Studies on Oxovanadium (IV) Complexes

II. Absorption Spectra and Circular Dichroism

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Absorption spectra and circular dichroism of optically active oxovanadium(IV) complexes are reported. The experimental data are compared with the molecular orbital energy level diagram given by Ballhausen and Gray.[1] The agreement between the MO description and the observed bands is shown and discussed.

Recently, a number of papers have appeared on the interpretation of the electronic absorption spectra of oxovanadium(IV) complexes. Ballhausen and Gray [1] have discussed in detail the possible electronic structure of such complexes with C_{4v} symmetry. However, Selbin and co-workers [2,3] have questioned the generality of the proposed scheme. In this paper, an interpretation of the absorption spectra based on the circular dichroism (C.D.) spectra of some dissymmetric oxovanadium(IV) complexes is presented which lends support for the former authors' proposals.

It is a general experience that an optically active chelate which forms a puckered metal-chelate ring with one conformation preferred will cause the ligand field transitions to exhibit Cotton effects. Experiments indicate that transitions derived from a common degenerate transition in a closely related complex of higher symmetry nearly obey a sum rule: $\Sigma^i R_{g-n} = 0$ (R_{g-n} is the rotatory strength of the n'th split component from the i times 'degenerate' state). For example this implies that the CD of two split components may be observed even if the splitting is less than 100 cm^{-1}.[4] Thus CD studies may yield information about the number of components under an absorption band enveloping nearly degenerate transitions.

For the investigation of oxovanadium(IV) complexes the anion of R-lactic acid was preferred since it is not far from water in the spectrochemical series. Further its low pK_a enabled the work to be carried out under acid conditions (pH 3.3), so that the error due to hydrolysis was small. In order to obtain a firmer idea of the species studied the equilibrium constants of the system were
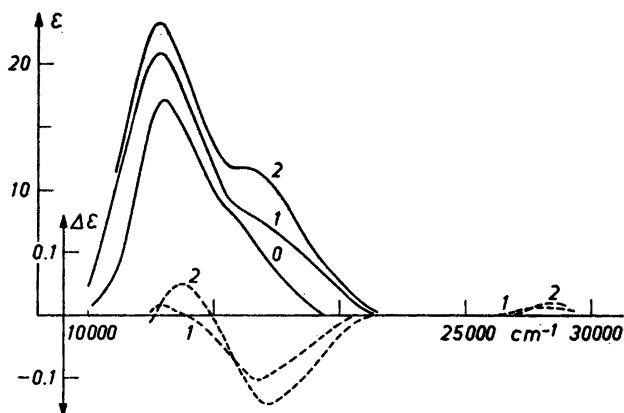
Fig. 1. ——: Absorption spectra of the aqua (0), the mono- (1) and the bis lactato oxovanadium(IV) complexes (2). - - - -: The circular dichroism of the mono- and bis lactato oxovanadium(IV) complexes (1 and 2, respectively).

determined.[5] This was also relevant as it is known that copper(II) (in many respects similar to oxovanadium(IV)) takes up more than two lactate ions causing the CD of the complex to diminish.[6]

ABSORPTION SPECTRA AND CIRCULAR DICHROISM

The absorption spectra and CD of the R-lactato complexes together with the spectrum of the aqua oxovanadium(IV) ion are shown in Fig. 1. The MO model predicts the following energy level scheme for the ligand field transitions. A ground state of symmetry $^2B_2$, and low excited states of ^2E, $^2B_1$ and $^2A_1$ symmetry. The ^2E state may be split in lower symmetries. The absorption
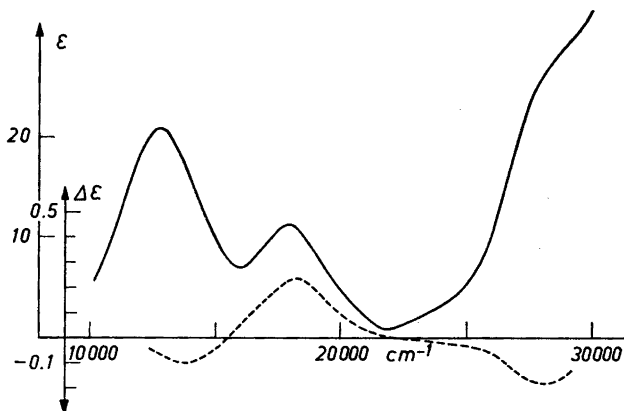

Fig. 2. ——: The absorption, and - - - -: the circular dichroism of a solution of 0.05 M oxovanadium(IV) sulfate and 0.5 M. sodium S,S-tartrate.

curves are in agreement with this scheme showing a slight shift of the second absorption peak at some 16 000 cm^{-1} (mainly a $d_{xy} \rightarrow d_{x^2-y^2}$ transition) towards higher wavenumbers when a negatively charged ligand is introduced.

The CD curves suggest that only in the bis complex has the E component (C_{4v}) split so much that two wing curves result. Unfortunately, it is not possible with our apparatus to confirm this directly (800 nm is maximum wavelength); but the situations of the CD extrema compared to the absorption maxima provide a strong indication.

The strong absorption in the ultraviolet region did not allow a more detailed investigation than that shown in Fig. 1.

The absorption and CD of a solution of 0.05 M oxovanadium(IV) sulphate and 0.5 M sodium S,S-tartrate (Fig. 2) are quite analogous to those of the bis R-lactato complex except for some irregularities near 24 000 cm^{-1}. Kar[7] has measured the CD of an ammoniacal solution of $(NH_4)_2VO(S,S\text{-tart})$, 2 H_2O. However, the corresponding copper(II) tartrate system is known to form polynuclear complexes in basic solution[8] and therefore, a similar behaviour is assumed for oxovanadium(IV) system.

