# ADDUCT FORMATION BETWEEN BIS(β-DIKETONATO) OXOVANADIUM(IV) COMPLEXES AND 4-METHYL-PYRIDINE N-OXIDE

### N. S. AL-NIAIMI, A. R. AL-KARAGHOULI, S. M. ALIWI and M. G. JALHOOM

Chemistry Department, Nuclear Research Institute, Iraqi Atomic Energy Commission, Tuwaitha, Baghdad, Iraq

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**Abstract**—Adduct formation between 4-methylpyridine N-oxide (MPO) and a series of bis( $\beta$ -diketonato)oxovanadium(IV) complexes has been studied spectrophotometrically in dichloromethane and their adduct formation constants ( $K_1$ ) have been determined. The  $\beta$ -diketones used are acetylacetone (Haca), benzoylacetone (Hbza), dibenzoylmethane (Hdbm), dipivaloylmethane (Hdpm), trifluoroacetylacetone (Htfa) and thenoyltrifluoroacetone (Htta). The results obtained show that the  $K_1$  values vary in following the order

tta > tfa > dbm > bza > aca > dpm.

Solid adducts have been isolated and their i.r. spectra in the region 200-4000 cm<sup>-1</sup> studied.

### INTRODUCTION

BIS( $\beta$ -DIKETONATO)OXOVANADIUM(IV), VO(DK)<sub>2</sub> are known to form adducts with a variety of bases. Monoaddition compounds of  $VO(aca)_2$  with pyridine [1, 2] and pyridine N-oxide[3] have been studied. VO(aca)<sub>2</sub> has been used rather extensively as a reference acid [3-6]. The heats of reaction of substituted pyridine N-oxides with VO(aca)<sub>2</sub> have been determined calorimetrically, and in the case of the 4-substituted derivatives, the  $\Delta H$  values correlate well with the substituent constants  $\sigma[3]$ . The shifts in the vanadyl stretching frequency  $\Delta v$  (V=O) and the  $\Delta v$  (V-O) shifts have also been found to correlate with the enthalpies of the reaction [3]. Selbin et al. [5] found no general correlation for VO(aca)<sub>2</sub> and a variety of bases. On the other hand, a study of the enthalpy change in the reaction of a number of nitrogen and oxygen donors with VO(aca)<sub>2</sub> showed no general correlation of  $\Delta H$ values with  $pK_a$  values of the bases [4].

However, Garvey and Ragsdale [6] have found that  $\Delta v(V=O)$  values correlate with  $\sigma$  when 4-substituted pyridine N-oxides coordinate with VO(aca)<sub>2</sub> and with VO(bza)<sub>2</sub>. The shifts in v(V=O) produced when substituted pyridines are added to VO(aca)<sub>2</sub> in chloroform have been discussed in terms of the equilibrium in solution between the *cis* and *trans* isomers [7]. Caira *et al.* [2] found that the solid adducts formed between VO(aca)<sub>2</sub> and several substituted pyridines could be classified on the basis of their i.r. spectra into either *cis*- or *trans*- isomers (with reference to acetylacetone rings) depending on the pyridine substituent. A study

of the addition compounds of  $VO(dbm)_2$  with pyridine has shown the existence of mono- and di-addition adducts [8].

Relatively few studies have been made of adduct formation constants of  $bis(\beta$ -diketonato)oxovanadium (IV) complexes, and the available data are largely for the VO(aca)<sub>2</sub> adducts. The object of the present investigation was to study the adduct formation between 4-methyl pyridine N-oxide (MPO) and each of VO(aca)<sub>2</sub>, VO(bza)<sub>2</sub>, VO(dbm)<sub>2</sub>, VO(dpm)<sub>2</sub>, VO(tfa)<sub>2</sub> and VO(tta)<sub>2</sub>. The adduct formation constants were determined in dichloromethane in the hope of correlating the results with the nature of the  $\beta$ -diketone and with other structural factors. In addition, the solid adducts were prepared and their i.r. spectra analysed.

