

## The Infrared Absorption Intensity of the V=O Vibration of the Vanadyl(IV) Ion and its Thiocyanato Complexes

RAGNAR LARSSON and GENNARO NUNZIATA\*

*Division of Inorganic Chemistry, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden*

The absorption intensity of the V=O vibration band has been measured in aqueous solutions 3 M (NaCl) and in solutions containing thiocyanate ions. From the shift of the absorption maximum the stability constants have been determined. The absorption bands of each of the complexes  $\text{VO}(\text{NCS})_n^{(2-n)+}$ , where  $n = 0-3$ , have been resolved (Fig. 5). The first complex is characterized by a decrease, the second one by an increase of the intensity of the V=O absorption band.

From the intensity obtained for the  $\text{VO}^{2+}$  ion the dipole moment derivative has been calculated ( $d\mu/dr = 1.8$  a.u.). This result is discussed in relation to recent models for the bonding in the  $\text{VO}^{2+}$  ion.

The chemistry of vanadyl(IV) complexes has attracted much attention in recent years.<sup>1</sup> Bonding schemes for the  $(\text{H}_2\text{O})_5\text{VO}^{2+}$  ion have been proposed by Ballhausen and Gray<sup>2</sup> and recently by Vanquichenborne and McGlynn.<sup>3</sup> Experimentally, several spectroscopic techniques, notably the study of ESR and electronic spectra, have been applied to vanadyl compounds. In the infrared region of the spectrum the most important absorption band is the one at about  $1000\text{ cm}^{-1}$ , corresponding to the V=O stretching vibration. This absorption band has previously been recorded by Evans<sup>4</sup> in a qualitative investigation on aqueous solutions of vanadyl(IV) compounds.

Although the above-mentioned MO calculations result in somewhat different distributions of the charges on the vanadyl and oxygen atoms of the V=O group, it seemed to us that they could be of considerable help in interpreting the absorption intensity of this band.

It is probably allowed as a first approximation to consider the vibrating unit as a diatomic molecule,<sup>5</sup> as this frequency is relatively far from the frequencies of the other metal-ligand vibrations. This facilitates the calculation of the theoretically interesting quantity  $d\mu/dr$  from the measured intensity.

\* Present address: Product Research Department, European Technical Center, Procter & Gamble Co., Bruxelles, Belgium.

It is well-known <sup>5</sup> that the V=O stretching frequency is usually decreasing, when ligands other than water are introduced in the coordination sphere of the vanadium atom. This opens the possibility of determining the degree of complex formation for suitable ligands from a measurement of the frequency shift as developed in an earlier paper.<sup>6</sup> That investigation dealt with the  $\text{UO}_2^{2+} - \text{SCN}^-$  complex system.

The vanadyl-thiocyanato complex system is well suited for this type of measurement, as, *pro primo*, the vanadyl ion is known <sup>7</sup> to exist in acid solutions to quite high concentrations without polymerisation and, *pro secundo*, the thiocyanato ion is such a weak base that it exists as such in the moderately acidic medium that must be used. One has therefore a simple system and the infrared absorption band is composed only of components corresponding to the  $\text{VO}^{2+}$  and  $\text{VO}(\text{NCS})_n^{(2-n)+}$  species. The basic assumption in the determination of the complexity is that the position of the maximum of the composite absorption band is determined solely by the relative proportions  $\alpha_n$  of the complex species. As  $\alpha_n$  is determined only by the concentration of free ligand, (L), the principle of corresponding solutions can be applied to find related values of  $\bar{n}$  and [L] and hence, by usual methods, the stability constants.<sup>8</sup> A necessary condition for such a quantitative study is a careful temperature control of the solution. This was not applied in the previous investigation, but we have now tried to achieve such a control as is described below.