The absorption spectra of bis acetylacetonato oxovanadium(IV) in various glasses at 77 and 296°K have been measured by Selbin, Ortolano and Smith,[2] who found fine structure in the first absorption band at the low temperature. These authors interpreted the fine structure as being the four possible $d-d$ transitions. Basu, Yeranos and Belford[9] have reported the unpolarized spectrum of thin crystals of the same compound at 90°K. A similar fine structure was found but interpreted as resolved vibrational progressions. Some indication for a true splitting of the E component was found. As a new feature Belford and co-workers reported two narrow bands near 23 000 cm^{-1} and suggested that they are spin forbidden bands.
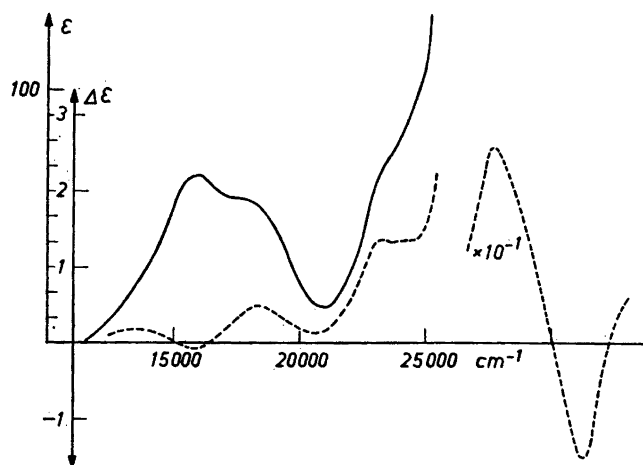

Fig. 3. ———: The absorption, and - - - -: circular dichroism of R-1,2-di-iminopropane-diacetylacetonato oxovanadium(IV) in chloroform.

Schiff bases of acetylacetone are known to be similar to the ketone in coordinating ability. Thus the R-propylenedi-imine-bisacetylacetonate ion (R-pnacac $^{2-}$) was used as an optically active model ligand for acetylacetonate. Martin et al. have prepared the racemic complex and partially resolved it by chromatography. This resolution was not sufficient for CD measurements and therefore, the optically active ligand was used. In Fig. 3 the absorption and CD curves of the complex in chloroform are given. It is seen that the first absorption band gives rise to three CD bands and that this part of the spectrum is completely analogous to that of the formerly discussed complexes.

At ca. 23 000 cm^{-1} a shoulder in the absorption curve and an indication of two sharp CD bands are found. These are believed to correspond to the narrow bands in VOacac$_2$. The intensity of the CD compared to the absorption certainly shows that the transitions are magnetically allowed as would be expected for spin forbidden transitions. In order to obtain a firmer basis for the assignment a luminescence spectrum was measured. For incident light of 26 000 cm^{-1} the only observable emission was a band having maximum at 22 200 cm^{-1}. This result is analogous to earlier obtained luminescence data for similar ligands. For example Crosby, Whan, and Alire [10] in a series of rare earth complexes of the type M^{III} (benzoylacetonate)$_3$ found the emitted light of frequencies 21 300—21 600 cm^{-1}. Therefore, it is assumed that the transitions at 23 000—24 000 cm^{-1} are indeed spin forbidden transitions, but more or less internal ligand transitions. Self-consistent field calculations [11] predict a spin forbidden transition in the acetylacetonate ion in this range.

CONCLUSION

The CD curves reveal beyond doubt that there are three electronic transitions in the oxovanadium(IV) complexes under the absorption band 10 000—20 000 cm^{-1}. For complexes of C_{4v} symmetry these transitions are a doubly degenerate $^2B_2 \rightarrow {}^2E$ transition and a nondegenerate $^2B_2 \rightarrow {}^2B_1$ transition. In this symmetry both transitions are magnetically allowed. The CD exhibited by the optically active complexes is for this range of considerable magnitude, especially when it is considered that large cancellations occur. The predicted $^2B_2 \rightarrow {}^2A_1$ transition (C_{4v}) is not magnetically allowed. It is a general experience that CD of such a transition in an asymmetric compound will give rise to only a very small Cotton effect. This is observed for the CD bands near 28 000 cm^{-1} for the lactate and tartrate complexes. Although this transition is rather isolated so that no cancellation occurs the magnitude of the CD bands are small. In [VO R-pnacac] the $^2B_2 \rightarrow {}^2A_1$ transition is hidden under ligand transitions and the CD pattern is disturbed.

EXPERIMENTAL

S,S-tartrato-oxovanadium(IV). A solution with the composition $C_{VO^{*+}} = 0.05$ M and $C_{Na,tart} = 0.5$ M was measured without foregoing equilibrium study of the system. Formal molar absorption and CD were calculated.

R-1,2-di-iminopropane-di-acetylacetone (R-pnacacH$_2$) was prepared by mixing R-1,2-diaminopropane and acetylacetone dissolved in diethyl ether in 1:2 molar proportion.

(R-1,2-di-iminopropane)-di-acetylacetonato oxovanadium(IV), [VO R-pnacac]. The complex has been prepared from the optically active ligand in analogy to the preparation of the racemic compound [11] by heating acetylacetonato oxovanadium(IV) and excess R-pnacacH$_2$ to 130°. (In the paper of Martin *et al.*[12] we assume a misprint of 230° instead of 130° for this temperature, to be present.) Absorption, CD and fluorescence of this complex were measured in chloroform solutions at room temperature.

Absorption measurements were performed with a Cary 14 recording spectrophotometer using a thermostated cell holder (20°). CD was measured with a Roussel-Jouan Dichrograph at room temperature. The fluorescence of [VO R-pnacac] in chloroform solutions was measured with an Aminco-Bowman Spectrophotofluorometer.

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