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245. Spectroscopic Evidence for Symmetry-Restricted π -Interaction in Vanadyl β -Keto-enolates

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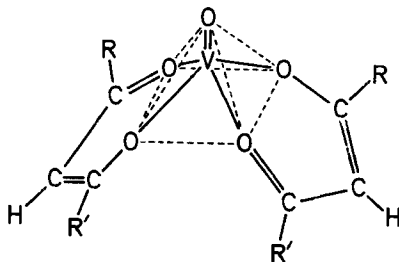
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Summary. Theoretical treatments of the distorted square pyramidal co-ordination observed in vanadyl β -keto-enolates predict restricted interligand conjugation and minimal π -interaction in the oxovanadium-ligand bonds. The effects of ligand substitution on the vibrational and electronic spectra of vanadyl β -keto-enolates yield evidence that strong σ -bonding and ionic contributions are chiefly responsible for the strong vanadium-ligand bonding.

Introduction. – Elsewhere [1] we were able to achieve a qualitative separation of the relative contributions of metal-ligand ($M \rightarrow L$) and ligand-metal ($L \rightarrow M$) π -interaction in transition metal(III) β -keto-enolates by examination of the electronic, IR. and NMR. spectroscopic data from these octahedral complexes, in which the metal d_e orbitals have full π -function. Vanadyl β -keto-enolates have distorted square pyramidal structure I, the vanadium atom being displaced from the basal plane of the four β -keto-enolate oxygen atoms towards the apical multiply-bonded oxygen atom [2] [3] [4]. Compared with regular square pyramidal structure, this distortion leads to some loss of π -function by the vanadyl $d\pi$ orbitals (d_{xz} , d_{yz}) and severely restricted interligand conjugation [5]. The latter implies a considerable limitation in the capacity of the substituents for resonance interaction with the V–O and V=O bonds. Quite apart from such symmetry constraints to π -interaction,

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the V^{IV} ion has only a single electron available for participation in $\pi(V \rightarrow O)$ bonding. Nevertheless, thermochemical measurements [6] show that the $V-O$ bond energy in vanadyl acetylacetonate ($77.2 \text{ kcal mole}^{-1}$) is at least 10% higher than the $M-O$ bond energies of the acetylacetonates of UO_2^{II} , Cu^{II} , Mg^{II} , Co^{III} and Fe^{III} . Furthermore, bond length data ($V=O$, 1.57 \AA ; $V-O$, 1.97 \AA) establish [3] a very short $V-O$ distance which has been attributed [7] to very strong σ -bonding. It was concluded that, while $L \rightarrow V$ π -bonding cannot be ruled out, there is probably an appreciable ionic contri-



I

bution to the short $V-O$ distance. In this paper we shall discuss the extent to which spectroscopic data on vanadyl complexes, particularly the β -keto-enolates I, are consistent with theoretical predictions [5] of restricted π -bonding.

Experimental. – Previously reported methods [8] were employed for the synthesis of $[VOL_2]$ ($L = \text{TFA, DBM, BA, AA, and DPM}$; for full names of ligands see Table 2). Hitherto unknown $[VO(\text{PTA})_2]$ and $[VO(\text{MDBM})_2]$ were synthesized by methods analogous with those used for $[VO(\text{TFA})_2]$ and $[VO(\text{DBM})_2]$, respectively. The complexes were dried over silica gel at 20° and 0.2 mm Torr . Vacuum sublimation was used to purify the complexes $[VOL_2]$ ($L = \text{TFA, AA, DPM, and PTA}$); the others melted without sublimation. Microanalyses are reported in Table 2. IR. spectra were determined on a *Beckman* IR-12 spectrophotometer calibrated against carbon dioxide and water vapour; samples were in the form of Nujol mulls between caesium bromide plates. For maximum precision, frequencies were read from the wave-number drum, not the chart paper. Replicate spectra yielded a maximum discrepancy of 1 cm^{-1} below and 2 cm^{-1} above 1000 cm^{-1} .

