

The Dipole Moment and Molar Kerr Constant of Vanadyl Acetylacetonate: Evidence for Bisacetylacetonato(oxo)vanadium–Dioxan Co-ordination

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Dipole moments and molar Kerr constants (for $\lambda = 500$ nm) are reported for bisacetylacetonato(oxo)vanadium $[\text{VO}(\text{acac})_2]$ as a solute in benzene and in dioxan. The data are analysed to provide evidence for complex formation between $\text{VO}(\text{acac})_2$ and dioxan by co-ordination in the sixth position of the vanadium atom.

BISACETYLACETONATO(OXO)VANADIUM $[\text{VO}(\text{acac})_2]$ is known to interact with amines to form addition compounds in which the vanadium has a roughly octahedral co-ordination sphere.¹⁻⁴ With oxygen-containing ligands, however, the evidence for such complex formation is less certain⁴⁻⁶ though recently Nyburg *et al.*⁷ isolated the complex $[\text{VO}(\text{acac})_2]_2(\text{dioxan})$ in which a dioxan molecule bridges two $\text{VO}(\text{acac})_2$ groups. They proved by X-ray analysis that, in the solid state at least, an oxygen atom in dioxan is bonded to the V atom at the sixth 'unoccupied' site. This paper provides further evidence for such interactions in the solution state from dipole moment and Kerr constant measurements. The experimental data are summarised in Tables 1 and 2.

EXPERIMENTAL

Materials, Apparatus, Etc.—Bisacetylacetonato(oxo)-vanadium was prepared by the method of Rowe and Jones⁸

¹ M. M. Jones, *J. Amer. Chem. Soc.*, 1954, **76**, 5995.

² R. T. Claunch, T. W. Martin, and M. M. Jones, *J. Amer. Chem. Soc.*, 1961, **83**, 1073.

³ K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, 1961, **83**, 4533.

⁴ J. Selbin, H. R. Manning, and G. Cessac, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1253.

⁵ R. L. Carlin and F. A. Walker, *J. Amer. Chem. Soc.*, 1965, **87**, 2128.

⁶ C. M. Guzy, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc. (A)*, 1969, 2791.

and recrystallised several times from acetone. The pyridine adduct was obtained by the procedure of Rosenheim and Mong.⁹ The purity of each compound was checked by microanalysis (C and H). The i.r. spectra agreed well with those reported by Martell *et al.*³

Apparatus, techniques, symbols used, and methods of calculation have been described before.¹⁰⁻¹³ Measurements of the Kerr constant B were made using light of wavelength 500 nm. The quantities $\Delta\epsilon$, Δd , Δn , and ΔB are the differences found between the dielectric constants, densities, refractive indices, and Kerr constants, respectively, of the solvent and of solutions containing weight fractions w_2 of solute. In all cases measurements were made on freshly prepared solutions to minimise the effects of slow solute decomposition. The constants shown in Table 1 apply for the solvents at 25°:

⁷ K. Dichmann, G. Hamer, S. C. Nyburg, and W. F. Reynolds, *Chem. Comm.*, 1970, 1295.

⁸ R. A. Rowe and M. M. Jones, *Inorg. Synth.*, 1957, **5**, 115.

⁹ A. Rosenheim and H. Y. Mong, *Z. anorg. Chem.*, 1925, **148**, 34.

¹⁰ C. G. Le Fèvre and R. J. W. Le Fèvre, *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 261.

¹¹ R. J. W. Le Fèvre, 'Dipole Moments,' Methuen, London, 3rd edn., 1953.

¹² C. G. Le Fèvre and R. J. W. Le Fèvre, in 'Physical Methods of Organic Chemistry,' ed. A. Weissberger, Interscience, New York, 3rd edn., vol. I, ch. XXXVI, p. 2459.

¹³ R. J. W. Le Fèvre and G. L. D. Ritchie, *J. Chem. Soc.*, 1963, 4933.

TABLE 1

	ϵ_1	d_1	$(n_1)\lambda^a$	$10^7(B_1)\lambda^a$	$10^{14}(K_1)\lambda^a$
Dioxan	2.2090 ^b	1.0280 ^b	1.4236 ^c	0.087 ^d	1.49 ^d
Benzene	2.2725 ^b	0.87378 ^b	1.5077 ^c	0.503 ^e	7.81 ^e

^a For $\lambda = 500$ nm. ^b From R. S. Armstrong, M. J. Aroney, R. J. W. Le Fèvre, R. K. Pierens, J. D. Saxby, and C. J. Wilkins, *J. Chem. Soc. (A)*, 1969, 2735. ^c From J. G. Foss and J. A. Schellman, *J. Chem. and Eng. Data*, 1964, 9, 551. ^d Determined relative to benzene for $\lambda = 500$ nm. ^e From R. J. W. Le Fèvre and S. C. Solomons, *Austral. J. Chem.*, 1968, 21, 1703.

