

cis-DIOXO(ACETYLACETONATO)(1,10-PHENANTHROLINE)VANADIUM(V)

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The reaction of oxobis(acetylacetonato)vanadium(IV) with 1,10-phenanthroline in methylene chloride under aerobic conditions afforded diamagnetic dioxo(acetylacetonato)(1,10-phenanthroline)vanadium(V). The cis configuration of this compound was concluded on the basis of IR and Raman data, and confirmed by the single crystal X-ray analysis. The geometry of this mixed ligand complex is a distorted octahedron. The V-O(oxide anion) distances are 1.613(4) and 1.670(5) Å, the O-V-O angle being 105.5(2)°. The appreciable trans influence of the oxide anion is reflected on the V-N and V-O(acetylacetonate) distances.

In a course of our study on the reactions of oxobis(acetylacetonato)vanadium(IV),  $\text{VO}(\text{acac})_2$ , with some bidentate nitrogen bases, an interesting phenomenon was observed. The reaction of  $\text{VO}(\text{acac})_2$  with a slight excess of 1,10-phenanthroline in methanol yielded a mixed ligand V(IV) complex of the composition  $\text{VO}(\text{acac})_2(\text{phen}) \cdot 2\text{MeOH}$ ,<sup>1)</sup> but the same reaction in methylene chloride under aerobic conditions resulted in a V(V) complex,  $\text{VO}_2(\text{acac})(\text{phen})$ . Although the detailed pathway of the oxidation reaction is not clear as yet, the product is the first example of the dioxo-vanadium(V) complex containing mixed ligands as evidenced by the correct analysis and diamagnetic behavior.

The IR spectrum of this compound shows two strong bands assignable to the V-O(oxide) stretching vibration at 916 and 886  $\text{cm}^{-1}$  together with a band due to the O-V-O bending mode at 340  $\text{cm}^{-1}$ . The Raman spectrum also exhibits two stretching bands, indicating the cis configuration of two oxide ligands, since the trans complex is expected to show two IR bands ( $\nu_{\text{as}}$  and  $\delta$ ) and one Raman band ( $\nu_{\text{s}}$ ) due to the  $\text{VO}_2$  vibrations.<sup>2)</sup> As is seen in Fig.1 the higher-frequency  $\nu(\text{V-O})$  band is weaker in IR but is much stronger in Raman than the lower-frequency one, revealing that the former is attributed to the symmetric vibration and the latter to the anti-symmetric vibration. In many bent triatomic molecules the  $\nu_{\text{as}}$  band is observed

in the higher frequency region than the  $\nu_s$  band, but the present compound shows an opposite pattern. A similar situation is also observed in  $(\text{NH}_4)_3[\text{VO}_2(\text{ox})_2] \cdot 2\text{H}_2\text{O}$ ,<sup>2)</sup> while  $\text{VO}_2\text{Cl}$ ,  $\text{VO}_2\text{F}$  and  $\text{VO}_2\text{SbF}_6$  show the  $\nu_{as}$  (V-O) band in the higher frequency region than the  $\nu_s$  (V-O) band.<sup>3)</sup>

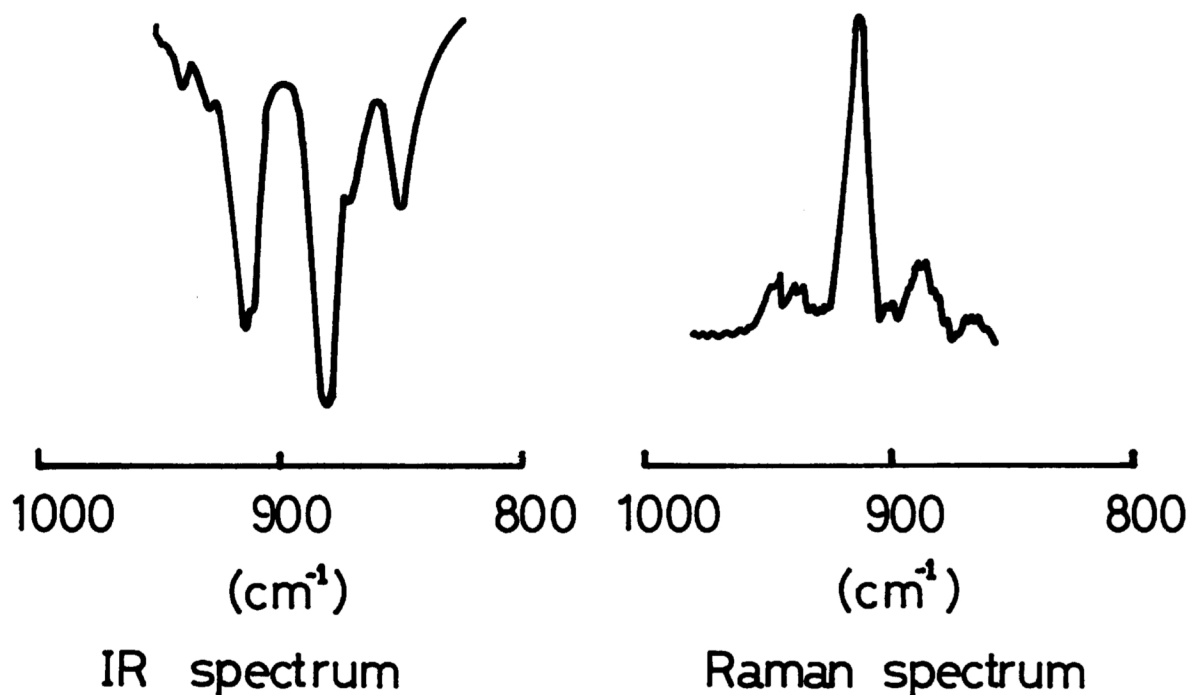


Fig. 1. The IR (in Nujol) and Raman (in solid state) spectra of  $\text{VO}_2(\text{acac})(\text{phen})$  in the V-O(oxide) stretching region.

