On the Infrared Intensity of the V=O Stretching Vibration in Some Vanadyl Complexes

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In a previous study,[1] it was suggested that the absorption intensity of the V = O stretching vibration band for vanadyl complexes was characteristic for the type of metal-ligand bonding. Two cases were distinguished, one where the intensity increased as the frequency $\nu_{V=O}$ decreased, the other where both intensity and frequency decreased. In order to further substantiate this observation, we have measured the infrared intensity of vanadyl ethylxanthogenate, VO(exan)$_2$,and vanadyl diethyldithiocarbamate, VO(dtc)$_2$, extracted into carbon tetrachloride or carbon disulphide. The extraction was performed from aqueous solutions of vanadyl sulphate to which aqueous solutions of the extraction reagent (exan or dtc) were added. In all cases a precipitate was formed, which, however, was dissolved when extracted into the organic phase.

By varying the ratio of the volumes of the organic and the aqueous phases, the molar absorption coefficients (ε_{org}) of the species in the organic phase could be determined as described in another context.[2] This is demonstrated in Fig. 1. where $dC_M'/(\log T_0/T)_{org}$ is plotted *versus* q for VO(exan)$_2$ in carbon tetrachloride at two values of the total metal concentration C_M'. ε_{org} is then determined from the slope of the lines.
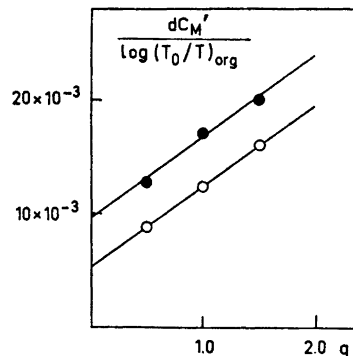

Fig. 1. Determination of ε_{org} at the maximum of the V = O absorption band (926 cm^{-1}) in VO(exan)$_2$ in carbon tetrachloride ($C_M' = 15$ mM (●) and $C_M' = 20$ mM (○)).

Because of a slow decomposition, three spectra were recorded after each other and the absorbance of the V = O band was extrapolated to zero time. The results are given in Table 1. The integrated intensity A has been calculated from the expression[3]

$$A = \pi/2 \times 2.303 \times \varepsilon \times \Delta\nu_{\frac{1}{2}}$$

in order to make the data directly comparable with the figures already[1] given.

In Fig. 2 we reproduce a typical spectrum of VO(exan)$_2$ in CCl$_4$ and also one of Zn(exan)$_2$ extracted into the same solvent. By comparison it is obvious that two absorption bands appear in the frequency range where V = O vibrations are expected. Because of the much greater difference (48 cm^{-1}) between the two bands and because of the constancy of this difference with respect to a change of solvent, we hesitate to describe this effect as being similar to the solvent association considered

Table 1. Spectral data of the vanadyl thiocomplexes.

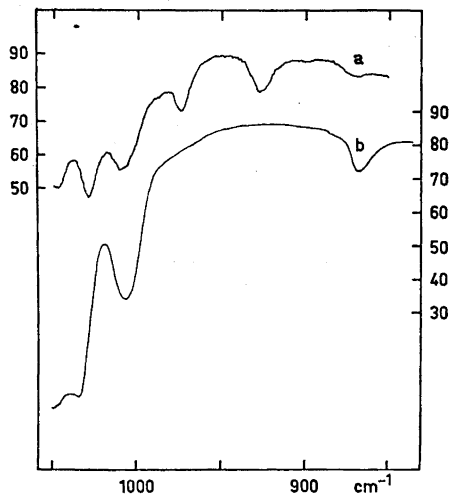| Complex	Solvent	$\nu_{V=O}$ cm^{-1}	ε M^{-1} cm^{-1}	$\Delta\nu_{\frac{1}{2}}$ cm^{-1}	$A \times 10^{-4}$ M^{-1} cm^{-2}	$A_{tot} \times 10^{-4}$ M^{-1} cm^{-2}	$\nu_{V=O}$ mean cm^{-1}
VO(dtc)$_2$	CS$_2$	958	440 ± 40	7.8 ± 0.3	1.24 ± 0.10	1.24 ± 0.10	
VO(exan)$_2$	CS$_2$	922	130 ± 10	12.0 ± 0.2	0.57 ± 0.04	0.75 ± 0.05	935
		970	70 ± 5	7.0 ± 0.5	0.18 ± 0.01		
VO(exan)$_2$	CCl$_4$	926	145 ± 15	12.5 ± 0.5	0.65 ± 0.06	0.94 ± 0.09	941
		974	85 ± 8	9.5 ± 0.5	0.29 ± 0.03		

Fig. 2. Comparison of spectra of VO(exan)$_2$ ((a), left scale) and Zn(exan)$_2$ ((b), right scale) in CCl$_4$.

before. In lieu of a complete equilibrium analysis one can but speculate that two different VO^{2+} species coexist in the organic phase (*e.g.* VO(exan)$_2$ and VO(exan)$_2^-$).