### **EXPERIMENTAL**

#### Preparations and materials

The complexes VO(aca)<sub>2</sub>, VO(bza)<sub>2</sub>, VO(dbm)<sub>2</sub>, VO(dpm)<sub>2</sub>, VO(tfa)<sub>2</sub> and VO(tta)<sub>2</sub> were prepared by the neutralization of an acidic solution of oxovanadium (IV) sulfate or chloride with sodium acetate in the presence of the respective  $\beta$ -diketone [9, 10]. The resulting precipitates were collected, washed, dried and purified by recrystallization from ether, ethanol or chloroform, or by vacuum sublimation.

The diketones Haca, Hbza, Hdbm, Hdpm, Htfa and Htta were obtained commercially from Fluka AG Chemische Fabrik and used without further purification.

4-Methyl pyridine N-oxide was prepared by a method similar to that for 3-methyl pyridine N-oxide [11], by the

Compounda	D.P.		Found %		Calculated %				
Compounds	± 2°	С	Н	N	C	Н	N		
VO(dpm) <sub>2</sub>	193	60.60	9.01		60.94	8.77			
VO(dpm) <sub>2</sub> MPO <sup>†</sup>	141	62.50	8.16	3.51	61.99	8.30	2.57		
VO(aca) <sub>2</sub>	257	45.27	5.27		45.24	5.28			
$VO(aca)_2$ . MPO	178	50.58	5.48	4.02	51.30	5.66	3.74		
VO(bza),	211	61.65	4.61		61.65	4.62			
$VO(bza)_2$ . MPO	59	62.08	4.97	3.81	62.65	5.02	3.81		
VO(dbm) <sub>2</sub>	253	70.66	4.31		70.18	4.28			
$VO(dbm)_2 . (MPO)_2$	120	69.61	5.15	4.09	68.93	4.96	3.83		
$VO(tfa)_2^c$	226	32.32	2.18		32.17	2.14			
$VO(tta)_2$	290	37.74	1.63		37.69	1.57			
VO(tta) <sub>2</sub> . MPO	68	43.54	2.69	2.30	42.72	2.45	2.26		

Table 1. Data on vanadyl chelates VO(DK)<sub>2</sub> and their 4-methyl pyridine N-oxide adducts

\*Microanalysis was carried out by "Alfred Bernhard" Microanalytisches Laboratorium, Germany.

<sup>†</sup>The result of N analysis is high as compared to the calculated value. This is most probably due to the difficulties encountered in the purification of this compound. <sup>‡</sup>Solid adduct of VO(tfa)<sub>2</sub> could not be isolated. A thick green layer was obtained.

oxidation of 4-methyl pyridine with peracetic acid (a mixture of glacial acetic acid and 30% hydrogen peroxide).

Adducts of the  $VO(DK)_2$  complexes with 4-methyl pyridine N-oxide were prepared by refluxing equimolar quantities of the respective  $VO(DK)_2$  complex and the base in ether (or ether-cyclohexane mixture) for few minutes until reaction was completed. The reaction mixture was then dried over magnesium sulfate, filtered and concentrated by evaporation under vacuum and the resulting precipitate was recrystallized from cyclohexane, isooctane or carbon tetrachloride. All solvents used in the preparation were sodium-dried to ensure anhydrous conditions. Results of microanalyses for C, H and N are given in Table 1.

### Apparatus and procedure

In each system weighed quantities of the VO(DK)<sub>2</sub> complex and known volumes of a stock solution of MPO in dichloromethane were made up to 10 ml with dichloromethane. The spectra of these solutions were immediately measured on a Beckman i.r. 12 spectrophotometer in the v(V=O) region using variable pathlength cells with KBr windows or on Unicam SP 500 and SP 700 spectrophotometers using silica cells at a predetermined wavelength. The choice of wavelength ensuring maximum change in absorbance upon adduct formation was made by recording the spectrum of a solution of VO(DK)<sub>2</sub> of an appropriate concentration superimposed on to the spectrum of a mixture of VO(DK)2 and a high concentration of MPO. Only one wavelength was used for the measurement in order to minimize the time required and so reduce the decomposition which was evident from the fairly rapid change of absorbance with time and the formation of a dark residue. This decomposition has also been observed by other workers [4] and assumed to be accompanied by oxidation [12] of V(IV) to V(V). Blank correction was not found necessary since the ligand absorption was negligible in the concentration range used. The dichloromethane was of spectro quality and was not further purified.

