Ligand-field Analysis of the Ion VO^{2+}: Application of the Angular Overlap Model to the Electronic Absorption Spectrum of Bis(acetylacetonato)oxovanadium(IV) in Various Solvents

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A ligand-field analysis employing the angular overlap model of the electronic *d–d* spectrum of $[VO(acac)_2]$ (acac = acetylacetonate) is presented. A consistent set of e_λ values has been determined through statistical procedures. First, the constancy of the parameters was assumed when solid $[VO(acac)_2]$ is dissolved in different solvents. Then, the results were compared with those obtained when variability of the parameters with the solvent is allowed. Variations in the electronic spectra are primarily dependent on modifications in the chromophore topology induced by the solvent. Earlier calculations using the point-charge electrostatic model are discussed on the basis of the formal equivalence between the models.

Controversial features concerning the electronic structure of oxovanadium(IV)-containing species have recently been emphasized by Lever.[1] Despite the apparent simplicity which might be expected for d^1 species, a variety of divergent assignments for the observed electronic absorption spectra is found in the literature.[2] Three *d–d* type transitions are expected for both five- and six-co-ordinated VO^{2+} complexes having the highest C_{4v} symmetry $[3d_{xz}^*, 3d_{yz}^* \longleftarrow 3d_{xy}^*$ (I), $3d_{x^2-y^2}^* \longleftarrow 3d_{xy}^*$ (II), and $3d_{z^2}^* \longleftarrow 3d_{xy}^*$ (III)].[3] Upon symmetry reduction, splitting of the band I only becomes noticeable (at room temperature) under grossly asymmetric fields.[4] It has been suggested that one single assignment scheme cannot work for all the vanadyl(IV) compounds, but it also seems unreasonable that the electronic structure of the VO^{2+} group undergoes changes as diverse as suggested by the wide variety of schemes proposed.[2,5] Disagreements refer to the energy of band III with respect to charge-transfer type transitions and also to the relative position of bands I and II. From the results of Collison *et al.*[2] on single-crystal polarized electronic absorption spectra, it seems clear that for the five-co-ordinated complexes all three *d–d* bands occur below 30 000 cm^{-1}, but band III might move to relatively higher energies upon addition of a sixth ligand *trans* to V=O that increases the ligand-field strength along the molecular z axis. More confusion remains as to the relative energy of bands I and II.[6] Indeed, it has been empirically argued that even a crossover between the e_π^* doublet ($3d_{xz}^*, 3d_{yz}^*$) and the b_1^* singlet ($3d_{x^2-y^2}^*$) levels might occur by varying the oxygen–vanadium–equatorial ligand angles[7] and/or the π-acceptor ligand character.[8] Thus only a well grounded argumentation can lead to a reliable assignment scheme from which chemical conclusions could be inferred, mainly when working with conventional electronic absorption spectra. Otherwise, the angular overlap model (a.o.m.),[9] as redirected by Gerloch and co-workers,[10] has become a useful theoretical tool to perform accurate ligand-field analysis. For vanadyl(IV) derivatives, one a.o.m. analysis has recently been reported on bis(2-methylquinolin-8-olato)oxovanadium(IV), but the experimental electronic absorption spectrum is not accurately reproduced.[11] Bis(acetylacetonato)oxovanadium(IV) has been the subject of several conflicting crystal-field treatments.[5,6a,7] In view of this we report a detailed a.o.m. analysis on it trying to benefit from the chemical appeal[10a] of the model.

Experimental

Preparation of $[VO(acac)_2]$.—Vanadyl acetylacetonate was prepared as described elsewhere.[12] All solvents were of analytical grade or spectroscopic quality.

Electronic Absorption Spectra.—These were obtained at room temperature (25.0 ± 0.5 °C) between 300 and 1 000 nm using a Perkin-Elmer LAMBDA 9 spectrometer, 1-cm quartz cells, and solutions typically in the range 10^{-2}—10^{-3} mol dm^{-3} in complex. The diffuse reflectance electronic spectrum of solid $[VO(acac)_2]$ was recorded using the aforementioned apparatus.