TABLE 2

Incremental dielectric constants, densities, refractive indices, and Kerr constants for solutions at 25°

VO(acac) ₂ in benzene					
$10^6 w_2$	830	1535	2395	2520	3297
$-10^{11} \Delta B$	219	435	641	688	858
$10^4 \Delta \epsilon$		74	112	115	156
$10^5 \Delta d$		48	74	77	99
$10^4 \Delta n$		1			2
	3365	4567			
	1192				
	104	219			
		140			
		3			
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -26.6$; $\Sigma \Delta \epsilon / \Sigma w_2 = 4.72$; $\Sigma \Delta d / \Sigma w_2 = 0.307$; $\Sigma \Delta n / \Sigma w_2 = 0.06_4$					
VO(acac) ₂ in dioxan					
$10^6 w_2$	1969	2167	4069	4445	
$-10^{11} \Delta B$	736			1631	
$10^4 \Delta \epsilon$		170	325	346	
$10^4 \Delta d$	5			11	
	4963	5364	5554	6008	10,306
		2043	2061	2176	3743
	391		444	474	846
		15	15	16	28
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -36.8$; $\Sigma \Delta \epsilon / \Sigma w_2 = 7.99$; $\Sigma \Delta d / \Sigma w_2 = 0.267$					
$10^6 w_2$	2208	3254	5492	6770	10,727
$10^4 \Delta n$	3	5	7	10	14
whence $\Sigma \Delta n / \Sigma w_2 = 0.13_8$					

DISCUSSION

The mean values of the experimental dipole moment estimates are 3.2₁ D for VO(acac)₂ in benzene and 3.9₈ D for VO(acac)₂ in dioxan. The coefficients $\alpha \epsilon_1$, β , γ , δ , listed in Table 3 for VO(acac)₂ were calculated from the

Selbin *et al.*⁴ have reported the moment of VO(acac)₂ as 4.3 D but they do not give details of the solvent used or the atom polarisation allowance. No other relevant dipole moment or Kerr constant determinations appear to have been published.

The structure of VO(acac)₂ was established by X-ray analysis¹⁴ to be tetragonal pyramidal with the V atom being slightly displaced from the plane of the four ligand oxygen atoms and in the direction of the apical oxygen. The complex is monomeric in the solid state and in solution.¹ The co-ordination number of vanadium can be increased from five to six by the addition of a ligand base in the vacant sixth position of the vanadium co-ordination sphere. Such co-ordination to ligands which are strong Lewis bases increases the electron density in the vanadium *d*-orbitals and this, in turn, reduces the amount of *p* π -*d* π donation from O to V in the V=O group. The lowering of the V=O bond order would be reflected in a shift to lower frequencies of the V-O stretching frequency in the i.r. spectrum.^{3,4} The dipole moment will also be affected by the formation of the six-co-ordinated species VO(acac)₂base primarily be-

cause the moment vector $\mu(\text{base}-\overrightarrow{V})$ associated with the highly polar co-ordinate bond would reinforce the dipole moment of VO(acac)₂. Secondary effects would also be operative, *viz.* an enhancement of $\mu(\overrightarrow{V=O})$ because of the reduction in the *p* π -*d* π back donation from O to V, and, most likely, a greater degree of vector cancellation of the two V(acac) group dipoles.⁷ The increase in μ so predicted is found in the dipole moment quoted above for VO(acac)₂ in dioxan (4.0 D) relatively to the moment of the 'isolated' VO(acac)₂ molecule as measured in benzene (3.2 D). Co-ordination of VO(acac)₂ with benzene, if it occurs at all, is not significant,^{4,5} while the formation of VO(acac)₂benzene collision complexes, arising through long-range electrostatic interactions, do not affect the magnitude of the solute dipole moment. We regard the dipole moment increase in dioxan as definite evidence for the existence in

TABLE 3

Polarisations, refractions, dipole moments, and molar Kerr constants (from observations on solutions at 25°) for VO(acac)₂

Solvent	$\alpha \epsilon_1$	β	γ	δ	∞P_2 (c.c.)	R^a (c.c.)	μ (D) ^b	μ' (D) ^c	$10^{12} \infty (mK_2)$
Benzene	4.72	0.351	0.04	-52.9	291	67.1	3.31	3.10	-1128
Dioxan	7.99	0.260	0.09	-421	404	66.7	4.06	3.89	-1676

^a Determined using refractive index measurements made with the solutions as filters. ^b Calculated taking the distortion polarisation as equal to the measured molecular refraction. ^c The moment values μ' were obtained if, in estimating the distortion polarisation, an allowance of 14 c.c. is made for each acac ring to take into account anomalous atomic polarisations (A. E. Finn, G. C. Hampson, and L. E. Sutton, *J. Chem. Soc.*, 1938, 1254).

