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Short Communication

Solvent Effects on the Electronic Spectra of Oxovanadium(IV) β-Diketonates

Comments on the Papers of Ebraheem et al.

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Summary. Solvent effects on the electronic absorption spectra of oxovanadium(IV) β-diketonates are discussed. It has been found that positions of the long-wave-length bands can be described in terms of the donor-acceptor concept including the donor numbers and the acceptor numbers.

Keywords. Electronic spectra; Oxovanadium β-diketonates; Solvent effect.

Lösungsmitteleffekte bei den Elektronenspektren von Oxovanadium(IV)-β-diketonaten. Kommentar zu den Arbeiten von Ebraheem et al. (Kurze Mitt.)

Zusammenfassung. Es werden Lösungsmitteleffekte bei den Elektronenspektren von Oxovanadium(IV)-β-diketonaten diskutiert. Dabei wurde gefunden, daß die Lage der langwelligen Banden auf Basis eines Donor-Akzeptor-Modells unter Berücksichtigung der Donor- und Akzeptor-Nummern beschrieben werden kann.

The electronic spectra of oxovanadium(IV) β-diketonate complexes, especially bis(acetylacetonato)oxovanadium(IV), VO(*acac*)$_2$, have been the subject of extensive investigations in a variety of solvents. Generally speaking, these spectra exhibit three distinct bands (labelled ν_1, ν_2, and ν_3) which were attributed to e_π (d_{xz}, d_{yz}) $\leftarrow$ b_2 (d_{xy}), b_1 ($d_{x^2-y^2}$) $\leftarrow$ b_2 (d_{xy}) and a_1 (d_{z^2}) $\leftarrow$ b_2 (d_{xy}) transitions, respectively [1, 2]. Quite often attention has been paid to the solvent effect on the intensity and positions of bands I and II; a discussion of these problems has been undertaken anew in a recent paper [3].

The work of Ebraheem et al. [3] is devoted to the correlation of the $\Delta\nu_{1,2}$ values ($\Delta\nu_{1,2} = \nu_I - \nu_2$) of VO(*acac*)$_2$ and VO(*tfa*)$_2$, bis(trifluoro-acetylacetonato)oxovanadium(IV), with solvent parameters. The authors have suggested that the solvent induced spectral shifts in VO(*acac*)$_2$ are dominated by the donor-acceptor interactions, and, therefore, a linear relationship exists between $\Delta\nu_{1,2}$ and DN, the Gutmann donor number. The correlation equation for nine solvents was found to be [3]

$$DN = -12.37 + 10.42\,\Delta\nu_{1,2}, \tag{1}$$

with a correlation coefficient of $r = 0.97$ and a standard deviation of $s = 0.198$ (the energy differences $\Delta\nu_{1,2}$ were expressed in kK units; $1\text{kK} = 1\,000\,\text{cm}^{-1}$).

Correlation (1) seems to be satisfactory; we assume, however, that it needs some comments. To understand the reasons we return to the results of Ebraham et al. It can be seen from Table 1 that the authors [3] have used donor numbers different from real DN values. It should be pointed out in this place that Ebraheem's values of DN were earlier achieved from the solvent effect on the energy difference $\Delta\nu_{1,2}$ in VO(*acac*)$_2$ spectra. However, several of Gutmann's DN values are not in agreement with this estimation. What is then the significance of Eq. (1)?

To clarify the problem we have reanalyzed the data from Table 1 using real Gutmann's donicities (for these DN values see e.g. Refs. [4–6]. Consequently we find the correlation equation to be

$$\Delta\nu_{1,2} = 0.089\,(\pm 0.018)\,\text{DN} + 1.711\,(\pm\, 0.321) \tag{2}$$

with number of measurements: n = 9, correlation coefficient: r = 0.880 and errors are standard deviations. It is then clear, by contrast to the proposition reported in [3], that donor numbers should not be directly used to interpret VO(*acac*)$_2$-solvent interactions. Anyway this finding was not surprising: in our previous communication [8] we have postulated that the $\Delta\nu_{1,2}$ values are dependent on the Lewis acidic and basic properties of a solvent. Thus, we try to analyse the solvent effect by planar regression including both DN and AN parameters [see also 9]. Such analysis performed for the same set of solvents used to calculate Eq. (2) gives the following equation,

$$\Delta\nu_{1,2} = 0.070\,(\pm 0.009)\,\text{DN} + 0.047\,(\pm 0.008)\,\text{AN} + 1.019\,(\pm 0.186), \tag{3}$$

with a correlation coefficient of $R = 0.982$. Comparison of the correlation coefficients for Eqs. (2) and (3) shows a very important improvement in accuracy of