Table 1. Experimental and calculated band maxima[a] (cm^{-1}) for $[VO(acac)_2]$ in various solvents and some derived parameters

Solvent	$T_{\mathrm{I}}{}^{a}$	$T_{\mathrm{I}}{}^{b}$	$T_{\mathrm{II}}{}^{a}$	$T_{\mathrm{II}}{}^{b}$	$T_{\mathrm{III}}{}^{a}$	$T_{\mathrm{III}}{}^{b}$	$D_{\mathrm{II-I}}$	θ^{c}	θ^{d}
Solid	14 500	14 694	16 700	16 549	24 500	24 835	2 200	106.2[e]	106.2[e]
H_2O	12 439	12 549	17 670	17 919	25 258	24 885	5 231	101.6	103.1
CH_3OH	12 913	13 232	17 442	17 484	24 775	24 852	4 529	103.2	103.8
C_2H_5OH	13 304	13 277	17 422	17 456	24 969	24 850	4 118	103.3	103.9
C_5H_5N	13 233	13 414	17 523	17 368		24 840	4 290	103.6	103.6
CH_3NO_2	13 976	13 984	17 184	17 004	24 658	24 834	3 208	104.8	104.7
CH_3CN	14 561	14 590	16 850	16 616	24 865	24 834	2 289	106.0	105.8
CCl_4	16 881	17 300	14 538	14 862	24 957	25 013	−2 343	110.8	111.9
C_6H_6	17 338	17 361	14 879	14 823	24 909	25 021	−2 459	110.9	111.1
$CHCl_3$	17 453	17 421	14 752	14 783	25 109	25 029	−2 701	111.0	111.4

[a] As resulting from deconvolution. [b] Transition energies calculated by means of the a.o.m. treatment. [c] Azimuthal (statistical) angles. [d] Azimuthal angle, calculated from equation (6). [e] From the crystal structure.[14]

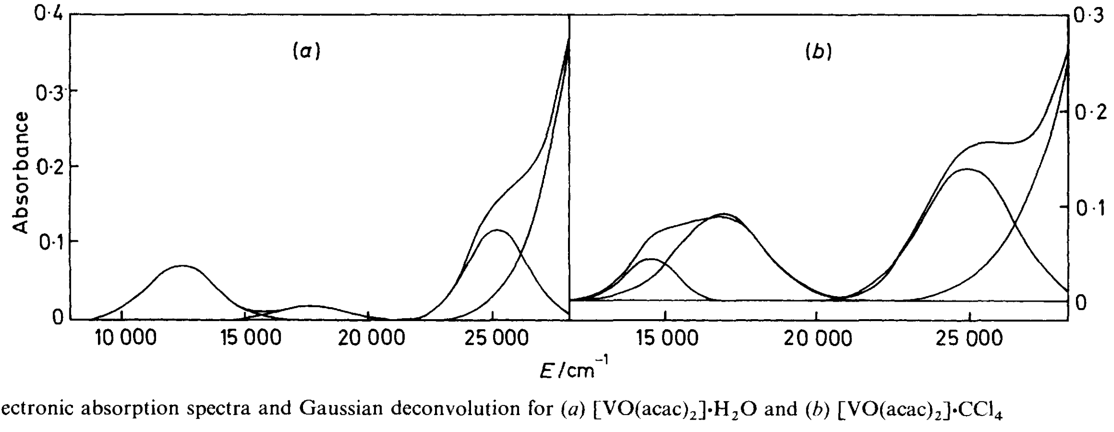

Figure 1. Electronic absorption spectra and Gaussian deconvolution for (*a*) $[VO(acac)_2]\cdot H_2O$ and (*b*) $[VO(acac)_2]\cdot CCl_4$

