

J. Synchrotron Rad. (1999), **6**, 364–366

The observation of unusual polarization dependence in single-crystal vanadium K-edge spectra of $[\text{H}_2\text{tmen}][\text{VO}(\text{malonato})_2\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$

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Unusual 2π dependence of the intensity of one of the pre-edge features in the single-crystal vanadium K-edge spectra of $[\text{H}_2\text{tmen}][\text{VO}(\text{malonato})_2\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$ has been observed.

Keywords: single crystal; V K-edge, unusual polarisation dependence

1. Introduction

The use of single-crystal polarisation dependent X-ray absorption spectroscopic data can greatly add to the understanding of the electronic structure of transition metal complexes (Brouder, 1990). As part of a study on a range of vanadium complexes we decided to investigate the applicability of single crystal V K-edge XANES spectroscopy to the determination of electronic structure. An ideal candidate for this study was $[\text{H}_2\text{tmen}][\text{VO}(\text{mal})_2\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$ (H_2tmen = N,N,N',N'-tetra methylethylenediammonium and mal = malonato), as the structure has been determined using single-crystal X-ray diffraction, giving a $Pnma$ (64) space group (Pajunen & Pajunen, 1980). The bc and ab planes used for the single crystal work are shown in Fig. 1. The structure is based on a 2D layer structure with all the $\text{V}=\text{O}$ vectors alternating parallel and anti-parallel to the c axis to within 0.5° . Single crystal EPR spectroscopy has identified a weak ferromagnetic coupling within the layers parallel to the ac plane of ca. 0.02 cm^{-1} at 300 K, which changes to weak anti-ferromagnetic coupling below 190 K. (Collison *et al.*, 1983). Previous V K-edge single crystal work on related compounds has been reported by Templeton and Templeton (1980) and Poumellec *et al.* (1993).

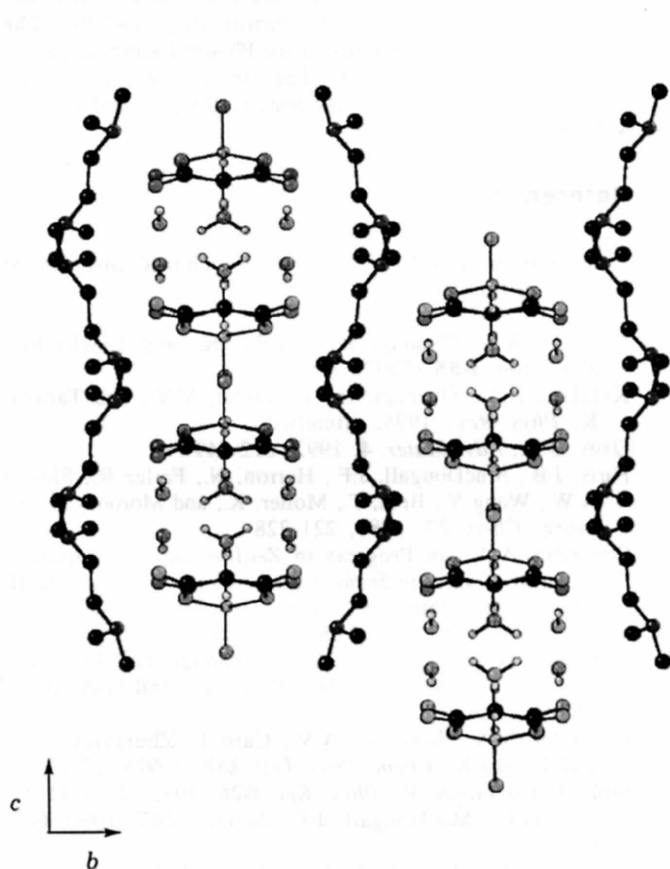


Figure 1(a)
Projection of $[\text{H}_2\text{tmen}][\text{VO}(\text{mal})_2\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$ in the bc plane V - green; C - black; N - blue; O - red; H - grey. (The H atoms from the $[\text{H}_2\text{tmen}]$ have been omitted for clarity).