Solid i.r. spectra were recorded on the Beckman i.r. 12 spectrophotometer for Nujol mulls between polythene discs  $(200-650 \text{ cm}^{-1})$  and KBr disks  $(400-4000 \text{ cm}^{-1})$ .

All spectral measurements were conducted at room temperature (25  $\pm$  2°).

#### **RESULTS AND DISCUSSION**

#### Adduct formation constants

The reaction between  $VO(DK)_2$  and MPO in dichloromethane proceeds according to:

$$VO(DK)_2 + j MPO \rightleftharpoons VO(DK)_2 (MPO)_i$$
. (1)

The absorption spectra of a series of solutions containing a fixed total concentration of VO(DK)<sub>2</sub>,  $M_{T}$ , and varied concentrations of the base were determined. The spectrum of VO(DK)<sub>2</sub> in dichloromethane exhibits two maxima, the longer wavelength of which falls within the range 670-700 nm depending upon the type of VO(DK)<sub>2</sub>, and shifts to a longer wavelength upon addition of the base. The magnitude of this bathochromic shift also depends upon the type of VO(DK)<sub>2</sub> and lies within the range 75-130 nm. Within the range of added base concentration investigated, the spectra of the mixed solutions for each of the systems  $VO(aca)_2$ ,  $VO(bza)_2$  and  $VO(dpm)_2$  exhibited isosbestic points consistent with 1:1 adduct formation. However in the system involving VO(dbm)<sub>2</sub> addition of the base beyond the isosbestic region caused a large increase of the absorbance at the shorter wavelength band and deviation from the isosbestic point was significant, indicating the formation of both 1:1 and 2:1 adducts. Similar observations have been reported for the reaction of VO(dbm)<sub>2</sub> with pyridine [8].

For each system and within the isosbestic region the apparent absorbance, A, was measured as a function of the added total base concentration,  $B_T$ , at a fixed wavelength chosen to ensure maximum variation in absorbance. The adduct formation constant,  $K_1$ , of the 1:1 adduct is given by [13]:

$$K_1 = \frac{(A - A_0)}{(A_\infty - A)} \cdot \frac{1}{B_T - M_T (A - A_0) / (A_\infty - A_0)}$$
(2)

where  $A_0$  and  $A_{\infty}$  are the absorbances measured for

	Vis	sible w	ork	Infrared work						
Vanadyl chelate	range of $\frac{B_T}{M_T}$	λnm	<i>K</i> <sub>1</sub>	range of $\frac{B_T}{M_T}$	v(V = O $cm^{-1}$	) K <sub>1</sub>				
VO(dpm) <sub>2</sub>	1.9 -19.0	860	$9.8 \pm 0.5$	1.4410.5	999	$10.8 \pm 0.5$				
VO(aca) <sub>2</sub>	0.3 - 5.0	830	$76 \pm 3$	0.67- 2.7	1004	$65 \pm 6$				
$VO(bza)_2$	0.71-2.85	746	$98 \pm 7$	0.48 3.8	1001	$94 \pm 10$				
VO(dbm) <sub>2</sub>	0.34-3.42	880	$151 \pm 6$	0.51 2.93	1001	$186 \pm 10$				
VO(tfa)2	0.15-0.74	460	$500 \pm 150$							
$VO(tta)_2$	0.2- 0.7	500	$2000 \pm 1000$							

Table 2. Formation constants of the adducts formed between the vanadyl chelates VO(DK)<sub>2</sub> and 4-methyl pyridine N-oxide in dichloromethane