Results and Discussion

Electronic Absorption Spectra.—The electronic absorption spectral data for solid $[VO(acac)_2]$ and its solutions in a variety of solvents are summarized in Table 1 along with several derived parameters which are described below. As can be noted, according to previous observations,[6a,7] the resulting spectra depend markedly on the solvent. Initially, it can be reasonably assumed that on dissolution of $[VO(acac)_2]$ a pseudo-six-co-ordination may be achieved with a solvent molecule approaching the vanadium atom along the axial direction *trans* to the V=O bond.[1] Steric and/or ligand-field effects along the *z* molecular axis may lie behind these changes. While the highest possible actual symmetry for $[VO(acac)_2]$ adducts would be C_{2v}, the room-temperature spectra do not show the predicted splitting of band I because of the broadness of the experimental bands. In such a situation, and given the evident lack of geometrical information on the solvated species, to assume an idealized pseudo-C_{4v} symmetry is a convenient and usual way to approach ligand-field analysis.[5,6a,7] On this assumption, the only orbitally allowed *d-d* transition is the $e_\pi \longleftarrow b_2{}^*$ $(3d_{xz}{}^*, 3d_{yz}{}^* \longleftarrow 3d_{xy}{}^*)$.[1] Then, once it is accepted that band III generally occurs as a shoulder to an intense charge-transfer band in the range 21 000—27 000 cm^{-1},[2,5,6] the assignment of bands I and II should be consistent with the selection rules. Thus, taking into account the aforesaid possibility of $e_\pi{}^* - b_1{}^*$ crossover, a coherent assignment criterion is to associate initially the allowed transition to the more intense band. Regardless of their relative position, band I would be more intense than band II. The results in Table 1 reflect this choice. An illustrative example is provided by comparison of the spectra in Figure 1. There is an inversion in the relative position of the more intense band. From the ratio of intensities, it seems clear that the allowed band I in the spectrum of $[VO(acac)_2]\cdot H_2O$ [Figure 1(*a*)] must be that centred at 12 439 cm^{-1}, but in the case of $[VO(acac)_2]\cdot CCl_4$ [Figure 1(*b*)] the $e_\pi{}^* - b_1{}^*$ crossover is apparent. It is noticeable that such an intensity transposition occurs when non-basic solvents are involved. Even though this effect was reflected in the results of Stoklosa and Wasson,[7] their assignments overlooked it. As we shall see, the whole results are fitted better by the assignment proposed here.

Table 2. Dependence of the transition energy on the a.o.m. parameters; $K = 3e_\sigma{}^{eq} - 4e_\pi{}^{eq}$

Transition	Band	a_i	b_i	c_i
$3d_{xz}{}^*, 3d_{yz}{}^* \longleftarrow 3d_{xy}{}^*$	I	$K/2 + e_\pi{}^{eq} + e_\pi{}^{ax}$	$3e_\pi{}^{eq}$	$-K/2$
$3d_{x^2-y^2}{}^* \longleftarrow 3d_{xy}{}^*$	II	$K/4$	$-K/2$	$K/4$
$3d_{z^2}{}^* \longleftarrow 3d_{xy}{}^*$	III	$e_\sigma{}^{eq}/4 + e_\pi{}^{eq} + e_\sigma{}^{ax}$	$\frac{1}{2}(3e_\sigma{}^{eq} + 4e_\pi{}^{eq})$	$3/4\ K$

$$Ed_{xy}{}^* = (4\sin2\theta)e_\pi{}^{eq} \tag{1}$$

$$Ed_{xz}{}^* = Ed_{yz}{}^* = \tfrac{3}{4}(1 - \cos4\theta)e_\sigma{}^{eq} + (2 + \cos4\theta + \cos2\theta)e_\pi{}^{eq} + e_\pi{}^{ax} \tag{2}$$

$$Ed_{x^2-y^2}{}^* = \tfrac{3}{4}(1 - \cos2\theta)^2 e_\sigma{}^{eq} + (\sin2\theta)^2 e_\pi{}^{eq} \tag{3}$$

$$Ed_{z^2}{}^* = \tfrac{1}{4}(1 + 3\cos2\theta)^2 e_\sigma{}^{eq} + 3(\sin2\theta)2e_\pi{}^{eq} + {}^2 2e_\sigma{}^{ax} \tag{4}$$

Angular Overlap Model Analysis.—Our a.o.m. treatment includes the required simplifying assumptions whose validity is widely accepted for linear ligating ligands, namely $e_\sigma > e_{\pi x} = e_{\pi y} \gg e_\delta$.[10] On this basis, under the assumed C_{4v} symmetry, the *d*-orbital energies can be expressed as functions of four a.o.m. parameters (*i.e.*, $e_\sigma{}^{eq}$, $e_\pi{}^{eq}$, $e_\sigma{}^{ax}$, and $e_\pi{}^{ax}$) and the azimuthal angle θ (O=V–O$_{eq}$).[13] Schaffer's expressions[9] can be arranged to give equations (1)—(4). From these, assuming a $d_{xy}{}^*$ orbital ground state, all three *d–d* transition energies can be written in the parabolic form (5), a_i, b_i, and c_i being a.o.m. parameter linear

$$T_i = a_i + b_i \cos2\theta + c_i \cos^2 2\theta \tag{5}$$

combinations listed in Table 2. Thus, we have sets of three equations involving five unknowns, namely the four a.o.m. parameters and the angular parameter θ. At this point, the system is undetermined having infinite solutions. To restrict them, further chemical insight must be developed.