In order to confirm the molecular structure of this complex, a single crystal X-ray analysis was carried out. Crystal data:  $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}_4\text{V}$ ,  $M=362.3$ , monoclinic, space group  $\text{P}2_1/c$ ,  $a=8.037(5)$ ,  $b=16.058(6)$ ,  $c=12.285(5)\text{\AA}$ ,  $\beta=90.53(6)^\circ$ ,  $Z=4$ . Intensities were measured from the multiple-film equi-inclination Weissenberg photographs taken around  $a$  and  $b$  axes using  $\text{Cu-K}\alpha$  radiation. A total of 2831 reflections were collected and used for structure analysis. The crystal structure was solved by the Patterson and Fourier techniques and refined by the least-squares method to an  $R$  factor of 0.108, isotropic temperature factors being used except for the hydrogen atoms.

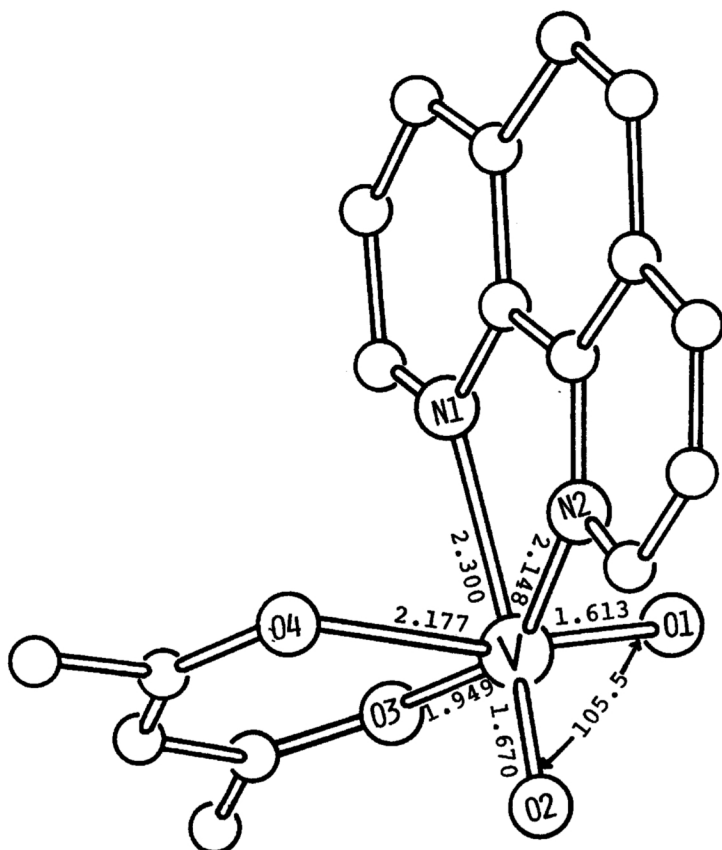


Fig. 2. The molecular structure of  $\text{VO}_2(\text{acac})(\text{phen})$ .

The molecular structure is displayed in Fig.2. The ligating atoms form a distorted octahedron and the vanadium atom is displaced from the center of the octahedron toward the midpoint of the edge joining O(1) and O(2). The  $\text{VC}_2$  group is in the cis configuration with an O-V-O angle of  $105.5(2)^\circ$ ; the V-O distances of  $1.613(4)$  and  $1.670(5)\text{\AA}$  are comparable to  $1.635$  and  $1.648\text{\AA}$  in  $(\text{NH}_4)_3[\text{VO}_2(\text{ox})_2] \cdot 2\text{H}_2\text{O}$ <sup>4)</sup> and  $1.623$  and  $1.657\text{\AA}$  in  $\text{NH}_4[\text{VO}_2(\text{edtaH}_2)] \cdot 3\text{H}_2\text{O}$ ,<sup>5)</sup> implying substantial double bonding. In either case the two V-O distances are not equal, but the difference is most pronounced in the present case (ca.  $0.06\text{\AA}$ ).

The chelating acetylacetonate anion is planar, but the two V-O bond lengths are not equivalent. The O(3) atom is cis to both oxo ligands but the O(4) atom is trans to one, and the V-O(4) length ( $2.177(4)\text{\AA}$ ) is significantly longer than V-O(3) ( $1.949(4)\text{\AA}$ ). Similar situation is also observed for the V-N(1) ( $2.300(4)\text{\AA}$ ) and V-N(2) ( $2.148(4)\text{\AA}$ ) distances.

## References

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