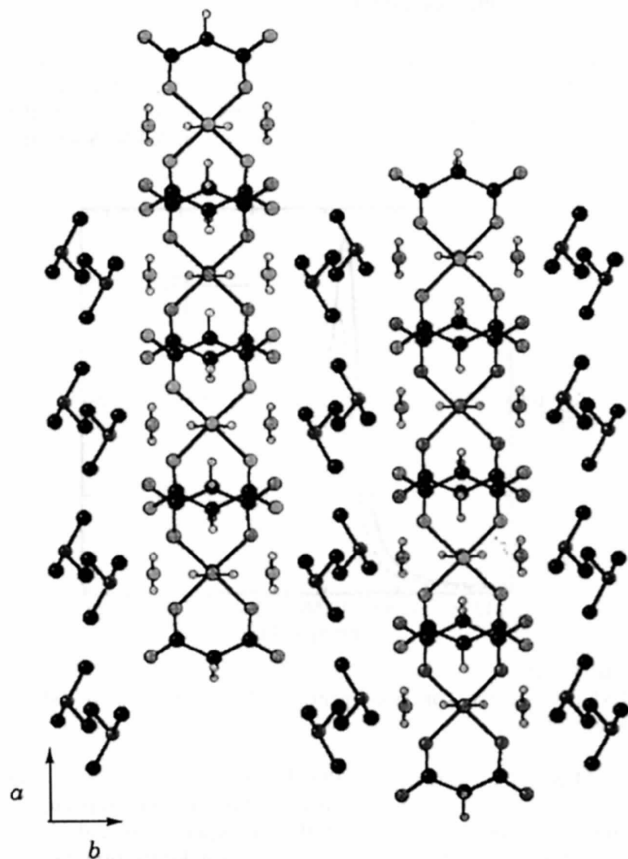


Figure 1(b)
Projection of $[\text{H}_2\text{tmen}][\text{VO}(\text{mal})_2\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$ in the ab plane V - green; C - black; N - blue; O - red; H - grey. (The H atoms from the $[\text{H}_2\text{tmen}]$ have been omitted for clarity).

2. Experimental

The compound was prepared using the method of Pajunen and Pajunen (Pajunen & Pajunen, 1980) and the blue crystals were obtained directly from the reaction mixture by allowing the aqueous solution to evaporate from an uncovered crystallising dish on the open bench. Large single crystals (*ca.* 4 x 4 x 4 mm), which exhibited clear extinctions and colour changes under a polarising microscope, were selected for study; the crystal habit and EPR properties were identical to those reported previously (Collison *et al.*, 1983).

The single crystals were mounted on a calibrated rotating disc on a xyz translation stage which allowed for the optimum alignment of the crystal at each angle. Fig. 2 shows the schematic arrangement used for the data collection with the source and detector being orthogonal, with the crystal rotation axis at 45° to both. The front face of the crystal was approximately flat and parallel with respect to the rotating disc.

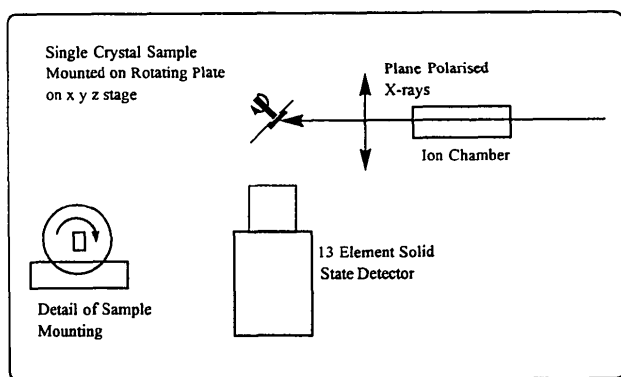


Figure 2
Schematic plan view of experimental set-up for V K-edge single crystal experiments.

The V K-edge spectra were collected in fluorescence mode using a 13 element solid state detector on station 8.1 of the Daresbury Laboratory SRS. The beam size at the crystal was reduced to less than the crystal size with lead masks. Calibration was carried out using a value of 5466.0 eV for the pre-edge feature in the spectrum of V foil. (Wong *et al.*, 1984)

3. Results

Fig. 3 shows the V K-edge XANES transmission spectrum obtained from a powdered sample ground and diluted in BN, compared to a fluorescence spectrum from a ground neat sample mounted on adhesive tape. As expected, the fluorescence spectrum is subject to self-absorption effects, especially with respect to the intensity of the pre-edge features compared to the EXAFS, but the spectra do provide a comparison with the polarisation dependent spectra which have to be collected in fluorescence mode because of the thickness of the crystal in all 3 dimensions. Fig. 4 shows the V K-edge spectra obtained from the rotation of a single crystal of $[\text{H}_2\text{tmen}][\text{VO}(\text{mal})_2\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$ in the *bc* plane around the *a* axis at a series of angles together with the angular intensity dependence of the pre-edge feature at 5469.7 eV. It is clear from these spectra that both the intensity of the pre-edge feature and the height of the edge show the expected π dependence.