We have chosen to use sodium chloride to create an ionic medium of constant ionic strength instead of the conventionally used sodium perchlorate. The reason for this is that perchlorate ions exhibit a strong infrared absorption in the actual spectral range. The complexity of the vanadyl(IV) chloride system is quite low <sup>9</sup> ( $\beta_1 \approx 1 \text{ M}^{-1}$ ), and the stability constants will be of the same order of magnitude as if they were determined in a perchlorate medium.

## EXPERIMENTAL

The infrared spectra were recorded with a Perkin Elmer Spectrophotometer Model 521. All spectra were recorded with a wavenumber scale expansion, so that 1 cm on the chart corresponded to 25  $\text{cm}^{-1}$ . The slit width regulation was put so (slit program <sup>10</sup> = 900 × 2) that the spectral slit width was about 2.1  $\text{cm}^{-1}$ . As the half-width of the absorption band under investigation was about 25  $\text{cm}^{-1}$  we have considered it unnecessary to correct the measured intensities for the finite slit-width effect.<sup>11</sup> The absolute intensity of the absorption band,  $A$ , was then calculated from the formula <sup>11</sup>

$$A = \pi/2 \times 2.303 \times \epsilon_{\text{max}} \times \Delta\nu_{1/2} \quad (1)$$

The temperature control is a difficult problem in infrared spectrometry as the flux of light through the cell is much greater than it is in spectrophotometers used for the ultra-violet-visible spectral range. Although it seems possible to construct cells embedded in a thermostated metal holder,<sup>12</sup> we considered it easier and — regarding the small volumes necessarily used for studies of aqueous solutions — safer to use a flow cell construction where the liquid was thermostated outside the cell and was then continuously passed through the cell with the help of a peristaltic pump. No difference in the spectrum was observed between streaming and non-streaming solutions. The details of this arrangement are given in Fig. 1. Further advantages of this construction were that it was possible to avoid contact between the acidic solutions and any metallic parts that could be corroded and thus introduce impurities in the solutions and also that it was possible to perform a series of measurements by a titration procedure. The temperature of the

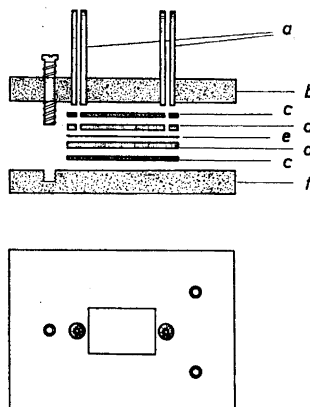


Fig. 1. Diagram of the flow cell. a=capillary glass tubes, extending about 0.1 mm from the bottom surface of b (exaggerated here); b=perspex upper plate; c=hard rubber gasket; d=IRTRAN-windows; e=platinum spacer; f=standard lower plate of stainless steel.

The tubes "a" are joined to tygon-tubes of the same inner diameter as "a" through a glass tube, one end of which was ground to have a smaller outer diameter to fit the tygon tube.

thermostat bath was 30°C. The cell-thicknesses were determined interferometrically and were found to be 28.4  $\mu$  and 28.6  $\mu$ , respectively, for the reference and sample cells.

**Chemicals used.** A vanadyl(IV) chloride solution was prepared from vanadyl(IV) sulphate (Merck *p.a.*) following the procedure described by Rossotti<sup>7</sup> with the only exception that hydrochloric acid was used instead of perchloric acid. To remove any vanadium(V) species possibly present, the solution was treated with sulphur dioxide, and then the excess of this agent was expelled by passing carbon dioxide through. The sulphate ions formed in this process were removed by passing the solution through a column of Dowex 1-X4 anionic exchange resin in the chloride form. No sulphate ions could be detected in the final solution. The concentration of vanadium(IV) was determined by a potentiometric titration<sup>13</sup> with a standard Ce(IV) solution. The excess of hydrochloric acid was determined by passing the solution through a column of Dowex 50W-X8 in its acid form, titrating the eluate with standard sodium hydroxide (to the methylred endpoint) and correcting for the vanadyl concentration,  $C_M$ . This excess of hydrochloric acid was found to be 0.257  $C_M$ .