 $M_T$  when the species B is absent  $(B_T = 0)$  and when it is present in such excess that adduct formation is complete ( $[VO(DK)_2(MPO)] = M_T$ ). the calculation of  $K_1$  from Eqn (2) was carried out by systematically varying the value assumed for  $A_{\infty}$ , the experimentally inaccessible value for the adduct, until the standard deviation in the calculated average value of  $K_1$  for all the data points was minimized. The computer-based solution given by Gans and Irving [13] was adopted. The results are given in Table 2. Although the standard deviation obtained from the computation was less than 5 per cent in some systems, the reproducibility in the experimental data was not very good owing to the lack of stability of the absorbance reading with time; consequently the error in the values of  $K_1$  could be as high as 10 per cent.

To gain further support for these values of  $K_1$  they were redetermined using the i.r. spectroscopic technique by following the decrease in intensity of the vanadyl stretching frequency v(V = O) of VO(DK)<sub>2</sub> on addition of the base. This band, occurring at about 1000 cm<sup>-1</sup>, shifts upon adduct formation to about 960 cm<sup>-1</sup> depending upon the type of VO(DK)<sub>2</sub>. A representative example of the shift and decrease in



Fig. 1. Reduction in intensity of the original unperturbed v(V = O) band (999 cm<sup>-1</sup>) and growth of the shifted band (948 cm<sup>-1</sup>) of 0.0208 mole/l. VO(dpm)<sub>2</sub> with increasing MPO concentration in CH<sub>2</sub>Cl<sub>2</sub>.1, [MPO] = 0: 11-V1. [MPO] = 0.01, 0.03, 0.08, 0.12 and 0.22 mole/l. respectively. Dotted lines represent the base lines used in the absorbance measurement.

intensity of the v(V=O) band is reproduced in Fig. 1 for the VO(dpm)<sub>2</sub>-MPO system. Eqn (2) was used for the calculation of  $K_1$  values as before. The absorbance  $A = \log (I_0/I)$  was calculated for each measurement from values of  $I_0$  and I measured by the base line method. This method was found to be convenient since the band under consideration was reasonably symmetrical and the base line did not vary appreciably on addition of the base. The calculated values of  $K_1$ given in Table 2 are in reasonable agreement with those obtained from the work in the visible region. It must be added, however, that greater accuracy in the values of  $K_1$  determined in the i.r. work could be achieved by measuring the area under the band after resolving it, though this may not be worth while in view of the standard deviations due to experimental error. Further examination of this problem is being made.

For the systems VO(tfa)<sub>2</sub>-MPO and VO(tta)<sub>2</sub>-MPO it was not possible to calculate adduct formation constants from the results in the visible region by using the peak around 800 nm owing to the very small variation in absorbance upon adduct formation. The work in the i.r. region did not give reproducible values either. It was thought worthwhile to utilize the large shifts in absorbance at 460 and 500 nm respectively. However, the absorbance lacked reproducibility when  $B_T/M_T$ increased beyond 0.5. The data obtained for the region  $B_T/M_T < 0.5$  were analyzed assuming the formation of a 1:1 adduct only, and only approximate  $K_1$  values can be reported. The value thus found for the VO(tfa)<sub>2</sub>. MPO adduct is  $500 \pm 150$ , while that for the VO(tta)<sub>2</sub>.

The results obtained show that the adduct formation constants,  $K_1$ , vary with the nature of the  $\beta$ -diketone in the VO(DK)<sub>2</sub> complex in the following order:

tta > tfa > dbm < bza > aca > dpm.

These adducts exist in solution as *cis*- and/or *trans*isomers of structures I and II.

The electron-accepting capacity of vanadium in the  $VO(DK)_2$  complexes should be markedly affected by the coordinated ligands. Thus the order of increase of  $K_1$  will depend upon factors such as (1) the order of basicities of the  $\beta$ -diketones (b) the order of stabilities of the  $VO(DK)_2$  complexes and (c) steric and structural factors.