Anyway, we presume that the sum of the intensities of the two bands is the

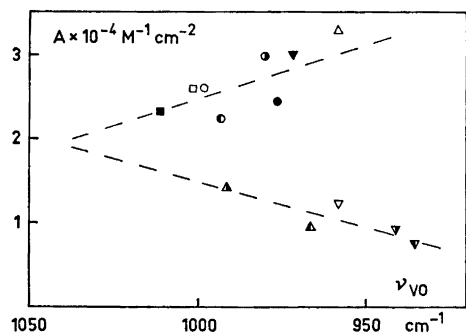*Fig. 3.* The absolute intensities from Ref. 1 and Table 1 plotted against the frequency. Symbols: VO(acac)$_2$ in ethanol △, in tetrahydrofuran ▲, in CCl$_4$ ■, in CHCl$_3$ □, in pyridine △; VO^{2+}aq ○, VONCS$^+$aq ◐, VO(NCS)$_2$aq ◑, VO(NCS)$_3^-$aq ●, VO(dtc)$_2$ in CS$_2$ ▽, VO(exan)$_2$ in CS$_2$ ▼, in CCl$_4$ ▽, (VO)$_2$[Fe(CN)$_6$] solid ▼.

relevant figure to consider. When plotting these results (Fig. 3) in a way similar to that used before,[1] we have used for the frequency a weighted mean of those observed. In Fig. 3 is also included an intensity value for the V=O absorption of the compound ideally formulated as (VO)$_2$[Fe(CN)$_6$], measured in the solid (dried) state in KBr pellets. The data of interest here are $\varepsilon_{max} = 310$ M^{-1} cm^{-1}; $\Delta\nu_{1/2} = 41$ cm^{-1}, and $\nu_{max} = 971$ cm^{-1}. This gives $A = 4.55 \times 10^4$ M^{-1} cm^{-2}. This value is valid for the total number of VO groups in the compound. The value per VO group is then 2.3×10^4 M^{-1} cm^{-2}. This is, of course, the true, experimental value, but in order to make it comparable to the other results from measurements on species in solution, we may recall the following observation. In many instances,[4,5] measurements of the same species in solution and in KBr immersion show that the intensity is larger in the former by a factor of about 1.3. Consequently, we have increased the observed value to $1.3 \times 2.3 = 3.0$.

It can now be noticed that the generalisation made in the earlier paper still is valid: Two distinctly different groups of complexes are distinguished, one whose intensities fall on a line with positive slope and one where they fall on a line with negative slope. These lines intersect at $\nu = 1 040$ cm^{-1} and $A = 2.0 \times 10^4$ M^{-1} cm^{-2}, supposedly representing the totally undisturbed VO^{2+} unit.

The most interesting observation is that VO(acac)$_2$ dissolved in ethanol and tetrahydrofuran fall on the lower line, where the complexes with "soft" ligands [6] are found. Is this a coincidence, or does it imply that the presence of, *e.g.*, ethanol turns the acetylacetonate ligand into a "soft" one? Or is the coordination of ethanol itself a "soft" interaction, similar to that preceding *e.g.*, the formation [7] of Ir(PPh$_3$)$_2$COCl from ethanol?

It seems to us that in the answer to these questions is hidden the explanation of the catalytic action of VO(acac)$_2$ in the autooxidation of alcohols.[8]

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NMR Studies on Cyclic Arsenites. Spectral Analysis of the NMR Spectrum of 2-Chloro-1,3,2-dithiarsenane

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In recent years a great deal of effort has been expended in NMR studies of the conformations of six-membered heterocycles.[1] For rigid molecules, analyses of observed NMR spectra yield chemical shifts and coupling constants which can be correlated with a particular conformation.

This paper reports preparation and NMR analysis of 2-chloro-1,3,2-dithiarsenane (I). Hitherto no analyses of six-membered arsenites have been reported. The effective "decoupling" of the arsenic nucleus simplifies the spectrum but reduces its information content as compared to cyclic phosphites. The reported NMR studies on 1,3,2-dioxaphosphorinanes and 1,3,2-dithiaphosphorinanes are of particular relevance to this work.[2,3]

The NMR spectrum of I was analyzed as an AA'BB'CD spin system by means of the

computer programs LAOCN3 [4] and KOM-BIP.[5] The latter sub-routine generated "stick"- and Lorentzian line-shape plots. The stick-plots based on trial parameters facilitated the rather tricky analysis.

The iterated spectral parameters of I are listed in Table 1. The root-mean-square deviation was 0.059 for 136 assigned transitions. The calculated probable errors in the thirteen varied parameter sets were 0.014 or less. The excellent fit between the experimental and calculated spectra in Figs. 1 and 2 confirms the correctness of
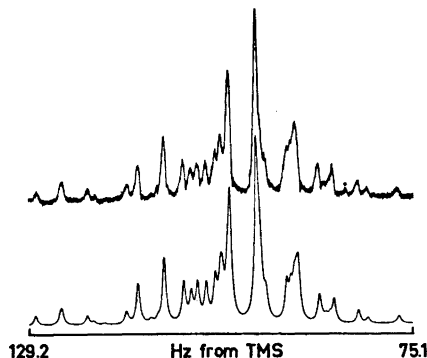

Fig. 1. Experimental (upper part) and calculated (lower part) 60 MHz spectrum of the protons at carbon 5 in I. The asterisk indicates an impurity.

the parameters. The NMR spectrum can be divided into three distinct regions. The region at higher field is, of course, due to the two protons at carbon 5.
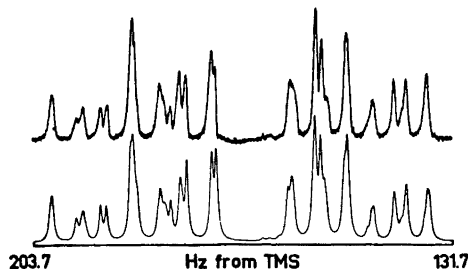

Fig. 2. Experimental (upper part) and calculated (lower part) 60 MHz spectrum of the protons at carbons 4 and 6 in I. The low-field and high-field spectrum traces represent the axial and equatorial protons, respectively.