A stock solution of sodium thiocyanate was prepared from A. R. NaSCN (Malincrodt) and standardized by Volhard titration. The sodium chloride (Merck *p.a.*) used as the inert electrolyte was dried at least 2 h at 160°C and a stock solution (3 M) was prepared.

From these stock solutions the actual solutions of measurement were prepared, so that in all cases the ionic strength was 3 M. The excess of hydrochloric acid was sufficiently large to prevent the hydrolysis of the vanadyl ion.<sup>7</sup> The spectrum of each solution was recorded three times to minimize random errors in intensity and position of absorption maximum. As each combination  $C_M, C_L$  was produced twice by totally independent mixing (starting from the stock solutions) the spectra used for calculations were the mean of six determinations.

## RESULTS AND CALCULATIONS

The results of spectral measurements for solutions of composition  $C_M$  M  $\text{VOCl}_2$ ,  $C_L$  M NaSCN,  $C_H$  M HCl, and  $C_{\text{NaCl}} = 3 - 3C_M - C_L - C_H$  M NaCl are given in Table 1.

**Determination of  $\bar{n}$  and the stability constants.** In Fig. 2 a graphical representation of the frequency shifts  $\Delta\nu$  is given for the three values of  $C_M$  that were used. The curves were cut at a number of suitably chosen values of  $\Delta\nu$ , and the resulting values of  $C_L$  were plotted against  $C_M$ . Within the experimental accuracy these functions were found to be linear. From our above-mentioned

Table 1.  $C_M = 203.2$  mM.

$C_L$ mM	$\nu_{\max}$ $\text{cm}^{-1}$	$\epsilon_{\max}$ $\text{M}^{-1}\text{cm}^{-1}$	$\Delta\nu_{1/2}$ left $\text{cm}^{-1}$	$\Delta\nu_{1/2}$ right $\text{cm}^{-1}$
0	997.0	285.4	11.8	12.7
109	993.0	254.0	13.0	14.0
200	991.3	251.7	14.0	15.0
311	987.5	248.8	19.2	14.6
400	986.1	247.9	14.8	14.3
494	983.5	245.4	15.3	14.0
600	982.1	247.5	15.0	14.0
720	980.6	249.8	14.8	13.2
800	979.0	253.2	15.3	13.4
1000	978.0	256.7	14.3	13.2
1200	976.5	260.8	13.6	12.6
1440	975.4	269.4	14.0	12.8
1600	974.4	272.5	13.7	11.6
1815	973.2	277.8	14.5	11.1

 $C_M = 304.8$  mM

$C_L$ mM	$\nu_{\max}$ $\text{cm}^{-1}$	$\epsilon_{\max}$ $\text{M}^{-1}\text{cm}^{-1}$	$\Delta\nu_{1/2}$ left $\text{cm}^{-1}$	$\Delta\nu_{1/2}$ right $\text{cm}^{-1}$
0	997.0	281.1	11.3	12.9
109	993.8	243.5	13.2	13.3
200	992.1	239.9	13.9	14.1
311	989.5	236.8	14.5	14.6
400	988.3	237.5	15.3	14.1
494	986.5	238.9	14.8	14.2
600	984.1	240.3	15.1	13.0
720	982.6	242.6	14.9	14.3
800	981.2	245.1	15.2	14.1
865	980.6	249.1	14.9	14.0
1050	979.0	258.3	14.8	14.0
1260	977.5	264.0	14.8	13.2
1400	979.0	270.2	14.2	13.3
1575	976	272.1	14.2	12.4