A review of the published  $pK_a$  values of these  $\beta$ -diketones indicates the following order [14]:

dbm > bza > aca > tta > tfa.



No data are available on the stabilities of the  $VO(DK)_2$ complexes and it cannot be stated with certainty what their order would be. In general the stabilities of the metal chelates fall in the same order as the basicities of the chelating agents. On this basis  $VO(tta)_2$  and VO $(tfa)_2$  are expected to be less stable than VO(aca)<sub>2</sub> and this to be less stable than VO(dpm)<sub>2</sub>. The trend within the series  $VO(aca)_2$ ,  $VO(bza)_2$  and  $VO(dbm)_2$  cannot be so directly correlated with the order of basicities of the  $\beta$ -diketones since factors such as the resonance of the chelate ring and structural considerations become important. The crystal structure of VO(bza)<sub>2</sub>[15] shows that the two phenyl rings are twisted by 18° and 6° out of the plane of the two chelate rings. It is expected that in  $VO(dbm)_2$  the angles between the phenyl rings and the plane will be even larger. Such a structure will decrease the effect of the extended conjugation introduced by the phenyl groups, and tend to increase the basicity of the enolic ring to such an extent that the inductive effect of the phenyl groups outweighs the effect of conjugation. It is quite likely therefore that the order of stability of these vanadyl complexes is

 $VO(aca)_2 > VO(bza)_2 > VO(dbm)_2.$ 

As the stability of the VO(DK)<sub>2</sub> complex increases, the electron density on the vanadium atom increases and consequently its coordinating ability with the MPO decreases. Thereby the observed order of increase of  $K_1$  is parallel to the expected order of decrease of the stability of the VO(DK)<sub>2</sub> complexes. In the VO(dpm)<sub>2</sub>. MPO adduct the observed large decrease in the adduct formation constant could also be attributed in part to steric hindrance to adduct formation introduced by the *t*-butyl group in the  $\beta$ -diketone.

### Infrared studies

The i.r. results for the solid VO(DK)<sub>2</sub> complexes and VO(DK)<sub>2</sub>. MPO adducts and their solutions in dichloromethane are given in Table 3. These results include the v(V=O) bands and the V-O sensitive modes. The last mentioned, occurring at 611, 485, 423 and 365 cm<sup>-1</sup>, for the VO(aca)<sub>2</sub> complex, have been assigned to v(V-O),  $v(V-O) + v(C--CH_3)$ ,  $\sigma(O-V-O)$  and v(V-O) respectively [2].

It is now generally accepted that the V=O bond consists of a combination of  $\sigma$ -bond and  $p_{\pi}-d_{\pi}$  donation of electrons from the vanadyl oxygen to the vanadium atom. Donation of electron pairs from ligand atoms increases the electron density in the vanadium d

CH

II

aca:  $R = R' = CH_3$ bza:  $R = CH_3$ ;  $R' = C_6H_5$ dbm:  $R = R' = C_6H_5$ dpm:  $R = R' = C(CH_3)_3$ tfa:  $R = CH_3$ ;  $R' = CF_3$ tta:  $R = CF_3$ ;  $R' = C_4H_3S$ 

Compound	v(V=O) Nujol CH <sub>2</sub> Cl <sub>2</sub>		v(V - O) sensitive modes (Nujol) 200-650 cm <sup>-1</sup>										
VO(dpm),	1005	999	648m		524s			488s		- 439m		3735	
VO(dpm), MPO	958	948	633m		494s			478s	441w	426m	394w	3428	
VO(aca),	998	1004	611w		585s			423w				365m	
VO(aca) <sub>2</sub> . MPO	965	964>951	602w		565s			418w				365m	
$VO(bza)_2$	997	1001	574s		457m			449m				3775	
VO(bza) <sub>2</sub> . MPO	954	962 < 952	553s	497w	458w			431s		362m		3435	
VO(dbm) <sub>2</sub>	995	1001	587s		551m			463m				370s	
VO(dbm) <sub>2</sub> (MPO) <sub>2</sub>	950	962≪952	557s		651m	537m	496m	463m		417m		3358	
VO(tfa)	932	1015	601s		535m			448s				396m	260m
VO(tfa) <sub>2</sub> .MPO	965	968	590s	575m	502s			427s	4	112(sh)		361m	
VO(tta).	900	1012	607s		559w			541w				3795	266m
$VO(tta)_2$ . MPO	963	969	594s		541 m			503m		425m		3378	

