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Oxovanadium Complexes with Substituted Chalcone Oximates

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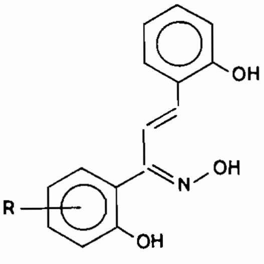
Two 2′-dihydroxychalcone oximes are known bidentate chelating agents [1], forming 1:2 (metal: ligand) complexes with divalent metal ions. In an attempt to further explore the coordination chemistry of these ligands, vanadyl complexes were synthesized in order to evaluate the metal–ligand and ligand–ligand bonding. Elemental analysis, conductivity, magnetic moment and molecular weight data were obtained, along with electronic and infrared spectra.

Experimental

All chemicals used were reagent grade. 2-Hydroxyacetophenone and the substituted methyl and chloro analogues were prepared by a known method [2]. Chalcones were prepared by reacting salicylaldehyde with substituted acetophenones according to the method of Dhar [3–5]. The ligands were recrystallized from benzene. The chalcone oximes were prepared by refluxing for one hour 0.01 mol of chalcone, 0.01 mol of hydroxylaminehydrochloride and 0.01 mol of sodium acetate in about 50 ml of ethyl alcohol. The refluxed solution was poured on crushed ice and the chalcone oxime was then filtered and recrystallized from ethanol. The following ligands were prepared:



Ligand	R
A	H
B	3-methyl
C	4-methyl
D	5-methyl
E	5-chloro

The vanadium complexes were prepared by adding 10 mmol of oxovanadium(IV) chloride to a slight excess of chalcone oxime (22 mmol) and sodium acetate (22 mmol) in a minimum amount of water. The resulting solution was vigorously stirred. The buff-colored complexes **I**–**V** corresponding to the ligands **A**–**E** were filtered and washed repeatedly with aqueous alcohol, and then dried in vacuo over anhydrous calcium chloride.

The elemental analyses were carried out using a standard procedure [6]. Vanadium was gravimetrically estimated as V_2O_5. Kjeldahl's method was used to determine the nitrogen content of the complexes. Molecular weights were determined in nitrobenzene by a cryoscopic method. The molar conductivities were measured in dimethylformamide (DMF) at concentrations of 10^{-3} M using an Elico-CM-82 conductivity bridge. The magnetic measurements on solid vanadyl complexes were made at room temperature on a Guoy balance with a split sample tube. The electronic spectra were obtained using a Cary-17 recording spectrophotometer in the region 11 100–28 600 cm^{-1}. The infrared spectra of the ligands, **A**–**E**, and the vanadium complexes **I**–**V** were recorded on a Beckman IR-S spectrophotometer in the region 650–4000 cm^{-1} using the Nujol mull technique. Table I reports the elemental analysis data for all the complexes as well as the magnetic moment and molecular weight.

Results and Discussion

It is evident from the elemental analyses that oxovanadium(IV) forms compounds with a 1:2 (metal:ligand) stoichiometry. In each case by using excess ligand, the formation of binuclear complexes was avoided. All complexes are soluble in benzene, chloroform, nitrobenzene, pyridine, dimethylformamide and dimethylsulfoxide. The molecular weights agree with the empirical formulae. All molecular conductivities are in the range of 5–15 ohm^{-1} cm^2 mol^{-1} suggesting nonelectrolyte behavior in dimethylformamide.

The magnetic moments obtained at room temperature are low, ranging from 1.35 to 1.48 BM, as compared to a normal range of 1.7 to 1.8 BM for a doublet ground state. Ginsberg *et al.* [7] have suggested that the low magnetic moment is due to a d–d orbital interaction within a dimeric compound. The present molecular weight determinations rule out this explanation, and the observed low values of the magnetic moment are attributed to a delocalization of d-electron density into the conjugated ligand.