 $C_M = 406.4$  mM

$C_L$ mM	$\nu_{\max}$ $\text{cm}^{-1}$	$\epsilon_{\max}$ $\text{M}^{-1}\text{cm}^{-1}$	$\Delta\nu_{1/2}$ left $\text{cm}^{-1}$	$\Delta\nu_{1/2}$ right $\text{cm}^{-1}$
0	997.0	283.9	11.6	12.5
109	994.5	259.7	12.8	13.3
200	993.1	247.2	14.0	13.5
311	991.7	244.7	14.3	14.0
400	989.7	243.4	14.9	14.1
494	988.4	242.8	15.3	13.7
600	986.7	240.4	15.3	14.2
720	985.1	241.6	15.4	14.6
800	984.2	245.3	15.2	14.3
900	982.5	250.5	15.4	14.7
1080	981.2	255.6	15.1	14.1
1200	980.1	260.3	14.9	13.9
1350	979.1	263.2	15	12.9
1473	978.0	270.6	14.9	13.1

Table 2. Values of  $\bar{n}$ , [L] calculated by graphical method.

$\Delta\nu$ $\text{cm}^{-1}$	$C_L$ mM			[L] mM	$\bar{n}$
	$C_M=203.2$ mM	$C_M=304.8$ mM	$C_M=406.4$ mM		
1	25	36	49	2.0	0.114
2	54	75	100	7.3	0.228
3	85	116	154	15.3	0.340
4	117	168	207	21.0	0.455
5	150	202	263	29.0	0.580
6	184	246	320	38.0	0.699
7	219	293	380	50	0.822
8	259	340	443	56	0.969
9	291	390	507	62	1.112
10	330	444	575	77	1.240
11	370	498	645	88	1.357
12	412	556	722	100	1.519
13	459	619	797	114	1.680
14	510	685	881	136	1.823
15	574	761	975	170	1.963
16	648	849	1079	207	2.136
17	737	950	1200	262	2.297
18	840	1065	1333	341	2.428
19	955	1205	1485	421	2.605
20	1082	1370	1682	485	2.928

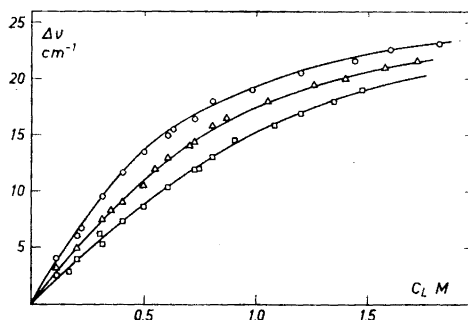


Fig. 2.  $\Delta\nu$  as a function of  $C_L$  for  $C_M=0.200$  (O),  $C_M=0.300$  M ( $\Delta$ ), and  $C_M=0.400$  M ( $\square$ ).

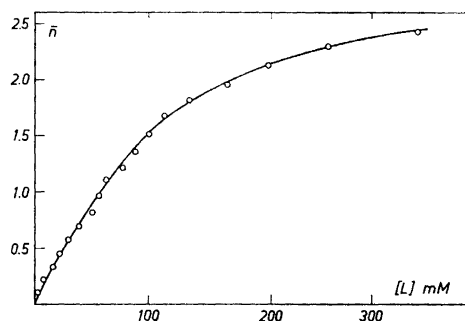


Fig. 3. The experimental values of  $\bar{n}$  (Table 2) plotted against [L].

assumptions it then follows that the slope is equal to  $\bar{n}$  and the intercept is equal to the free ligand concentration. The related values of  $\bar{n}$  and [L] thus found are given in Table 2. Fig. 3 gives a graphical presentation of  $\bar{n}$  as a function of [L]. The full-drawn curve has been used in the following calculations. As it holds<sup>8</sup> that

$$\ln X_{[L]_i} = \int_0^{[L]_i} (\bar{n}/[L])d[L] \quad (2)$$

the quantity  $\log X$  could be obtained from a graphical integration of  $\bar{n}/[L]$  plotted against  $[L]$ .

Then from the corresponding values of  $X$  and  $[L]$ , the stability constants were obtained graphically<sup>8</sup> by plotting the functions  $X_n = (X_{n-1} - \beta_{n-1})/[L]$  against  $[L]$ . The results are  $\beta_1 = 24 \pm 2 \text{ M}^{-1}$ ;  $\beta_2 = 175 \pm 20 \text{ M}^{-2}$ ;  $\beta_3 = 1200 \pm 300 \text{ M}^{-3}$ .