IR. Spectra. – Previous studies [9] [10] of ligation effects on the IR. spectra of uranyl and vanadyl complexes have led to the conclusion that the shift ($\Delta\nu$) in $\nu M=O$ ($M = U, V$) induced by various ligands, L , is given by

$$\Delta\nu = - (\text{electrostatic effect}) - \sigma(L \rightarrow M) - \pi(L \rightarrow M) + \pi(M \rightarrow L) \quad (1)$$

where the final term has significance only in the uranyl series in those compounds where the ligand orbitals are from the viewpoint of group theory and energetically suitable for participation in $U \rightarrow L$ π -bonding. In general, eq. (1) predicts that in a series of complexes (ideally an iso-structural and iso-stoichiometric series) substitution of one ligand by another of higher ligand field strength will shift $\nu M=O$ to lower frequency. Eq. (1) receives support from independent studies [9] [11] of two series of uranyl complexes, $[UO_2(\text{NO}_3)_2L_2]$ and $[UO_2(\beta\text{-keto-enolate})_2]$. The shift in $\nu V=O$ for a series of fifty-one vanadyl complexes has also been considered [10] to conform with eq. (1) but the results were far less conclusive than those for the uranyl complexes.

Representative values of $\nu V=O$ taken from the report [10] on vanadyl compounds are given in Table 1. Although a qualitative correlation between $\nu V=O$ and the position of the ligand in the spectrochemical series for various classes of vanadyl compounds was inferred, we shall employ the ligand parameter f obtained [12] from the factorization

$$10 Dq = fg \quad (2)$$

as a quantitative index of ligand field strength to show that there is no obvious relationship between the latter and $\nu V=O$. Thus, in the class of compounds $[VOL_5]$, similar values of $\nu V=O$ are obtained for $L = F$ and $L = CN$ which occupy opposed positions in the spectrochemical series. We suggest that the comparison between f and $\nu V=O$ cannot be considered as valid for several reasons. Firstly, the range of

Table 1. Ligand field parameters and vanadyl stretching frequencies ($\nu V=O$) for vanadyl complexes

L or (L—L) ^{a)}	$f^b)$	$\nu V=O$ (cm ⁻¹)			$\nu U=O$ (cm ⁻¹) ^{c)}
		$[VOL_5]$	$VO(\bar{L}-L)_2$	$VO(L-L)_2L'$	
F	0.90	947			960
mal	0.96			977	
ox	0.98		976	976	
H ₂ O	1.00	1003			945
NCS	1.03	997			898
AA	1.20		996	964	
NH ₃	1.25				895
py	1.25				926
en	1.28				888
bipy	1.43		979	965	
<i>o</i> -phen	1.43		987	982	
CN	1.70	953			873

a) Abbreviations: mal = malonate; ox = oxalate; AA = acetylacetonate; py = pyridine; en = ethylenediamine; bipy = bipyridyl; *o*-phen = *o*-phenanthroline.

b) Values from [12].

c) Values from [9].

vanadyl compounds represents a variety of structural types which include trigonal bipyramidal, square pyramidal, and distorted square pyramidal species. Secondly, compounds regarded as belonging to one class are not iso-stoichiometric; for instance, examples construed as belonging to the class $[VOL_5]$ are: $[NH_4]_3[VOF_5]$, $[VO(H_2O)_5]SO_4$, $[(C_2H_5)_4N]_3[VO(NCS)_5]$ and $Cs_3[VO(CN)_5]$. Finally, quoted frequencies are not all from the same source and have been determined with varying precision and by different sampling techniques. All of these difficulties were avoided in the corresponding study [9] of the uranyl nitrate complexes for which comparative data are included in Table 1 and which clearly conform with the requirements of eq. (1).

From the above discussion it is clear that a valid study of ligation effects on spectroscopic parameters must hinge on the choice of a suitable series of complexes. Vanadyl β -keto-enolates I represent an appropriate series in view of their analogous structures [2] [3] [4] and stoichiometry. The following discussion relates to the effect of varying the substituents (I; R, R') in the β -keto-enolate ring.

