XPS $2p_{3/2}$ binding energy of V_2O_5 at 516.9 eV.[30] The oxygen K-edge features starting at *ca.* 528 eV have been removed from the spectra for clarity. Whilst

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§ Hacac = Acetylacetone = pentane-2,4-dione; H_2salen = *N,N'*-bis(salicylidene)ethane-1,2-diamine.
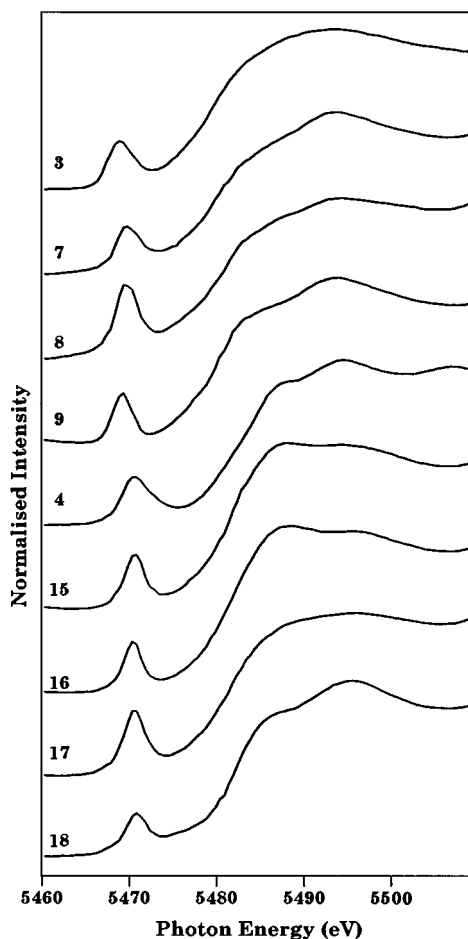
Fig. 2 Vanadium K-edge spectra of [VO(salen)] **3**, [VO(HL^H)$_2$] **7**, [VO(HL^{Me})$_2$] **8**, [VO(HL^{Et})$_2$] **9**, V$_2$O$_5$ **4**, [{VO-(HL^{Me})L^{Me}}$_2$] **15**, [{VO-(HL^{Et})L^{Et}}$_2$] **16**, [{VO(HL^H)L^H}$_2$] **17** and [{VO(HL^{Et})L^{Et}}$_2$] **18**

the accuracy of the *absolute* energy measurement is estimated to be ±0.2 eV, the *relative* energies are considered to be accurate to at least ±0.1 eV due to the use of *in situ* calibration.

Results and Discussion

Vanadium K-edge spectra

Vanadium K-edge spectra of [VO(salen)] **3** and V$_2$O$_5$ **4**, with pre-edge features of moderate intensity about 10 eV below the absorption edge, are shown in Fig. 2, and these were essentially identical to those observed previously.[2–5] The pre-edge feature in the spectrum of [VO(salen)] was at 5469.0 eV, compared to a literature value of 5469.1 eV,[¶,2] and previous workers have reported values for the position of the pre-edge features for molecular oxovanadium(IV) complexes of 5469.1 to 5469.8,[2] 5469.05 to 5469.8,[3] and 5469.7 to 5469.9 eV.[4] For V$_2$O$_5$ the pre-edge feature in the spectrum was observed at 5470.6 eV, *ca.* 1.5 eV higher in energy than the above values, as to be expected for vanadium-(V) *vs.* -(IV). Previously reported values of the positions of the pre-edge features for molecular oxovanadium(V) complexes are in the range 5470.1 to 5470.7,[2] 5469.9 to 5471.1 and 5470.2 to 5470.8 eV.[4] Therefore, the position of the pre-edge peaks in the vanadium K-edge spectra will be able to identify with reasonable certainty the oxidation state in the oxyoxime and oxyoximate complexes.