Solid $[VO(acac)_2]$. Solid $[VO(acac)_2]$ represents the most favourable situation in our case. The structure is well established[14] and this enables the angular parameter (θ = 106.2°) to be eliminated.* Notwithstanding, even in this case, there remain more unknowns (four) than equations (three). Two straightforward considerations allow us to rule out the chemically meaningless solutions. First, e_σ must be higher than e_π. Secondly, both $e_\sigma{}^{eq}$ and $e_\sigma{}^{ax}$ are taken as positive. While this is evident for σ-donor equatorial ligands, the vacant position *trans* to the V=O double bond might lead to some uncertainty in the $e_\sigma{}^{ax}$ values. Nevertheless, as a consequence of the holohedral

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* Actually, the azimuthal angles O=V–O$_{eq}$ (θ) range from 104.5 to 108.2° in solid $[VO(acac)_2]$.[14] We have used a single average θ value in the calculations. That this approximation does not induce significant perturbations can be checked *a posteriori*. Thus, the experimental spectrum of solid $[VO(acac)_2]$ is nicely reproduced by using the calculated a.o.m. parameters.

symmetry, only an average e_σ^{ax} value can be estimated. Because the negative e_σ^{ax} values corresponding to the vacant co-ordination sites are relatively low,[10] it can reasonably be assumed that the average e_σ^{ax} value in oxovanadium five-co-ordinated compounds is positive.

Otherwise, the energy of the $3d_{x^2-y^2}^* \longleftarrow 3d_{xy}^*$ transition (C_{4v} symmetry) provides the value of the inherently positive crystal-field radial integral Dq.[3] From data in Table 2, equation (6) can be written. Hence, $3e_\sigma^{eq} - 4e_\pi^{eq} > 0$. Thus

$$T_{II} = 10Dq = (3e_\sigma^{eq} - 4e_\pi^{eq})\sin^4\theta \qquad (6)$$

even for π-donor ligands e_π^{eq} cannot exceed 75% of e_σ^{eq}. Then, if we define p as the ratio e_π^{eq}/e_σ^{eq}, the only acceptable solutions of equation (5) are those for which $0 \leqslant p < 0.75$. In this way, the set of reasonable analytical $\{e_\sigma,e_\pi;p\}^{eq}$ solutions can be established.

Solvated [VO(acac)$_2$]. It has been previously stated that the V=O bond length is not appreciably modified by dissolution of [VO(acac)$_2$] in a variety of solvents.[4] Thus, the ν(V=O) i.r. frequency usually remains close to the value of the solid complex, and only some solvents having moderately strong basic properties yield significant frequency decreases.[4,15] Actually, on approach of a solvent molecule to the 'sixth' co-ordination site on the vanadium, only slight alterations of the strong axial perturbation of the vanadyl oxygen have been recognized.[6a] Moreover, even when six-co-ordination around the vanadium atom is clearly established, the ligand occupying the 'sixth' co-ordination site (*i.e. trans* to the V=O bond) displays an anomalously long V–L bond distance.[15,16] It seems therefore that in general the vanadium–solvent interaction is rather weak. Then, it is expected that no significant changes would occur in the V–O$_{eq}$ bond lengths. If this is so, the a.o.m. parameters must remain basically unchanged.[10] Notwithstanding, this weak interaction plus steric factors can induce variations in the O=V–O$_{eq}$ angles resulting in the observed spectral changes.

Accepting the quasi-constancy of the a.o.m. parameters, it can be concluded: (1) the analytical $\{e_\sigma,e_\pi;p\}^{eq,ax}$ solutions found in the foregoing section maintain their validity, and (2) spectral differences basically arise from solvent-dependent variations in the chromophore topology. Therefore, a single θ value must exist which is characteristic of each solvent (θ$_s$) and for which the same set of solutions are valid. This means that, by defining the reliability factor $R^{\theta,p}$ as $\Sigma(T_{i,\text{calc.}}^{\theta,p} - T_{i,\text{obs.}})/\Sigma T_{i,\text{obs}}$, a θ value (θ$_s$) should exist which minimizes the R factor independent of p (*i.e.* the θ$_s$ value leading to the best fit to the experimental spectrum should be independent of p). As can be observed in Figure 2, θ$_s$ = 110.8° in the case of CCl$_4$; θ$_s$ values calculated in this way are listed in Table 1. In fact, the availability of these θ$_s$ values supports the previous hypotheses.