The combined electronic effect ($\Sigma\sigma$) of the two substituents in the β -keto-enolate ring may be expressed [13] by

$$\Sigma\sigma = f\Sigma\mathcal{F} + r\Sigma\mathcal{R} \quad (3)$$

where \mathcal{F} and \mathcal{R} are the pure field and resonance capacities of the substituents and f and r are the relative weightings of each. Restricted interligand conjugation in vanadyl β -keto-enolates would imply that the field effects of the substituents will dominate the electron density distribution in the molecules. On the other hand, assumption of quasi-aromatic character for the β -keto-enolate ring would dictate the use of $\Sigma\sigma_m$ as an index of the electronic effects of the substituents, where σ_m is the Hammett parameter for *meta*-substitution in aromatic systems. Since $\Sigma\sigma_m$ is given [13] by

$$\Sigma\sigma_m = 0.78 \Sigma\mathcal{F} + 0.22 \Sigma\mathcal{R} \quad (4)$$

Table 2. Substituent parameters, analyses and vibrational frequencies of vanadyl β -keto-enolates [VOL₂]

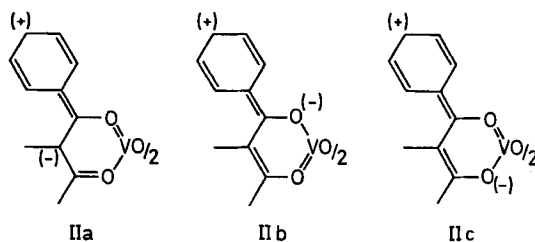
L ^{a)}	R	R'	Calcd.		Found		$\Sigma\mathcal{F}$	$\Sigma\mathcal{R}$
			% C	% H	% C	% H		
TFA	CF ₃	CH ₃	32.2	2.2	32.4	2.1	+ 0.58	+ 0.05
PTA	CF ₃	C(CH ₃) ₃	42.0	4.4	41.7	4.5	+ 0.53	+ 0.05
DBM	C ₆ H ₅	C ₆ H ₅	70.2	4.3	70.3	4.5	+ 0.28	- 0.18
BA	C ₆ H ₅	CH ₃	61.7	4.7	61.8	4.6	+ 0.08	- 0.23
AA	CH ₃	CH ₃	45.3	5.3	45.8	5.6	- 0.10	- 0.28
DPM	C(CH ₃) ₃	C(CH ₃) ₃	61.0	8.8	61.2	8.8	- 0.20	- 0.28
MDBM	<i>p</i> -CH ₃ O- C ₆ H ₄	<i>p</i> -CH ₃ O- C ₆ H ₄	64.5	4.8	64.8	4.8	—	—

L ^{a)}	R	R'	$\Sigma\sigma$	$\Sigma\sigma_m$	$\nu V=O$ (cm ⁻¹)	$\nu V-O$ (cm ⁻¹)	$\nu C-O$ (cm ⁻¹)	$\nu C-O$ (cm ⁻¹)
TFA	CF ₃	CH ₃	+ 0.50	+ 0.36	931	602, 449	1616	1540
PTA	CF ₃	C(CH ₃) ₃	+ 0.46	+ 0.33	945	607, 456	1604	1530
DBM	C ₆ H ₅	C ₆ H ₅	+ 0.21	+ 0.12	996	589, 467	1544	1531
BA	C ₆ H ₅	CH ₃	+ 0.03	- 0.01	998	575, 462	1562	1526
AA	CH ₃	CH ₃	- 0.13	- 0.14	999	611, 488	1564	1536
DPM	C(CH ₃) ₃	C(CH ₃) ₃	- 0.19	- 0.21	1006	648, 490	1552	1508
MDBM	<i>p</i> -CH ₃ O- C ₆ H ₄	<i>p</i> -CH ₃ O- C ₆ H ₄	—	—	991	652, 485	1531	1507

^{a)} Ligand abbreviations: TFA = trifluoroacetyl-acetonate; PTA = pivaloyl-trifluoroacetonate; DBM = dibenzoylmethanate; BA = benzoylacetonate; AA = acetylacetonate; DPM = dipivaloylmethanate; MDBM = bis-(*p*-methoxy)-dibenzoylmethanate.