The vanadium K-edge spectra (Fig. 2, Table 1) of the oxo-

¶ This value has been amended from the published value of 5459.1 eV, since the original work[2] used a value of 5456.0 eV for the pre-edge feature in vanadium foil, whereas a value of 5466.0 eV (see ref. 5) is more compatible with the calibration used herein. The other data taken from ref. 2 have been treated in a similar manner.
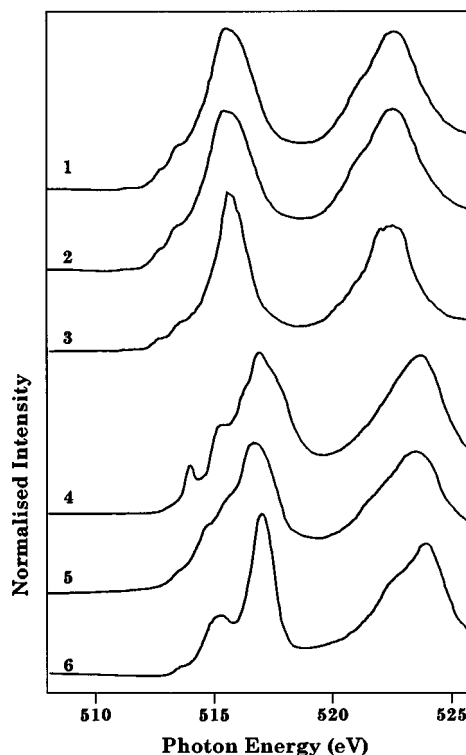

Fig. 3 Vanadium L-edge XAFS spectra of [VO(acac)$_2$] **1**, [VO(acac)$_2$-(py)] **2**, [VO(salen)] **3**, V$_2$O$_5$ **4**, [NH$_4$][VO$_3$] **5**, K$_3$[VO(O$_2$)$_2$(C$_2$O$_4$)] **6**

vanadium(IV) complexes containing oxyoxime ligands (**7–9**) have 1s $\longrightarrow$ 3d transitions in the range 5469.3 to 5469.8 eV, consistent with the presence of V^{IV}. In contrast, the position of the pre-edge features in the vanadium K-edge spectra (Fig. 2, Table 1) of the complexes formulated as dimeric oxovanadium(V) species (**15–18**) are in the range 5470.6 to 5470.8 eV, indicative of the presence of V^V. Therefore, vanadium K-edge XAFS confirms the presence of V^V in the dimeric species. The vanadium K-edge spectra of **15** and **16** are virtually identical, confirming the same type of structural motif (seven-co-ordinate, phenolate bridged dimer containing an η^2-N–O group [see Fig. 1(d)] is present in both complexes. The spectrum of **17** is different to those of **15** and **16**, indicating the presence of a different structural type (six-co-ordinate, V−N−O−V bridged dimers [see Fig. 1(c)]. The spectrum of **18** is broadly similar to that of **17** and very different from those of **15** or **16**, indicating that the same structural type is probably present in **17** and **18**.

Whilst the spectra of the dimeric complexes have indicated the sensitivity of vanadium K-edge XAFS to changes in structural type at the metal centre, the differences are fairly small and subtle. Therefore, we decided to investigate the applicability of vanadium L-edge XAFS to the identification of the structural form present in the oxovanadium(V) dimers, as this technique is very sensitive to changes in the electronic and geometric structure at the metal centre.

Vanadium L-edge spectra

Compounds for calibration and comparison. Fig. 3 shows the vanadium L-edge spectra obtained for several oxocompounds of V^{IV} and V^V. These spectra are split into the L$_3$ (2p$_{3/2}$) and L$_2$ (2p$_{1/2}$) components by spin–orbit coupling (*ca.* 7 eV) of the core–hole, and the structure on each of these components is related to the ligand field at, and site symmetry of, the vanadium. The structure on the higher energy L$_2$ feature is less well resolved than that at the L$_3$ edge due to interaction with the L$_3$ continuum states.[7] The maxima of the L$_3$ components for [VO(acac)$_2$] **1**, [VO(acac)$_2$(py)] **2** and [VO(salen)] **3** all occur at 515.7 eV, with shoulders at 512.7 (512.8 for **1**) and 513.4 eV in each case. The maxima of the broad, slightly asymmetric L$_2$

Table 1 Vanadium K- and L-edge XAFS data (eV) for some vanadium-(IV) and -(V) compounds