Table 3. Infrared data (cm<sup>-1</sup>) on vanadyl chelates VO(DK)<sub>2</sub> and their 4-methyl pyridine N-oxide adducts

orbitals and hence reduces donation from the vanadyl oxygen and reduces the V=O double bond character. This should imply a shift of v(V=O) to a lower frequency. On coordination of the MPO ligand to VO(aca)<sub>2</sub>. v(V=O) is lowered by 33 cm<sup>-1</sup>. In solution, however, the v(V=O) band of the above-mentioned VO(DK)<sub>2</sub> complexes gives rise on adduct formation to two shifted bands.

Da Silva et al. [7] have observed a similar phenomenon on adduct formation between  $VO(aca)_2$  and a number of pyridine bases. They suggest that the presence of two shifted bands provides evidence for the existence of an equilibrium between the two cis and trans isomers in solution. They also observed that trans coordination would be expected to have a larger effect on v(V=O) than cis coordination. However Caira et al. [2] proved from both i.r. and X-ray crystallographic evidence that the complexes which show the greatest reduction of v(V=O) are in the cis form. Our observation of two shifted bands implies the existence in solution of the two cis- and trans- isomers in equilibrium. For the VO(aca)2. MPO adduct in solution the band at 964 cm<sup>-1</sup> is much more intense than the one at 951 cm<sup>-1</sup> suggesting that the trans isomer is predominant. For the VO(bza)2. MPO adduct in solution the band at 952 cm<sup>-1</sup> is more intense than the one at  $962 \text{ cm}^{-1}$  indicating that the *cis* isomer is predominant. For the VO(dbm)<sub>2</sub>. MPO adduct in solution the band at 952 cm<sup>-1</sup> is very much more intense than the one at 962 cm<sup>-1</sup> indicating that the *cis* isomer is the predominant species. For the VO(tfa)<sub>2</sub>. MPO and VO (tta)<sub>2</sub>. MPO adducts in solution, only one frequency at low values was observed, suggesting the existence of only the cis isomer in solution. Likewise the VO(dpm)<sub>2</sub>. MPO adduct exhibits one band in solution at 948 cm<sup>-1</sup>, indicating the presence of the *cis* isomer only. The formation of this isomer rather than the *trans* could be attributed to steric hindrance introduced by the methyl groups in the ligand approaching the VO(dpm)<sub>2</sub> complex in the trans position.

It is interesting to note that the i.r. spectra of the solid VO(tfa)<sub>2</sub> and VO(tta)<sub>2</sub> complexes are remarkably dif-

ferent from those of other VO(DK)<sub>2</sub> complexes. While the v(V=O) band for the majority of the VO(DK)<sub>2</sub> complexes occurs at about 1000 cm<sup>-1</sup> both in the solid complex and for its solution, it is observed to occur at much lower frequencies for VO(tfa)<sub>2</sub> (932 cm<sup>-1</sup>) and for VO(tta)<sub>2</sub> (900 cm<sup>-1</sup>). The reported values for this band for the VO(tfa)<sub>2</sub> complex are 925 cm<sup>-1</sup> or 930 cm<sup>-1</sup> [10, 6]. However, no explanation was given for these low values. In dichloromethane solution the v(V=O) bands occur at 1015 cm<sup>-1</sup> and 1012 cm<sup>-1</sup> for the VO(tfa)<sub>2</sub> and VO(tta)<sub>2</sub> complexes respectively. This should be contrasted with the observation that the v(V=O) bands for all the adducts VO(DK)<sub>2</sub> MPO occur at roughly the same frequency both in the solid compounds and in their solutions.