it is clear that $\Sigma\sigma_m$ is itself governed largely by the field effects. However, in Cu^{II} and UO₂^{II} β -keto-enolates [11] [14] $\Sigma\sigma_m$ and $\nu Cu-O$ are qualitatively parallel except when phenyl substitution requires an increased weighting of \mathcal{R} to yield values of $\Sigma\sigma$ consistent with the observed values of $\nu M-O$ ($M = Cu, UO_2$). This arises from the significant contribution of forms equivalent to IIa, b, c (VO replaced by Cu, UO₂) to the resonance hybrid in the benzoylacetonates and dibenzoylmethanates. In the vanadyl complexes, the interligand conjugation implicit in the forms II is only allowed to a small extent [5], in accordance with observation (Table 2) that $\nu V=O$ correlates very reasonably with $\Sigma\sigma_m$ without assuming any increase in the weighting

of \mathcal{R} for vanadyl benzoylacetate and dibenzoylmethanate. In practice, it transpires that the $\nu\text{V}=\text{O}$ values are qualitatively parallel to those of $\Sigma\mathcal{F}$ so that it is not necessary to assume any resonance contribution to the bonding.



Further evidence for diminished π -interaction in vanadyl β -keto-enolates arises from the opposed direction of shift in $\nu\text{U}=\text{O}$ and $\nu\text{V}=\text{O}$, induced by ligands spanning the range of $\Sigma\sigma_m$ values (Table 3). Thus substitution of $\text{L} = \text{DPM}$ for $\text{L} = \text{TFA}$ leads to an increase of 75 cm^{-1} in $\nu\text{V}=\text{O}$ and a decrease of 21 cm^{-1} in $\nu\text{U}=\text{O}$. In the uranyl series, electron releasing substituents transfer charge by $\sigma(\text{L} \rightarrow \text{M})$ and $\pi(\text{L} \rightarrow \text{M})$ contributions into orbitals which are pure uranium orbitals in $\text{D}_{\infty h}$ symmetry [9].

Table 3. Summary of differences in substituent sensitivity of vibrational frequencies (cm^{-1}) in vanadyl and uranyl β -ketoenolates

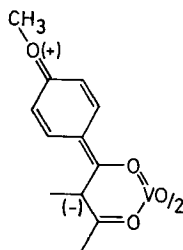
L	$\Sigma\sigma_m$	[VOL ₂]			[UO ₂ L ₂ (H ₂ O)] ^{a)}		
		$\nu\text{V}=\text{O}$	$\nu\text{V}-\text{O}$	$\nu\text{C}-\text{O}$	$\nu\text{U}=\text{O}$	$\nu\text{U}-\text{O}$	$\nu\text{C}-\text{O}$
TFA	+0.36	931	602, 449	1616	929	412	1624
AA	-0.14	999	611, 488	1564	922	404	1583
DPM	-0.21	1006	648, 490	1552	908	413	1548

a) Values from [11].

This charge transfer to uranium increases the electrostatic repulsion between the U and O atoms in the $\text{O}=\text{U}=\text{O}$ bonds leading to a decrease in $\nu\text{U}=\text{O}$. In the vanadyl series, a large ionic contribution to the bonding in the vanadium-acetylacetonate oxygen bond will (for electron releasing substituents) lead to a polarization of this bond in the sense O^--V^+ and thus promote the V to O attraction in the $\text{V}=\text{O}$ bond, increasing $\nu\text{V}=\text{O}$.

Electron withdrawing substituents will reduce the σ -donor capacity of the carbonyl oxygen atom for the metal ion, evident from the high values of $\nu\text{C}-\text{O}$ observed [14] for all metal trifluoroacetyl-acetonates. Superimposed on this effect will be substituent-induced $\pi(\text{M} \rightarrow \text{L})$ bonding, where allowed (*i.e.* in the uranyl but not in the vanadyl series). Thus $\nu\text{M}-\text{O}$ should serve as a sensitive index to detect differences in the relative significance of $\pi(\text{M} \rightarrow \text{L})$ bonding in the uranyl and vanadyl β -keto-enolates (Table 3). Accordingly, theoretical evidence for strong $\pi(\text{U} \rightarrow \text{O})$ bonding is supported by the observed high value of $\nu\text{U}-\text{O}$ in uranyl trifluoroacetyl-acetonate in contrast to a low value of $\nu\text{V}-\text{O}$ in the analogous vanadyl complex. At the opposite end of the $\Sigma\sigma$ scale, strongly electron releasing substituents will provide $\sigma(\text{L} \rightarrow \text{M})$ and $\pi(\text{L} \rightarrow \text{M})$ contributions to the total $\text{M}-\text{O}$ bonding. Both effects provide a positive