Compound	K edge 1s $\longrightarrow$ 3d transition[a]	L$_3$ edge[b]	L$_2$ edge[b]
1 [VO(acac)$_2$]	5469.05;[c] 5469.4[d]	512.8, 513.4, 515.7[e]	522.6[e]
2 [VO(acac)$_2$(py)]	f	512.7, 513.4, 515.7[e]	522.6[e]
3 [VO(salen)]	5469.0;[e] 5469.1[d]	512.7, 513.4, 515.7[e]	522.4[e]
4 V$_2$O$_5$	5470.6[e] 5470.6;[g] 5470.67;[c] 5470.3[d]	513.9, 515.3, (516.2), 516.9[e]	523.7[e]
5 [NH$_4$][VO$_3$]	5469.8;[g] 5470.1[d]	513.5, 514.7, 515.5, 516.7[e]	523.5[e]
6 K$_3$[VO(O$_2$)$_2$(C$_2$O$_4$)]	5470.61[c]	513.6, 515.3, 517.0[e]	522.4, 523.9[e]
7 [VO(HL^H)$_2$]	5469.8[e]	h	h
8 [VO(HL^{Me})$_2$]	5469.7[e]	512.8, 513.6, 515.7[e]	522.6[e]
9 [VO(HL^{Et})$_2$]	5469.3[e]	512.8, 513.6, 515.7[e]	522.6[e]
10 [VO(HL$^{(Cl)}$)$_2$]	f	512.7, 513.6, 515.6[e]	522.4[e]
11 [VO$_2$\{C$_6$H$_4$(O)CH=NOC(Me)=NH\}]	f	515.3, 516.9[e]	523.5[e]
12 [VO$_2$\{C$_6$H$_4$(O)CH=NOC(Ph)=NH\}]	f	515.0, 516.6[e]	523.3[e]
13 [VO$_2$\{C$_6$H$_4$(O)C(Me)=NOC(Ph)=NH\}]	f	514.9, 516.8[e]	523.4[e]
14 [VO$_2$\{C$_6$H$_4$(O)CH=NOC(4-O$_2$NC$_6$H$_4$)=NH\}]	f	515.0, 516.7[e]	523.3[e]
15 [\{VO(HL^{Me})L^{Me}\}$_2$] (η^2-N–O)[i]	5470.7[e]	514.9, 515.8, 516.8[e]	(522.6), 523.4[e]
16 [\{VO(HL^{Et})L^{Et}\}$_2$] (η^2-N–O)[i]	5470.6[e]	515.0, 515.8, 516.8[e]	523.3[e]
17 [\{VO(HL^H)L^H\}$_2$] (μ-N–O)[i]	5470.6[e]	514.0, 515.1, 517.1[e]	523.7[e]
18 [\{VO(HL^{Et})L^{Et}\}$_2$] (μ-N–O)[i]	5470.8[e]	(513.9), 514.9, (516.3), 517.1[e]	(522.2), 523.7[e]
19 [\{VO(HL^{oct})L^{oct}\}$_2$]	f	515.1, 517.1[e]	(522.7), 523.7[e]

[a] Peak maxima ± 0.25 eV, referenced to V$_2$O$_5$ 1s $\longrightarrow$ 3d transition at 5470.6 eV. [b] Peak maxima ± 0.1 eV referenced to L$_3$ maximum of V$_2$O$_5$ at 516.9 eV; figures in parentheses are poorly defined shoulders. [c] Ref. 3. [d] Ref. 2 [value amended from that given in the original work which used a value for the vanadium foil pre-edge feature of 5456.0 eV; a value of 5466.0 eV was used herein (see ref. 5)]. [e] This work. [f] Vanadium K-edge data not recorded. [g] Ref. 5. [h] Reliable vanadium L-edge data could not be obtained. [i] The bonding mode of the deprotonated oxime moiety (see Fig. 1).