Statistical treatment. Once the θ$_s$ value for each of the nine solvents used had been estimated, and assuming the constancy of the a.o.m. parameters, we now have a superabundant set of equations (30 for only four unknowns). To solve the system we have carried out a multiple linear regression analysis by a standard procedure.[17] The analysis yields a consistent parameter set showing admissible standard deviations (Table 3). An illustration of the quality of fit to the experimental data is shown in Figure 3. At the 95% significance level, it may be significant that the best fit depends mainly on the e_σ^{eq} [Figure 3(*a*)] and the e_π^{ax} [Figure 3(*b*)] values. Indeed, for a given e_σ^{eq} or e_π^{ax} value, the possible e_π^{eq} and e_σ^{ax} values become highly restricted. This could be associated to the relative sensitivity of the σ- and π-bond strengths towards the bond length variation: a short V=O double bond might be referred as 'e_π controlled' while a longer V–O one should be 'e_σ controlled.' We could also arrive at this conclusion by considering that $p = e_\pi^{eq}/e_\sigma^{eq} = 0.33 \ll e_\pi^{ax}/e_\sigma^{ax} = 0.62$. This result, being in line with previous observations on the variability of the e_σ and e_π parameters,[10b] supports what Gerloch called the 'chemical appeal' of the a.o.m. model,[10a] and as he stated 'although ... the ligand-field and molecular orbital approaches to the a.o.m. are fundamentally distinct, it remains perfectly legitimate to use qualitative molecular orbital concepts in order to help visualize the structure of the defined, ligand-field version of the a.o.m.'[10c] Finally, from data in Table 3, and using the appropriate θ$_s$ value, equation (5) allows us to calculate the *theoretical d–d* transition energies. Calculated values are listed in Table 1 in parentheses.

The simplifying assumptions made so far lead to a rather satisfactory fit to the experimental transition energies (Table 1). Notwithstanding, a rough correlation is observed between the solvent donor ability and the calculated θ$_s$ values. In fact, a practically constant θ$_s$ value is found for the non-co-ordinating solvents (benzene, carbon tetrachloride, and chloroform). This θ$_s$ value is higher than θ$_{\text{Solid}}$ which, in turn, is higher than the value calculated for the remaining solvents. This is related to the mentioned band crossover. Then, from a chemical point of view, it might be thought that the nature of the 'sixth' ligand molecule is important enough to be considered throughout the whole

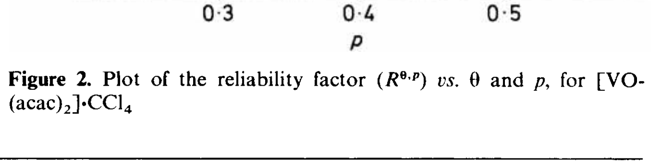

Figure 2. Plot of the reliability factor ($R^{\theta,p}$) *vs.* θ and p, for [VO(acac)$_2$]·CCl$_4$

Table 3. A.o.m. parameters (cm^{-1})

	e_λ (s.d.)[a]	Non-co-ordinating solvents, e_λ (s.d.)[b]	e_λ[c]					
			H_2O	CH_3OH	C_2H_5OH	C_5H_5N	CH_3NO_2	CH_3CN
e_σ^{eq}	11 603 (337)	12 064 (874)	12 064	12 064	12 064	12 064	12 064	12 064
e_π^{eq}	3 837 (353)	4 160 (680)	4 160	4 160	4 160	4 160	4 160	4 160
e_σ^{ax}	28 867 (586)	29 609 (931)	29 978	29 492	29 685		29 544	29 366
e_π^{ax}	17 782 (554)	18 459 (1 335)	17 571	17 506	18 057	18 130	18 239	18 333

[a] Average values resulting from the statistical treatment involving all solvents. [b] Statistical values calculated for the non-co-ordinating solvents. [c] Values calculated assuming possible variations in the axial parameters.

