848. *Magnetic and Spectral Studies of Vanadium Tetrachloride.*

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Magnetic studies over a temperature range, together with spectral studies, on vanadium tetrachloride are interpreted as implying that the molecule consists of essentially non-interacting tetrahedral species with a ^2E ground term.

VANADIUM TETRACHLORIDE, having a single *d*-electron and an essentially tetrahedral stereochemistry,[1] should display interesting spectral and magnetic properties. The vapour spectrum of the molecule was reported recently [2] at the same time as a study of the molecule in condensed phases was being carried out in these laboratories. The molecule is believed to be monomeric in the vapour phase [3] and, from a comparison of its vapour and solution spectra in the 8000 cm.$^{-1}$ region, we have concluded that it consists of essentially non-interacting tetrahedral species in condensed phases also, in agreement with the conclusions drawn by Whittaker and Yost [4] from magnetic studies in carbon tetrachloride solution

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[1] Lipscomb and Whittaker, *J. Amer. Chem. Soc.*, 1945, **67**, 2019.
[2] Blankenship and Belford, *J. Chem. Phys.*, 1962, **36**, 633.
[3] Tchukarev, Oranskaya, Tolmatcheva, and Yakhkind, *Zhur. neorg. Khim.*, 1956, **1**, 30.
[4] Whittaker and Yost, *J. Chem. Phys.*, 1949, **17**, 188.

over a range of concentrations. The absorption spectrum of vanadium oxide trichloride has also been recorded in the 8000 cm.$^{-1}$ region, in order to be certain that no bands in the absorption spectrum of vanadium tetrachloride arise from vanadium oxide trichloride, an impurity which confused the interpretation of the spectrum reported by Blankenship and Belford;[2] the very strong band which they observed at 1030 cm.$^{-1}$ must clearly be the V–O fundamental stretching frequency[5] of vanadium oxide trichloride impurity, and not a triple combination band as suggested.[2]

The magnetic moment of vanadium tetrachloride has been recorded over the range 315—87°K, and at three field strengths at room temperature. The results have been analysed on the basis that any antiferromagnetic interactions are small, and a range of possible values for the spin–orbit coupling constant and the orbital delocalisation factor of vanadium(IV) in the molecule are suggested below.

Results and Discussion

Spectral Measurements.—The absorption spectrum of vanadium tetrachloride (Fig. 1) was recorded at 20° in carbon tetrachloride solution at 3·87 × 10^{-2}M. The solvent had been redistilled from a dehydrating agent under oxygen-free nitrogen immediately before use. The absorption bands for the solution were at 9010, 7880, and 6600 cm.$^{-1}$ (ε 130, 124, and ~65), whilst the corresponding data[2] for the vapour are 9250, 7850, and 6600 cm.$^{-1}$ (ε ~145, ~135, and ~70, respectively). A solution of vanadium oxide trichloride in carbon tetrachloride does not absorb in this region, and hence all three bands appear to belong to the vanadium tetrachloride molecule. The similarity between the spectra in the two phases strongly suggests that the molecule consists of non-interacting monomeric species in solution as well as in the vapour.[3] The energy separation between the e and t_2 orbitals is thus ~7900 cm.$^{-1}$, which is consistent with the typical value of ~21,000 cm.$^{-1}$ for $10Dq$ found[6] for octahedrally co-ordinated vanadium(IV). The splitting of the T_2 term is much greater than is expected from spin–orbit coupling; it is also in three components, and not two as would be expected by the above mechanism. Hence it appears that the splitting must arise from distortion of the molecule from T_d symmetry to D_2 at least.

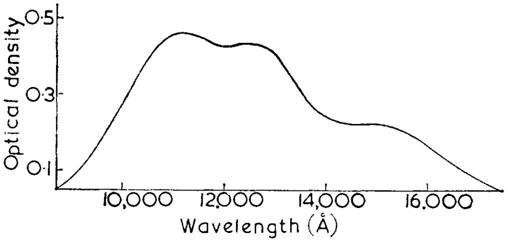

Fig. 1. Absorption spectrum of vanadium tetrachloride in the 8000 cm.$^{-1}$ region.

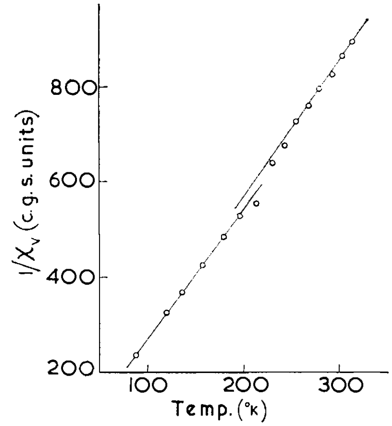

Fig. 2. Inverse magnetic susceptibility per g.-atom plotted against temperature, for vanadium tetrachloride.

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[5] Eichhoff and Weigel, *Z. anorg. Chem.*, 1954, **275**, 267.

[6] Clark, *J.*, 1963, 1377.