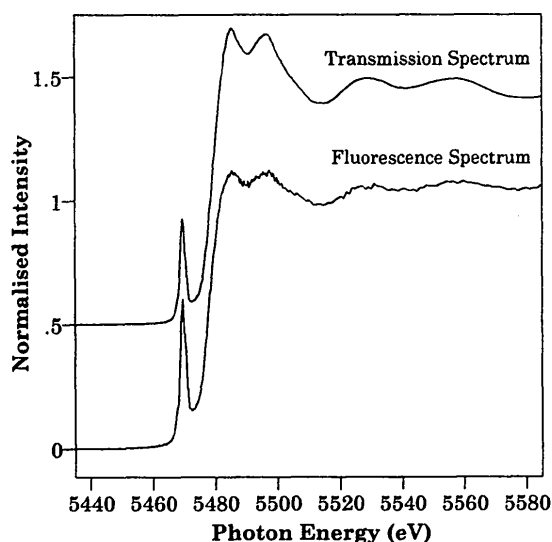


Figure 3
V K-edge spectra of $[\text{H}_2\text{tmen}][\text{VO}(\text{malonato})_2\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$ recorded in transmission and fluorescence mode.

In particular, the intensity of the pre-edge feature is at a maximum when the V=O unit lies in the plane of the polarisation vector of the incident X-rays, and is at a minimum when the V=O unit is perpendicular to the plane of the X-rays. On closer inspection, the spectra also reveal that there are two pre-edge features in the spectra at 0 and 180°, but that only one of these appears to be orientation dependent with the lower energy feature at 5468.2 eV being swamped by the orientation dependent feature at 5469.7 eV. It should be noted that this energy difference (*ca.* 1.5 eV, 12000 cm^{-1}) is of the order of the crystal field splitting, and Poumellec *et al.* (1993) have previously observed better resolved structure in the pre-edge region for single crystal samples as compared to powder samples. None of the polarisation dependent observations are unexpected, given the favourable alignment of the molecular axes of the vanadium complexes with the *a*, *b*, and *c* lattice parameters.

In contrast, the polarisation dependent spectra (Fig. 5) for the rotation of the *ab* plane around the *c* axis, reveal a 2π dependence of both the pre-edge feature at 5469.4 eV and also the edge structure. As in the above case there are two pre-edge features at 5467.7 and 5469.4 eV, with the lower energy one being swamped by the polarisation dependent higher energy feature. The small differences between these values and those observed for the *bc* crystal plane, are probably not significant as they are of the order of the calibration uncertainty and the resolution limit of the spectrometer, and it should be noted that the gap between the two features is very similar in both cases. The ordering of d-orbitals in related complexes has been shown to be $3d_{xy} < 3d_{xz}$, $3d_{yz} < 3d_{x^2-y^2} < 3d_{z^2}$ with approximate energy differences of 1.5, 2 and 4 eV from the $3d_{xy}$ orbital. (The *z* co-ordinate is directed along the V=O unit and the *x* and *y* co-ordinates are taken as directed along the V-O directions projected onto the plane perpendicular to V=O) (Collison *et al.*, 1980). Therefore, these differences are of the order of those expected for transitions into the various d-orbitals.