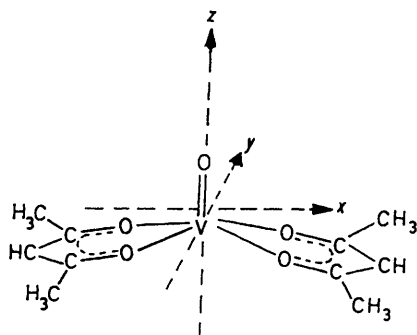
measured data of Table 2 on the basis that the solute in each case exists in solution in a non-complexed form and the μ and mK values were derived accordingly. If, however, the true solute species were the 1:1 complex VO(acac)₂solvent molecule, then a similar analysis of the data of Table 2, using now the corrected 'solute' weight fractions, would result in dipole moment and molar Kerr constant estimates which are virtually identical with those obtained for the 'isolated' solute.

solution of the VO(acac)₂dioxan complex. Associations involving the simultaneous co-ordination of one dioxan and two VO(acac)₂ molecules are unlikely for the low VO(acac)₂ concentrations examined; they would, moreover, tend to lower the apparent solute dipole moment of VO(acac)₂ rather than to increase it. Polarisation and refractivity measurements were made also for the

¹⁴ R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, 1961, 35, 55.

VO(acac)₂ pyridine complex in benzene solution but the moment estimate so obtained (~4.1 D) is not that of the adduct alone since an i.r. spectral study of the solutions shows clearly that the complex is appreciably dissociated in benzene at 25°.

The experimental molar Kerr constant of VO(acac)₂ in benzene and in dioxan is in each case large and algebraically negative. If the moment is directed along the V=O longitudinal axis, *i.e.* the Z direction in the Figure, then it follows, from the Langevin-Born interpretation of the Kerr effect, that $b_{xx} + b_{yy} > 2b_{zz}$, where the elements b_{ii} are the diagonal components of the molecular polarisability tensor with reference to the X, Y, Z system of axes.¹⁵ It follows also, from the



geometry¹⁴ of VO(acac)₂, that within each V(acac) chelate ring grouping, the in-plane polarisabilities, and by inference the electron mobilities, are greater than that in a direction perpendicular to the plane. Estimates of the molecular polarisability anisotropy of VO(acac)₂ can be derived from the molar Kerr constant (if we assume $b_{zz} \neq b_{xx} = b_{yy}$) using equation (1) in which the ratio

$${}_mK = 4\pi N \left[\frac{{}_D P (b_{zz} - b_{xx})^2}{{}_E P + \mu_z^2 (b_{zz} - b_{xx}) / kT} \right] / 405 kT \quad (1)$$

distortion polarisation/electron polarisation was taken as 1.1, k is the Boltzmann constant, N Avogadro's number, and T is the absolute temperature. Since solubility limitations do not allow the experimental determination of the molar Kerr constant of VO(acac)₂

in an inert solvent environment we have utilised in the calculations the ${}_mK$ values in benzene and in dioxan to derive estimates ($b_{zz} - b_{xx}$) of $-10.5 (\pm 0.8)$ and $-10.0 (\pm 0.5)$ respectively. The polarisabilities are expressed throughout in 10^{-24} c.c. units. The equations were solved using in turn the moments μ and μ' of Table 3. The figures quoted above are mean values and the maximum errors arising from the uncertainty in the dipole moment in each case, are given in parentheses. The close accord between these two estimates is a consequence of (a) the near isotropically polarisable nature of the dioxan molecule¹⁶ which when associated with VO(acac)₂, does not greatly change the VO(acac)₂ polarisability anisotropy, and (b) the low incidence of stereospecific VO(acac)₂ benzene electrostatic association since the attraction of the benzene π electrons towards the positive end of the V=O dipole would be counterbalanced by repulsions by the lone pairs of the four neighbouring oxygen atoms. The Kerr constant measurements can thus be reconciled with the formation in dioxan of the VO(acac)₂ dioxan complex. The sum b_{ii} for VO(acac)₂ may be obtained from the electron polarisation which we take as 0.95 times the measured molecular refraction [equation (2)]:

$${}_E P = 4\pi N (2b_{xx} + b_{zz}) / 9 \quad (2)$$

Thus for VO(acac)₂ in benzene we calculate the (mean) values $b_{xx} = 28.8$ and $b_{zz} = 18.3$. A similar calculation for VO(acac)₂ in dioxan leads to $b_{xx} = 28.5$ and $b_{zz} = 18.5$ but these estimates, derived from ${}_E P$ for the VO(acac)₂ alone, do not include the polarisability contributions of co-ordinated dioxan molecules.

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¹⁵ R. J. W. Le Fèvre, *Adv. Phys. Org. Chem.*, 1965, **3**, 1.

¹⁶ R. J. W. Le Fèvre, A. Sundaram, and R. K. Pierens, *J. Chem. Soc.*, 1963, 479.