Magnetic Measurements.—The essentially tetrahedral structure of vanadium tetrachloride in both the liquid and the solid phase is indicated by a study of its magnetic properties over a temperature range (see Table 1). Vanadium tetrachloride is a liquid which freezes at 245°K, and down to the freezing point $\mu_{\text{eff.}}$ is independent of temperature; this is the behaviour expected for the ^2E ground term of tetrahedral vanadium(IV). A small deviation from Curie-law behaviour is to be expected as the result of a temperature-independent term. There appears to be a small change in the magnetic behaviour on freezing. However, this may be due to uncertainty as to the length of the solid sample, or to crystallisation in a preferred direction in the tube. A plot of $1/\chi_V$ against temperature for the liquid and the solid phase is shown in Fig. 2; the values of θ for the two lines are -1°K and 1°K, respectively, for the liquid and the solid phase, so that any antiferromagnetic interaction must be small. Because of the small temperature ranges involved, the extrapolations used to obtain these values of θ are not very reliable. The Curie–Weiss law is expressed here as $\chi_V \propto 1/(T + \theta)$. Whatever the reason for this break in the plot, $\mu_{\text{eff.}}$ remains independent of temperature in the solid phase, indicating that the structure is either a regular or a distorted tetrahedron. The latter would have a singlet ground term with similar magnetic properties to the ^2E ground term of the regular structure, so that it is not possible magnetically to distinguish between the two structures.

TABLE 1.

Magnetic measurements on vanadium tetrachloride.

T (°K)	$10^6\chi_V$	$1/\chi_V$	T (°K)	$10^6\chi_V$	$1/\chi_V$	T (°K)	$10^6\chi_V$	$1/\chi_V$
315·4	1123	890·5	256·7	1377	726·2	179·7	2065	484·2
306·0	1160	862·1	244·2	1483	674·3	157·1	2347	426·1
293·8	1215	823·0	232·4	1565	638·9	135·5	2710	369·0
281·4	1263	791·8	214·5	1810	552·5	118·9	3080	324·7
269·0	1318	758·7	197·1	1898	526·8	87·2	4190	238·7

The magnetic moment of the compound has been measured accurately with as large a sample as possible at three field strengths. The results are given in Table 2.

TABLE 2.

Magnetic measurements on vanadium tetrachloride at several field strengths.

Field strength (oersteds)	$10^6\chi_M$	$10^6\chi_M'$ *	$10^6\chi_M' - 132$	T (°K)	$\mu_{\text{eff.}}$ (B.M.)
10,000	1115	1209	1077	296·9	1·607
7000	1147	1241	1109	291·5	1·618
5000	1143	1237	1105	291·2	1·612

* χ_M' is the value of χ_M corrected for diamagnetism of the ligands (-94×10^{-6} c.g.s. units).

The contribution of temperature-independent paramagnetism to $10^6\chi_M'$ is taken as $4N\beta^2/10Dq$ which is 132 c.g.s. units for $10Dq = 7900$ cm.$^{-1}$. If the resultant average value for $\mu_{\text{eff.}}$ (1.612 B.M.) is inserted in the formula $\mu_{\text{eff.}} = \mu_{\text{spin-only}}(1 - 2\lambda'/10Dq)$, where $\mu_{\text{spin-only}} = 1{\cdot}73$ B.M. and $10Dq = 7900$ cm.$^{-1}$, then a value of 270 cm.$^{-1}$ is obtained for the spin–orbit coupling constant, λ', of vanadium(IV) in vanadium tetrachloride, *i.e.*, a value greater than the free-ion value[7] of $\lambda = 250$ cm.$^{-1}$, whereas λ is normally reduced slightly on co-ordination.[6]

The temperature-independent contribution to the paramagnetism can be reduced if the *d*-electron of vanadium(IV) is partially delocalised on to the ligands, *i.e.*, if the electron is contained in a metal–ligand π molecular orbital. This effect is discussed by, *e.g.*, Figgis;[8] the temperature-independent term is reduced to $4k^2N\beta^2/10Dq$ where k, the orbital delocalisation factor, is the probability of finding the unpaired electron in a metal *d*-orbital. No results are available to suggest what value should be assigned to k in a tetrahedral

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[7] Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441.

[8] Figgis, *Trans. Faraday Soc.*, 1960, **56**, 1553.

vanadium(IV) complex, but for octahedral titanium(III) and vanadium(IV) complexes[6,9] k is $\sim 0{\cdot}8$. It is reasonable to suggest that k may also be of this order in a tetrahedral molecule. Putting $k = 0{\cdot}9$ and $0{\cdot}8$ in turn, the following values are obtained: $4k^2N\beta^2/10Dq = 107$, and 85×10^{-6} c.g.s. units; $\mu_{\text{eff.}} = 1{\cdot}629$ and $1{\cdot}645$ B.M.; and $\lambda' = 231$ and 194 cm.$^{-1}$, respectively. Thus λ' has a more reasonable value if one allows for such electron delocalisation. The assignment of the 8000 cm.$^{-1}$ band system to the $^2T_2 \longleftarrow {}^2E$ transition is thus consistent with the magnetic measurements.

EXPERIMENTAL

The absorption spectra were recorded on a Cary model 14 recording spectrophotometer with 1 cm. cells. The measurement of the absolute value of the magnetic susceptibility was carried out by the Gouy method at room temperature. The sample (Johnson Matthey) was redistilled *in vacuo* at room temperature directly into the Gouy tube, the latter being kept at liquid-nitrogen temperature. The sample (3·06 ml., 8·10 cm. long) was sealed off immediately after distillation and before being allowed to liquefy. The magnetic field was provided by an electromagnet and the force on the specimen was measured on a semimicro chemical balance. The equipment was calibrated against redistilled water. The relative susceptibility of the compound was measured on equipment described previously.[9] The density of vanadium tetrachloride was 1·829 g./c.c. at 20°, in close agreement with the value (1·820 g./c.c. at 25°) reported previously.[3]

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[9] Clark, Lewis, Machin, and Nyholm, *J.*, 1963, 379.