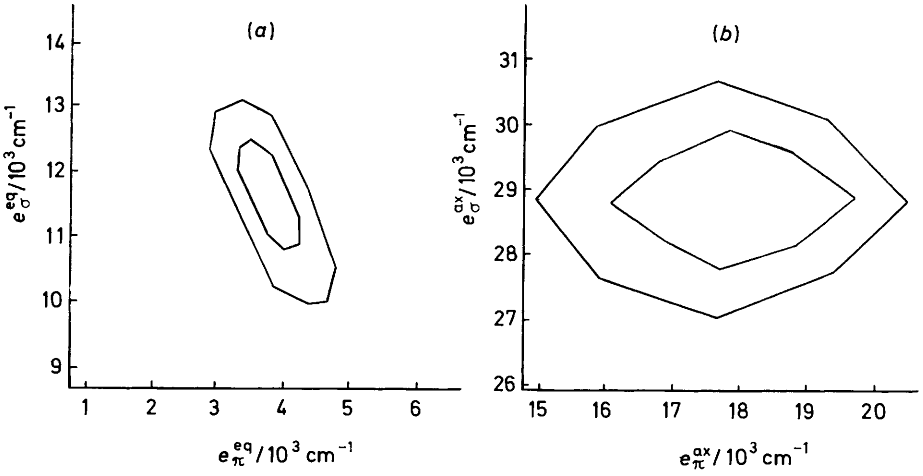

Figure 3. Contour plot for the confidence limit regions (95 and 90%) for (*a*) equatorial parameters and (*b*) axial parameters

Table 4. Radial integrals (cm^{-1}) for [VO(acac)$_2$]

	α_2^{ax}	α_4^{ax}	R^{ax}	α_2^{eq}	α_4^{eq}	R^{eq}
Ref. 7.	85 050	94 500	0.9	10 728	11 920	0.9
This work	46 649	9 283	5.02	15 440	11 677	1.32

calculations. In other words, the axial a.o.m. parameters might depend on the basic properties of the solvents. Thus, an improvement of our calculations can be achieved by handling separately both solvent groups. To carry out this new treatment we proceed as follows: (1) using as reference the θ_{Solid} value (106.2°), θ_s values were estimated from equation (6) (see Table 1); (2) all three transition energies for each non-co-ordinating solvent and the solid have been statistically treated[17] to find the single a.o.m. parameter set which would describe the effective five-co-ordination cases; (3) taking the equatorial parameters as constant, the axial ones were determined separately for each co-ordinating solvent from equation (5). Calculated values are listed in Table 3. From these, it can be concluded that the equatorial parameters are essentially independent of the mathematical treatment, and allowing the variation of the axial parameters, all the new e_σ^{ax} and e_π^{ax} values fall into the 95% confidence interval corresponding to the standard deviation associated with the values previously calculated assuming their constancy. Notwithstanding, some reasonable tendencies become apparent. As expected, the relative variations of e_π^{ax} are appreciably higher than those of e_σ^{ax}. Moreover, e_π^{ax} (statistical) $<$ e_π^{ax} (non-co-ordinating solvents) $>$ e_π^{ax} (donor solvents). Thus, although the absolute variations cannot be overemphasized, it seems that a slight weakening of the V=O bond occurs as the donor ability of the solvent increases. However, as predicted, this weakening is too small to alter significantly the a.o.m. parameters. Then, for simplicity, it is adequate to work henceforth with the statistical unified e_λ values for [VO(acac)$_2$].

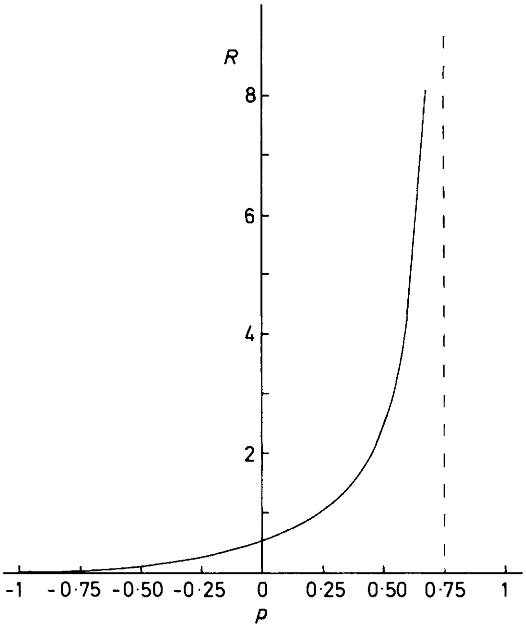

Figure 4. Plot of the ratio $p = e_\sigma^i/e_\pi^i$ *vs.* $R = \alpha_2^i/\alpha_4^i$ from equation (9)