The lower frequencies observed for the v(V=O) bands in the VO(tfa)<sub>2</sub> and VO(tta)<sub>2</sub> solid compounds are most probably due to a polymeric chain structure of the type

The lowering of the v(V=O) frequency upon formation of the polymeric species is analogous to the decrease in the frequency upon adduct formation. This polymerization could be attributed to the inductive effect of the trifluoro group tending to increase the electro-negativity of the vanadium atom and resulting in intermolecular V.....O bonding in the solid compounds to meet the crystal packing requirements. The rather high v(V=O)values observed in dichloromethane solution for the VO(tfa)<sub>2</sub> and VO(tta)<sub>2</sub> complexes is a result of the increase in the V=O double bond character as a consequence of the increase in the extent of  $p_{\pi}$ - $d_{\pi}$  donation of electrons by the vanadyl oxygen to the vanadium atom. Polymeric linkages have similarly been proposed [16, 17] for compounds of the type  $VO(OOCR)_{2}$ where R is H, CH<sub>3</sub>,  $C_2H_5$ ,  $n-C_3H_7$ ,  $n-C_8H_{17}$ , ClCH<sub>2</sub>, Cl<sub>2</sub>CH, Cl<sub>3</sub>C, C<sub>6</sub>H<sub>5</sub>, (O–I)–C<sub>6</sub>H<sub>4</sub> and  $n = C_4H_9$ . Evidence for polymeric structure in vanadyl monothiodiketonate complexes has also been reported [18].

The bands in the region 200–650 cm<sup>-1</sup> corresponds to the V–O sensitive modes. Caira *et al.* [2] have assigned the bands at 611, 488, 425 and 367 cm<sup>-1</sup> for

the VO(aca)<sub>2</sub> complex to v(V-O),  $v(V-O) + v(C-CH_3)$ ,  $\delta(O-V-O)$  and v(V-O) respectively. Nakamoto et al. [1] have only assigned the band at  $480 \text{ cm}^{-1}$  to the v(V–O) vibration. Assignment of the bands in this region for the complexes studied will not be attempted. For the  $VO(aca)_2$  complex the bands observed appear at 611, 485, 423 and 365  $cm^{-1}$ . The bands in this region for the VO(DK)<sub>2</sub> complexes shift to lower frequencies in the adducts  $VO(DK)_2$ . MPO, the magnitude of the shifts being the least for the VO(aca)<sub>2</sub>. MPO. Also in all VO(DK)2. MPO adducts, except VO(aca)2. MPO, new bands appeared in this region that were absent in the VO(DK)<sub>2</sub> complexes. Adducts that gave new peaks in this region are also those that exhibited the greatest weakening of the v(V=O) and v(V-O) stretching frequencies.

It has been reported [2] that the appearance of new bands and the large shifts observed upon adduct formation are a consequence of a change in geometry and that the adducts formed have the *cis* structure (II). Following this deduction VO(aca)<sub>2</sub>.MPO has the *trans* structure (I) while all other VO(DK)<sub>2</sub>.MPO adducts have the *cis* structure. It is also to be noted that the band around 370 cm<sup>-1</sup> undergoes the greatest shift ( $\Delta v37 \pm 5$  cm<sup>-1</sup>) in all the adducts except VO(aca)<sub>2</sub>. MPO where no shift is observed.

An appreciable change in the spectrum of VO(dbm)<sub>2</sub> upon adduct formation is observed, which may be attributed to the formation of the 2:1 adducts. In the complexes VO(tfa)<sub>2</sub> and VO(tta)<sub>2</sub> a peak of medium intensity observed at 260 and 266 cm<sup>-1</sup> respectively disappeared upon adduct formation. This may be assigned to the bridging v(V....O) in the polymeric structures suggested earlier for these complexes.

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