features are observed at 522.6 eV for [VO(acac)$_2$] and [VO(acac)$_2$(py)] and 522.4 eV for [VO(salen)]. The spectra for all three complexes are very similar, implying that vanadium L-edge XAFS is not sufficiently sensitive to discriminate between the small changes in the ligand field experienced by the vanadium in these compounds. (Single crystal electronic absorption measurements have shown that the 3d$_{z^2}$ orbitals is at least 4000 cm^{-1} higher in energy in six-co-ordinate VO^{2+} complexes than in their five-co-ordinate counterparts.[31]) Therefore, we believe that the profile observed could be useful as a spectroscopic signature for VO^{2+} bound to O,N-donor ligands. For V$_2$O$_5$ **4** the L$_3$ maximum was observed at 516.9 eV, with well defined features at 513.9 and 515.3 eV and a weak shoulder at 516.2 eV. In the case of [NH$_4$][VO$_3$] **5** the L$_3$ maximum was at 516.7 eV together with shoulders at 513.5, 514.7 and 515.5 eV. For K$_3$[VO(O$_2$)$_2$(C$_2$O$_4$)] **6** the L$_3$ maximum at 517.0 eV was accompanied by a well defined shoulder at 515.3 eV and a weaker feature at 513.6 eV. The L$_2$ features for V$_2$O$_5$, [NH$_4$][VO$_3$] and K$_3$[VO(O$_2$)$_2$(C$_2$O$_4$)] were observed at 523.7, 523.5 and 523.9 eV, respectively. For the last of these features there was a shoulder at 522.4 eV, whereas in the other two spectra the L$_2$ band was asymmetric. The shift of *ca.* 1 eV in the maxima of both the L$_3$ and L$_2$ peaks on going from V^{IV} to V^V clearly indicates the sensitivity of vanadium L-edge XAFS spectra to changes in oxidation state. Chen *at al.*[16] have previously observed a shift of 0.68 eV per oxidation state for vanadium oxocomplexes, but the resolution obtained was very poor (*e.g.* the spectrum of V$_2$O$_5$ contained only a broad feature at both the L$_3$ and L$_2$ edges) casting some doubt on the accuracy of this value. Whilst the L-edge spectra of the oxovanadium(IV) compounds appear to be very similar, there are significant differences between the spectra of the vanadium(V) systems, presumably related to the differences in the local environment of the vanadium which affect the relative energies of the 3d orbitals. Previously, it has been noted that the simulation of L-edge spectra for d^0 configurations is complicated because of the large number of individual dipole-allowed 2p $\longrightarrow$ 3d transitions.[7] Although polarisation-dependent, single crystal measurements on V$_2$O$_5$ have been used to identify the spectroscopic features arising from the different 3d orbitals,[15] we have been unable to collect polarisation-dependent data on *molecular complexes* due to the loss of crystallinity, presumably related to

the loss of solvent from the top (*ca.* 30–50 Å) layer of the compounds under the ultra-high vacuum conditions required for the experiment. The complexity of the L-edge spectra observed for the vanadium(V) systems reported herein also calls into question the approach previously used for identification of oxidation state in vanadium-containing minerals.[18,19] This assumed that any V^V present would be represented by a single peak in the L$_3$-edge region of the spectrum. Thus, whilst we have observed one major peak at the L$_3$ edge, lower energy shoulders associated with the vanadium(V) spectra may overlap with, or could be misassigned to, features from lower oxidation state species.

Oxovanadium oxyoxime and oxyoximate complexes. The vanadium L-edge spectra obtained from the oxovanadium-(IV) and -(V) complexes containing oxyoxime and oxyoximate ligands are shown in Fig. 4. Essentially identical spectra were observed for all of the oxovanadium(IV) oxyoxime complexes studied (**8**–**10**) and representative spectra of [VO(HL^{Me})$_2$] **8** and [VO(HL^{Et})$_2$] **9** are given in Fig. 4. The L$_3$ maxima were observed at 515.7 eV, together with lower energy features at 512.8 and 513.6 eV, whilst the L$_2$ absorption band was observed at 522.6 eV for **8** and **9** and at 522.4 eV for **10**. These spectra and values are very similar to those observed for [VO(acac)$_2$], [VO(acac)$_2$(py)] and [VO(salen)], consistent with the presence of V^{IV} in these complexes, further supporting the idea that this spectroscopic motif is characteristic of VO^{2+} bound to O,N-donor ligands.

For the vanadium(V) complexes **11**–**19** a much wider variation in the nature of the L-edge spectra was observed. For the monomeric, five-co-ordinate, dioxovanadium(V) complexes **11**–**14** [see Fig. 1(e)] the spectra were similar, with the L$_3$ maxima at 516.6–516.9 eV with low energy shoulders at *ca.* 515.0 eV and the L$_2$ maxima at *ca.* 523.4 eV; Fig. 4 shows the spectrum obtained for **14**. The position of the L$_3$ maxima at *ca.* 516.7 eV suggests that this feature is indicative of V^V in such systems which have been shown unambiguously to be V^V from ^{51}V NMR spectroscopy, consistent with the lack of an EPR signal.[23]