contribution to $\nu\text{M}=\text{O}$ although their relative weightings undoubtedly differ in the vanadyl and uranyl series. Accordingly, high values of $\nu\text{M}=\text{O}$ are realized for vanadyl and uranyl dipivaloylmethanate (Table 3). We have cited evidence for the relatively small contribution of the quinonoid forms II to the bonding in phenyl-substituted vanadyl β -keto-enolates compared with their uranyl analogues. In both series substitution of methyl by phenyl groups leads to the expected decrease in $\nu\text{C}=\text{O}$ and $\nu\text{M}=\text{O}$. Furthermore, the smaller shifts in the vanadyl series are in accordance with the diminished rôle of quinonoid resonance in this series. We consider that it may be possible to induce an increased contribution from the forms II by incorporating a *p*-methoxyl substituent in the phenyl rings since this substituent participates in strong resonance interaction with an aromatic ring III, and find that in the series of complexes $[\text{VOI}_2]$, both $\nu\text{V}=\text{O}$ and $\nu\text{C}=\text{O}$ decrease in the order $\text{L} = \text{AA} > \text{BA} > \text{DBM} > \text{MDBM}$, *i.e.* as the resonance interaction of the substituent with the chelate ring increases.

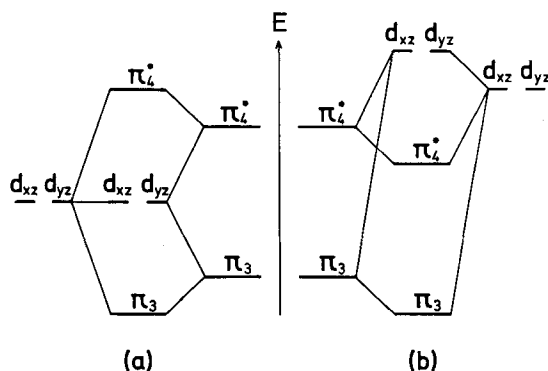


III

Infrared Band Assignments. Assignment of the sharp, intense band near 1000 cm^{-1} to $\nu\text{V}=\text{O}$ is based on theoretical and empirical studies [15] of vanadyl compounds, and that of $\nu\text{V}-\text{O}$ to the band at 488 cm^{-1} in the spectrum of $[\text{VO}(\text{AA})_2]$ follows that given by a normal co-ordinate treatment [15]. A further band at 611 cm^{-1} may also be assigned to (coupled) $\nu\text{V}-\text{O}$ on the basis of ^{18}O -labelling studies [16] and the fact that it corresponds with a band so assigned [14] in the spectra of transition metal acetylacetonates. All three bands exhibit similar substituent sensitivity as would be expected from their similar origin. Former assignments of $\nu\text{C}=\text{O}$ and $\nu\text{C}-\text{C}$ in metal β -keto-enolates by normal co-ordinate analyses [17] have recently been reversed by a further theoretical treatment [18] and by ^{18}O -labelling of the carbonyl oxygen atom [16]. Of the two bands in the range $1500\text{--}1620\text{ cm}^{-1}$, only that of higher frequency is appreciably shifted on substitution by the heavier isotope and is therefore assigned to $\nu\text{C}=\text{O}$.