Table 1. Spectral data of VO(*acac*)$_2$ and VO(*tfa*)$_2$ and relevant solvent parameters

Solvent	$\Delta\nu_{1,2}$ (kK) [3]		DN[a]		
	VO(*acac*)$_2$	VO(*tfa*)$_2$	Used in [3]	Real values	
CCl_4	1.554	1.612	0.0	0.0	8.6
Benzene	1.627	1.364	3.4	0.1	8.2
$CHCl_3$	1.916	3.024	10.9	0.0	21.3
ACN[c]	2.533	3.136	14.1	14.1	18.9
Acetone	2.493	2.756	17.0	17.0	12.5
DMF[d]	3.904	3.216	26.6	26.6	16.0
DMSO[a]	3.986	3.021	29.8	29.8	19.3
Ethanol	4.303	3.290	30.4	~20.0	37.1
Methanol	4.296	3.114	33.7	19.0	41.3

[a] DN = donor number

[b] AN = acceptor number [5, 7]

[c] *ACN* = acetonitrile

[d] *DMF* = N,N-dimethylformamide

[e] *DMSO* = dimethylsulphoxide

the planar regression. Statistical treatment with the Fisher-Snedecor *F*-test in a way proposed in [10] indicates strongly that addition of the AN parameter is significant even at the 0.001 level. The percentage of the explanation of variance for variation of $\Delta\nu_{1,2}$ is now 96.4%. It is then obvious that the solvent effect on the optical spectrum of VO(*acac*)$_2$ should be interpreted in terms of two parameter approach in the form of Eq. (3). More detailed discussion of this problem was presented in our paper [8].

Now, let us consider the question of VO(*tfa*)$_2$-solvent interactions. According to Ebraheem et al. [3] the solvent induced spectral shifts of this compound are dominated by non-specific solvent-solute interactions which are limited by the microscopic parameters, e.g. electric permittivity and refractive index. In our opinion, however, this seems to be wrong. As can be seen, a satisfactory linear relationship is observed between the $\Delta\nu_{1,2}$ and real DN values ($n = 9$; $r = 0.947$),

$$\Delta\nu_{1,2} = 0.053\,(\pm 0.009)\,\mathrm{DN} + 1.989\,(\pm 0.213). \tag{4}$$

Assuming that experimental errors in the determination of ν_1 and ν_2 are $\pm 25\,\mathrm{cm}^{-1}$ [3] and taking into account the possible errors in the estimation of solvent parameters, we stop our analysis at Eq. (4) since the percentage of the explanation of variance of $\Delta\nu_{1,2}$ is $r^2 \times 100 = 90\%$. In this light addition of AN, the second explanatory parameter, to eqn. (4) is not statistically significant. The suggested treatment can be applied also for the electronic spectra of bis(*p*-substituted) benzoyl-1,1,1-trifluoroacetonato)oxovanadium(IV) species. Analysing the spectra reported by Ebraheem and Fahad [11] we may conclude that for the five complexes of this group (numbered 1–5 in Ref. 11) the planar regression of the type of Eq. (3) exist; in all these cases the consideration of the Lewis acidity parameters (AN) is statistically significant at least at the 0.05 level.

It is to say that the results of Ebraheem et al. [3, 11] should be interpreted in terms of the donor-acceptor concept [4] including the donor numbers and acceptor numbers. In other words, the problem of the solvent effect on the visible spectra of bis(β-diketonato)oxovanadium(IV) complexes should be considered as a result of the electron charge density redistribution in the interacting molecules. In such a case electric permittivity or refractive index seem to be of little use.

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