For the oxovanadium(V) dimeric species **15**–**18**, two different structural forms have been identified using X-ray crystallography. Red-brown, [\{VO(HL^{Me})L^{Me}\}$_2$] **15** has a seven-co-
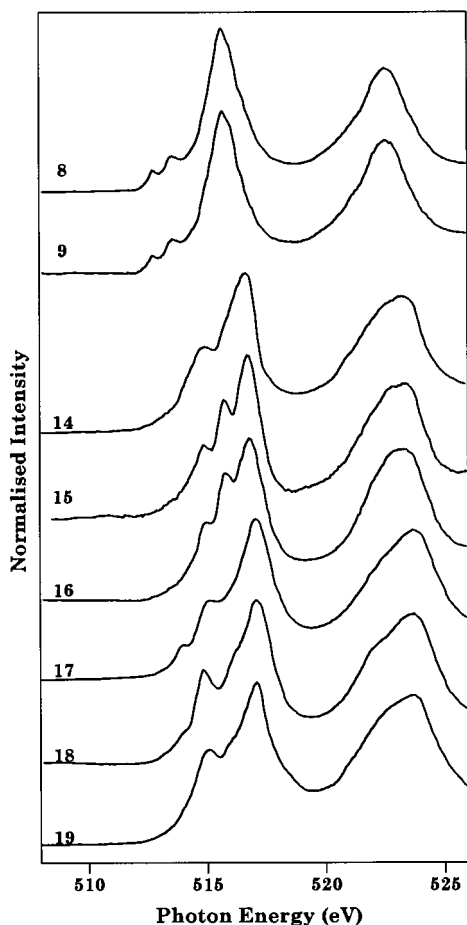
surface layer, rather than as a result of bulk decomposition of the sample.

Black, [{VO(HL^H)L^H}_2] **17** has a six-co-ordinate, dimeric structure [Fig. 1(c)] with V–N–O–V bridging.[20] The vanadium L-edge spectrum of this compound has an L_3 band with features at 514.0, 515.1 and 517.1 eV, and a broad asymmetric L_2 band with a maximum at 523.7 eV. There is no evidence of a feature at 515.8 eV, indicating the absence of any significant photoreduction. Of interest is the effect of changes in molecular geometry on the rate of soft X-ray photoreduction in these two oxovanadium(v) complexes. The L_3 maximum at 517.1 eV for **17** is 0.3 eV higher in energy than that for **15** and the L_2 band is also *ca.* 0.3 eV higher in energy. These shifts were consistently observed for different samples and are considered to be indicative of changes in the 3d orbital energies due to changes in bonding and site symmetry at the vanadium between the two structural forms. Deconvolution of the spectrum of the seven-co-ordinate species **15** using a vanadium(iv) spectrum **9** and a spectrum of the six-co-ordinate species **17** showed that this shift of *ca.* 0.3 eV cannot be accounted for by the presence of the 515.8 eV band in the spectrum of the seven-co-ordinate species. Therefore, we believe that the position of the L_3 maximum can be used to differentiate between the two types of dimeric structures.

In respect of the synthesis of complexes **15** and **17**, the same product was obtained from either oxidation of the corresponding vanadium(iv) complex or the addition of the proligand to a vanadium(v) precursor such as [NH_4][VO_3].[20,21] However, in the case of [{VO(HL^Et)L^Et}_2], the nature of the product depended on the synthetic route chosen. Oxidation of [VO(HL^Et)_2] in CHCl_3 led to the production of black crystals of [{VO(HL^Et)-L^Et}_2] **18** which have been shown by X-ray crystallography[21] to possess a structure of the type shown in Fig. 1(c). The vanadium L-edge spectrum of **18** is similar to that of **17**, with L_3 components at 514.9 and 517.1 eV, together with weak shoulders at 513.9 and 516.3 eV, and a broad asymmetric L_2 peak at 523.7 eV. The positions of the L_3 and L_2 maxima and the general form of the spectral profile are very similar to those observed for **17**, as expected since both **18** and **17** have the same structural form. The origin of the subtle change in relative intensity and slight energy shift of the shoulders at the L_3 peak is unclear, and it should be noted that there were also small differences between the vanadium K-edge spectra of these two complexes. Crystallographic studies have revealed that whilst both complexes have the structure type of Fig. 1(c), there are statistically significant differences in the angles subtended at the vanadium in the two compounds.[20,21] Thus, the experimental data indicate the sensitivity of L-edge spectroscopy to small changes in the local environment of d^0 systems.

Reaction of proligand H_2L^Et with [NH_4][VO_3] led to the synthesis of brown [{VO(HL^Et)L^Et}_2] **16**. Whilst we have not been able to determine the structure of **16** by X-ray crystallography, the spectroscopic data (IR, NMR, UV/VIS) indicate a structure of the type Fig. 1(d).[21] The vanadium L-edge spectrum of **16** was essentially identical to that of **15**, with L_3 features at 515.0, 515.8 and 516.8 eV and a broad L_2 peak at 523.3 eV, consistent with the structure of **16** being very similar to that of **15**, as indicated by other spectroscopic data.