The three bands appearing in the electronic spectra of the oxovanadium complexes are ascribed to d–d

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TABLE I Analytical and Physical Data for Bis(2,2′-dihydroxychalcone oxime)oxovanadium(IV)

Ligand	Complex	Molecular formula of complex	%V[a]	%N[a]	Molecular[a] weight	μ_{eff} (BM)[b]
A	I	$VO(C_{15}H_{12}O_3N)_2$	8.75 (8.87)	4.78 (4.87)	592 (575)	1.37
B	II	$VO(C_{16}H_{14}O_3N)_2$	8.53 (8.46)	4.55 (4.64)	615 (603)	1.42
C	III	$VO(C_{16}H_{14}O_3N)_2$	8.40 (8.46)	4.70 (4.64)	621 (603)	1.35
D	IV	$VO(C_{16}H_{14}O_3N)_2$	8.55 (8.46)	4.50 (4.64)	610 (603)	1.48
E	V	$VO(C_{15}H_{11}O_3NCl)_2$	7.85 (7.92)	4.42 (4.35)	660 (644)	1.45

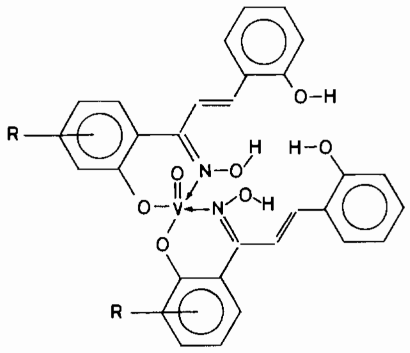
[a]Figures in the parentheses are theoretical values [b]Bohr magneton

transitions for oxovanadium in C_{4v} symmetry [8–10]. The prominent band at 12 700 cm^{-1} is assigned to a $^2B_2 \rightarrow {}^2E$ transition. A shoulder band at 14 700 cm^{-1} is due to a $^2B_2 \rightarrow {}^2B_1$ transition. The third band, generally not observed in many similar compounds [11] due to the intense charge transfer bands of the ligands, is observed as a shoulder at 27 800 cm^{-1} and is assigned to the $^2B_2 \rightarrow {}^2A_1$ transition.

The infrared spectra of the ligands and the metal complexes may be assigned as follows. The ligands exhibit two O–H stretching bands. a broad, medium-intensity band in the range 3150–3400 cm^{-1}, due to a hydrogen-bonded hydroxy group, and a second broad, low-intensity band in the range 2550–2700 cm^{-1} due to ν(O–H) but shifted to low frequency because of intermolecular hydrogen bonding. In the metal complexes the first band remains unchanged, but the second disappears. These facts appear to indicate that one of the phenyl hydroxy groups is not involved in bonding, precluding the possibility of a tridentate coordinating ligand; furthermore, the disappearance of the band in the range 2550–2700 cm^{-1} indicates that a hydroxy group has ionized and that oxygen is now coordinated to the oxovanadium.

Only one piece of evidence indicates that intramolecular hydrogen bonding continues to influence the overall metal complex structure. A comparison of the infrared spectra of the ligands and that of the respective oxovanadium complexes reveals that the fingerprint region of the metal complex spectra is shifted to lower frequency. This suggests that intramolecular hydrogen bonding may be enhanced upon complexation of the oxovanadium with the chalcone oxime. One structural representation consistent with the data postulates that the two phenyl and two oxime hydroxy groups of the two chalcone oxime ligands are involved in hydrogen bonding. The bonding may be partially responsible for the observed subnormal magnetic moment, since it might delocalize d-electrons into the two ligands.

In view of the previous assignments [12, 13] the high intensity band at 1605 cm^{-1} in the ligands as well as in the complexes is assigned to a mixture of a hydroxy deformation and ethylynic C=C stretching vibration. The medium intensity band around 1575–1580 cm^{-1} in the ligands shows a measurable shift in all the complexes and appears in the region 1540–1550 cm^{-1}. This band is assigned to ν(C=N) of the oxime and shifts toward lower frequency upon complexation, indicating a coordination of the C=N group to the oxocation through nitrogen. The high intensity band in the ligands around 1270–1280 cm^{-1} may be assigned to phenolic ν(C–O) [14, 15] and is shifted to higher frequency at 1300 cm^{-1} in all of the metal oxo-compounds due to the coordination through oxygen to the metal. An unusual, high-intensity, broad band around 1240 cm^{-1} in the ligands as well as in the complexes is attributed to a combination of ν(C–H) and ν(N–O) vibrations. A new, broad, intense band appears in the complexes around 980 cm^{-1} and is attributed to ν(V=O) which agrees with earlier observations [11].



The foregoing data suggest that vanadium metal is pentacoordinated. On the basis of the previous reports based on oxovanadium(IV) oximates [11, 16, 17] a square-pyrimidal structure around vanadium(IV) with a strongly hydrogen-bonded ring is proposed.

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