Electronic Spectra. - Evidence for the extent of π -interaction in metal complexes is generally sought from electronic rather than vibrational spectra. No universally acceptable energy level scheme has yet been proposed for the *d*-orbitals of the VI^{IV} ion and there are indications that their energy order may be transposed from one complex to another [7]. Accordingly, interpretational difficulties of the *d-d* spectra preclude any valid discussion of these bands in terms of π -bonding. The bands in the range $27\text{--}34\text{ kK}$ in the electronic spectra of metal β -keto-enolates are more reliably assigned to the $\pi_3-\pi_4^*$ intraligand transition on the basis of a *Hückel* LCAO-MO treatment [19] and their usefulness in determining π -bonding effects has been amply demonstrated [1] [20]. In C_{2v} symmetry this band will be split into two electronically-allowed components of which only the lower energy component is observable with precision in the spectra [21] of vanadyl β -keto-enolates. For simplicity, this component will therefore be referred to as the $\pi_3-\pi_4^*$ band.

The vanadium $d\pi$ orbitals (d_{xz} , d_{yz}) lie some 14–15 kK above the ground state which places them either between the π_3 and π_4^* or above the π_4^* ligand orbitals [21]. In the former case, increased π -interaction will shift this band to higher and in the latter to lower energy (Fig.). The π_3 – π_4^* transition of the vanadyl β -keto-enolates



Effect of π -interaction on π_3 and π_4^* ligand orbital energies in vanadyl β -keto-enolates

a) vanadyl $d\pi$ orbitals lie between π_3 and π_4^* levels; b) vanadyl $d\pi$ orbitals lie above π_4^* level

shifts to higher energy through the ligand series DBM < BA < TFA < DPM \sim AA. This is precisely the same order as that previously established [1] for the β -keto-enolates of eight transition and non-transition metal ions and now extended [21] to include the free ligands and their Na^{I} complexes (Table 4). Since this order is observed for transition metal(III) β -keto-enolates in which the metal ion $d\pi$ orbitals lie between the π_3 and π_4^* levels [19] it is clear that the $d\pi$ orbitals of the vanadyl ion almost certainly also lie between these levels.

The most significant aspect of the results in Table 4 is that the π_3 – π_4^* transition energies of the vanadyl β -keto-enolates are lower than those of the β -keto-enolates of all other ions studied. In fact, the values are comparable with those for the K^{I} and Na^{I} complexes, supporting Selbin's conclusion [7] that ionic contributions must be considered largely responsible for the short V–O bond length in vanadyl acetyl-

Table 4. π_3 – π_4^* Transition energies (kK) of metal β -keto-enolates

Metal ion	L \rightarrow DBM	BA	TFA	DPM	AA	Ref.
VO^{IIa})	27.4	30.3	32.7	33.1	32.6	[21]
Sc^{III}	28.2	30.6	33.4	–	33.8	[1]
Al^{III}	28.6	31.3	34.3	34.0	35.2	[1]
Na^{Ib})	29.1	31.8	33.8	34.8	35.0	[21]
K^{Ic})	29.4	32.6	34.2	36.2	36.2	[1]
Mn^{III}	29.1	32.4	34.2	36.5	36.8	[1]
H b)	30.3	32.3	35.3	36.2	36.6	[21]
Fe^{III}	30.0	33.2	36.5	36.2	36.8	[1]
Cr^{III}	31.2	34.2	35.8	–	36.5	[1]
Co^{III}	33.6	36.1	38.3	–	38.6	[1]

a) In CH_3CN ; similar values were obtained for a variety of solvents.

b) In $i\text{-C}_3\text{H}_7\text{OH}$.

c) In CH_3OH .

acetone and also in agreement with the theoretical predictions and evidence from the vibrational spectra for minimal π -interaction in vanadyl β -keto-enolates.

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246. Photochemical Reactions

Part 67 [1]

Photochemistry of Saturated Aliphatic and Cyclic β -Keto Sulfoxides (C_{α} -S)- and α -Cleavage – A New Case of Photostereomutation

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Summary. The photochemical behaviour of saturated aliphatic (**2**, **4**, and **5**) and bicyclic (**18** and **19**) β -keto sulfoxides has been studied. Photostereomutation of the sulfoxide group was observed on irradiation of **4a**, **4b**, **18**, and **19**. Most likely an internal energy transfer from the excited carbonyl to the sulfoxide group is operating on direct irradiation of such compounds.