Given the above results which show that vanadium L-edge XAFS is able to discriminate between the two structural forms observed for the oxovanadium(v) dimers, we employed this approach to investigate the nature of the vanadium centre present in a material that was only available as an amorphous solid but has industrial importance given the use of the proligand in metal extraction. Attempts to synthesize an oxovanadium(iv) complex using a 'octyl substituted hydroxyoxime proligand (R^1 = Oct^t, R^2 = H in Fig. 1(a)] invariably led to a rapid darkening of the reaction solution and the formation of an almost black amorphous product formulated as [{VO(HL^oct)L^oct}_2] **19** on the basis of microanalytical and IR data.[21] The vanadium

Fig. 4 Vanadium L-edge XAFS spectra of [VO(HL^Me)_2] **8**, [VO(HL^Et)_2] **9**, [VO_2{C_6H_4(O)CH=NOC(4-O_2NC_6H_4)=NH}] **14**, [{VO(HL^Me)L^Me}_2] **15**, [{VO(HL^Et)L^Et}_2] **16**, [{VO(HL^H)L^H}_2] **17**, [{VO(HL^Et)L^Et}_2] **18**, [{VO(HL^oct)L^oct}_2] **19**

ordinate, dimeric structure [Fig. 1(d)] with bridging phenolate ligands from two monodeprotonated hydroxyoxime ligands and the other two oximes co-ordinated *via* η^2-N–O units.[21] The vanadium L-edge spectrum (Fig. 4) of this material consists of three features (514.9, 515.8 and 516.8 eV) at the L_3 edge and a broad, asymmetric peak at 523.4 eV at the L_2 edge. The lowest and highest energy components at the L_3 edge, and the shape and position of the L_2 band, correlate very well with those observed for the monomeric dioxovanadium(v) complexes, confirming the presence of V^V in these dimeric complexes. We do not believe that the central component of the L_3 band at 515.8 eV is a genuine part of the spectral profile of the oxovanadium(v) dimer spectrum as its intensity was found to depend upon the length of time the sample was exposed to the soft X-ray beam (the intensity increased with successive scans) and whether epoxy- or graphite-mounted samples were used, even though the same batch of compound was used in both cases. The energy of this band (515.8 eV) is very similar to that observed for the vanadium(iv) complexes and therefore it is most likely to be due to the presence of some V^IV in the sample. Previously, we have observed soft X-ray induced spin state transitions and photochemistry in some iron complexes,[8] soft X-ray induced photoreduction and photoisomerisation in nickel complexes,[32] and different rates of photoreduction in a number of vanadium(v) compounds.[33] Therefore, the 515.8 eV feature in the spectra of some of the oxovanadium(v) oxyoxime oxyoximate complexes is probably due to V^IV caused by some photoreduction of the sample on exposure to soft X-rays. As 3d L-edge XAFS is essentially a surface sensitive technique (with a penetration depth of *ca.* 30–50 Å) the vanadium(iv) component in the spectra is most likely to be located in the

L-edge spectrum obtained for this product is shown in Fig. 4 with the L_3 maximum at 517.1 eV and a low energy shoulder at 515.1 eV, together with a broad asymmetric L_2 peak with a maximum at 523.7 eV. This spectrum is very similar to that obtained from the six-co-ordinate V−N−O−V bridged [{VO-(HL^{Et})L^{Et}}$_2$] dimer **18** at both the L_3 and L_2 edges and this, together with the observed colour, strongly implies that the structure of this compound is based on a six-co-ordinate vanadium(v) dimer with V−N−O−V bridging. This is in good agreement with the solid state IR spectroscopic experiments which also indicated a structure based on a six-co-ordinate dimeric structure.[21]

Conclusion

The position of the pre-edge features in the vanadium K-edge XAFS spectra gives a clear indication of the oxidation state in the molecular compounds. Subtle changes in the edge structure give a probable indication of the structural type present in the dimeric species, but this is not sufficiently diagnostic to be used as a fingerprint of co-ordination environment. In contrast, vanadium L-edge XAFS has been shown to be a powerful fingerprint of both the oxidation state and the local geometry of the vanadium in a range of oxyoxime and oxyoximate complexes.

In particular vanadium L-edge XAFS spectra have shown that the dimeric vanadium oxime oxyoximate complexes should be formulated as vanadium(v) systems with the L_3 maximum being diagnostic of the presence of either a V−N−O−V bridged structure with two six-co-ordinate pseudo-octahedral metal centres, or a phenolate-bridged structure with η^2-N−O bonding mode of the oxyoximate ligands and pseudo-pentagonal bipyramidal seven-co-ordination at each metal.

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