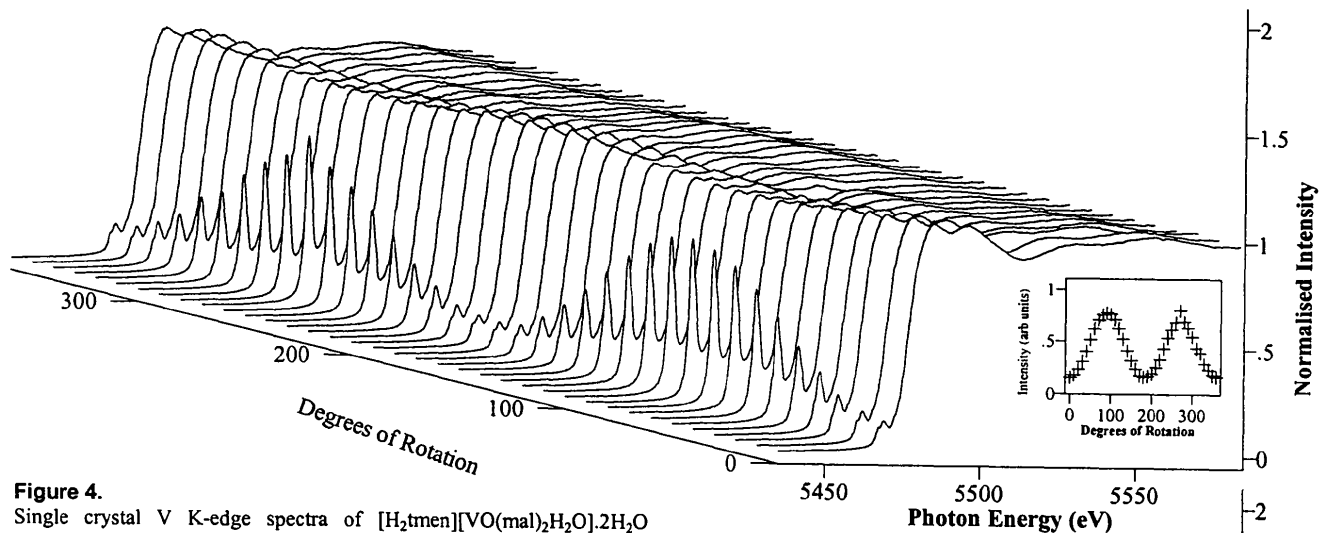


Figure 4. Single crystal V K-edge spectra of $[\text{H}_2\text{tmen}][\text{VO}(\text{mal})_2\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$ recorded in the bc plane at different angles. (0° , V=O perpendicular to polarisation vector) Inset shows intensity dependence of 5469.7 eV pre-edge feature.

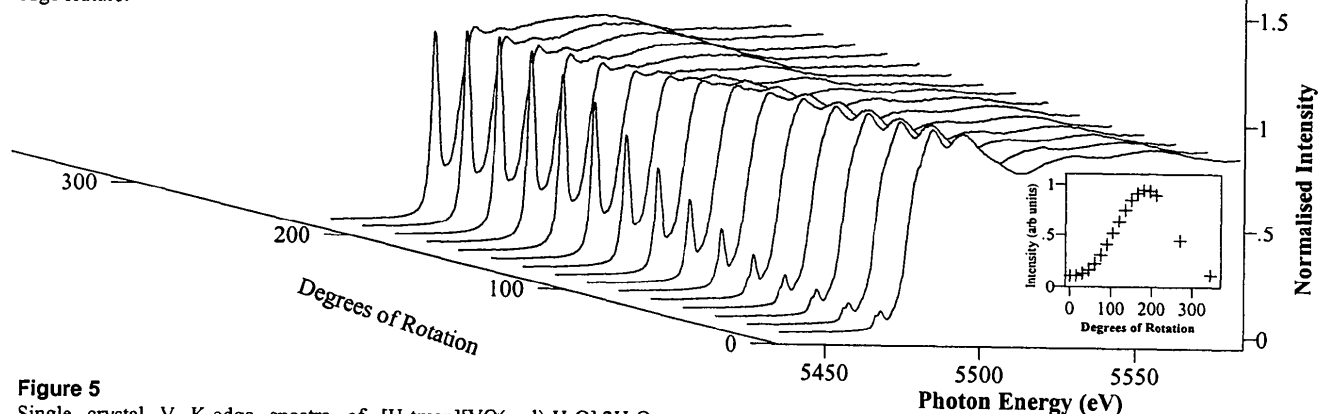


Figure 5 Single crystal V K-edge spectra of $[\text{H}_2\text{tmen}][\text{VO}(\text{mal})_2\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$ recorded in the ab plane at different angles. (0° , the polarisation vector bisects the V-O basal bonds) Inset shows intensity dependence of 5469.4 eV pre-edge feature.

4. Discussion

The 2π dependence of the V K-edge XAFS observed for rotation in the ab crystal plane is unexpected, and intriguing, with its origin not being immediately obvious. The space group is non-chiral, with an inversion centre, therefore the observation of an effective X-ray monopole transition must be the result of the introduction of apparent chirality by some other mechanism. The only ones that appear to account for this behaviour are either: (a) the molecule has been assigned to the wrong space group; (b) it arises as a result of the experimental configuration, with the orthogonal collection of the fluorescence, and the sample mounted at 45° to both incidence and detection; or (c) the ferromagnetic coupling of the unpaired electrons on the vanadium atoms within the sheets of vanadium complexes in the ac planes. At present we cannot make a definitive judgement, but our suspicions are that either (b) or (c) are largely responsible. We have also attempted polarisation dependent vanadium L-edge experiments using this compound, but under the UHV conditions required, the loss of solvent resulted in the loss of crystallinity, and hence no polarisation dependent spectral features were observed.

We gratefully acknowledge: the EPSRC/SERC for an Advanced Fellowship (NAY), equipment and SRS beamtime (GR/J 34200); The Royal Society for a University Research Fellowship (DC); The University of Manchester for a Rona Robinson Scholarship (EP); The University of Hull and The University of Manchester for equipment; and the Director of the Synchrotron Radiation Division at Daresbury Laboratory for access to synchrotron and computing facilities.

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(Received 10 August 1998; accepted 9 December 1998)