Comparison with Previous Studies.—With regard to previous crystal-field studies, the main differences arise from the fact that the analysis is based on a band assignment scheme which differs from that reported in the literature.[4,7] In this sense, Selbin[4,6a] suggested that the empirical quantity D_{II-I} ($T_{II} - T_I$, cm^{-1}) would allow a number of solvents to be ranked according to their tendency to occupy the 'sixth' co-ordinate site and Gutmann[18] used these D_{II-I} values to estimate the respective 'donor number' of the solvents. More recently, Stoklosa and Wasson[7] applied the same Gutmann relation not only to [VO(acac)$_2$] but also to other bis(β-diketonato)oxovanadium(IV) complexes. Whereas the correlations 'donor number' *vs.* D_{II-I} are not very good in the last case, they apparently work for [VO(acac)$_2$]. Our results parallel these observations, also showing a rough correlation between D_{II-I} and θ_s (Table 1). While the correlation 'donor number' *vs.* D_{II-I} is maintained, negative 'donor numbers' would result when $\theta_s > \theta_{Solid}$. Taking into account of the absence of the donor ability of the implied solvents, this is not a striking result.

On the other hand, based on the Companion and Komarinsky development,[19] Stoklosa and Wasson's crystal-field treatment of bis(β-diketonato)oxovanadium(IV) complexes might explain the two low-energy *d–d* transitions ($3d_{xz}^*$, $3d_{yz}^* \longleftarrow 3d_{xy}^*$, and $3d_{x^2-y^2}^* \longleftarrow 3d_{xy}^*$) but predict too high values for band III ($3d_{z^2}^* \longleftarrow 3d_{xy}^*$).[7,20] Because of the formal equivalence between the point-charge electrostatic and a.o.m. models,[1,21] the α_l^i (l = 2,4, radial integral order; i =

ligand index) crystal-field parameters can be calculated (under C_{4v} symmetry) according to equations (7) and (8). The resulting

$$\alpha_4{}^i = \tfrac{3}{5}(3e_\sigma{}^{ax,eq} - 4e_\pi{}^{ax,eq}) \qquad (7)$$

$$\alpha_2{}^i = e_\sigma{}^{ax,eq} + e_\pi{}^{ax,eq} \qquad (8)$$

$\alpha_l{}^i$ values are compared with Wasson's estimations[7,20] in Table 4. The latter values were determined assuming a ratio $R = \alpha_2{}^i/\alpha_4{}^i$ close to 1 for all ligands. This choice[20] has never been well grounded. Moreover, the theoretically allowed R values range from 0 to 7 and may vary not only from one transition metal to other but, for a given system, from one ligand to another.[22]

From equations (7) and (8), R can be written as in equation (9).

$$R^{ax,eq} = e_\sigma{}^{ax,eq} + e_\pi{}^{ax,eq}/\tfrac{3}{5}(3e_\sigma{}^{ax,eq} - 4e_\pi{}^{ax,eq}) = 1 + p/(3 - 4p) \qquad (9)$$

Thus, it becomes evident that bonds involving ligands having very different π-donor abilities such as V=O and V–acac do not give equal R. In such a situation, contrary to Wasson's results, $\alpha_2{}^i$ must always be higher than $\alpha_4{}^i$. While these results are not inferable from the charge-point model, they arise directly from a.o.m. arguments. A plot of R *vs.* p is shown in Figure 4. It can be noted that R rises very sharply ($1 < R < 8$) as the π-donor character of the ligand ($0 < p < 0.6$) increases. The R values from our analysis are listed in Table 4. The usual choice of $R = 1$ may be appropriate for 'normal' single bonds. Nevertheless, R *ca.* 0.5 is expected for 'semi-co-ordinated' ligands and R values higher than 1 are reasonable when the ligand is involved in a double bond.

Conclusions

In the a.o.m. context, the strongest support to our working hypothesis lies in the 'sum rule' recently clarified by Woolley.[23] This rule establishes that $\Sigma e_\lambda{}^{exp}$ is approximately constant when the number, nature, and bond distances of the ligands about the metal ion are similar for a given oxidation state.

The main problem with the a.o.m. model is its possible overparametrization associated with restricted experimental information. We think that a treatment similar to that reported here can overcome this inherent difficulty when working with high-symmetry systems.

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