*Resolution of the absorption bands of the complexes  $\text{VO}(\text{NCS})_n^{(2-n)+}$ .* Now when the stability constants are known it is possible to resolve the experimentally observed absorption bands into the components that correspond to the successively formed  $\text{VO}(\text{NCS})_n^{(2-n)+}$  complexes. For each couple of  $(C_M, C_L)$ -values the corresponding  $[L]$  was calculated from the stability constants using an Olivetti 101 electronic computer. Furthermore, for a number of frequencies the quantity  $\varepsilon = (1/C_M d) \log(T_0/T)$  was calculated (where  $T_0$  is percent transmission of the base line). Now it holds for each wave number that

$$\varepsilon = \sum_{n=0}^N \alpha_n \varepsilon_n \quad (3)$$

By forming the function

$$\varepsilon' = \frac{\varepsilon - \varepsilon_0 \alpha_0}{\alpha_1} = \varepsilon_1 + \frac{\beta_2}{\beta_1} \varepsilon_2 [L] + \frac{\beta_3}{\beta_1} \varepsilon_3 [L]^2 \quad (4)$$

and plotting this function against  $[L]$ ,  $\varepsilon_1$  could be obtained as the limiting value when  $[L] \rightarrow 0$ . A typical example of this procedure is given in Fig. 4. Then the function  $\varepsilon''$  was formed

$$\varepsilon'' = \frac{\varepsilon' - \varepsilon_1}{[L]} = \frac{\beta_2}{\beta_1} \varepsilon_2 + \frac{\beta_3}{\beta_1} \varepsilon_3 [L] \quad (5)$$

When plotting  $\varepsilon''$  against  $[L]$ ,  $\varepsilon_2$  and  $\varepsilon_3$  could be calculated from the intercept and slope, respectively, of the resulting straight line.

Hence the absorption bands corresponding to the thiocyanato complexes could be constructed as represented in Fig. 5. From these graphs the integrated absorption intensities were calculated and were found to be

$$\begin{aligned} A_1 &= 2.23 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}; & A_2 &= 2.98 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2} \\ A_3 &= 2.45 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2} \end{aligned}$$

These values can be compared with the corresponding value for the free vanadyl ion  $A_0 = 2.62 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$ , which of course could be determined separately.

*Determination of  $d\mu/dr$  for the  $\text{VO}^{2+}$  ion.* If, as we have proposed above, one can consider the vibrating unit causing the observed absorption band as the two-atomic entity  $\text{V}=\text{O}$ , one can easily calculate the quantity  $d\mu/dr$  from the formula (cf., e.g., Ref. 14)

$$A = \frac{N \pi}{3c^2 \times 10^3 \mu_{\text{red}}} \left( \frac{d\mu}{dr} \right)_{r=r_e}^2 \quad (6)$$

Here  $N$  and  $c$  stand for the Avogadro number and the velocity of light,  $\mu_{\text{red}}$  is the reduced mass,  $r$  is the interatomic distance and  $r_e$  signifies the equilibrium value of that distance. Introducing the relevant atomic masses and  $A = 2.62 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$  one obtains

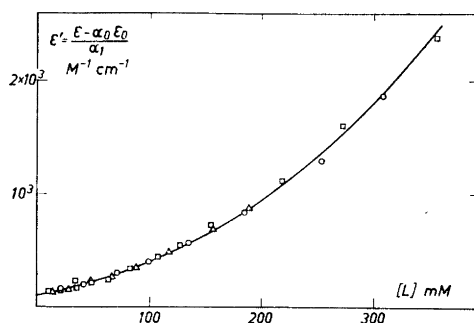


Fig. 4. A representative example of the function  $\varepsilon'$  versus  $[L]$ . The wave number in this case was  $975 \text{ cm}^{-1}$ .  $C_M$  values are represented as in Fig. 2.

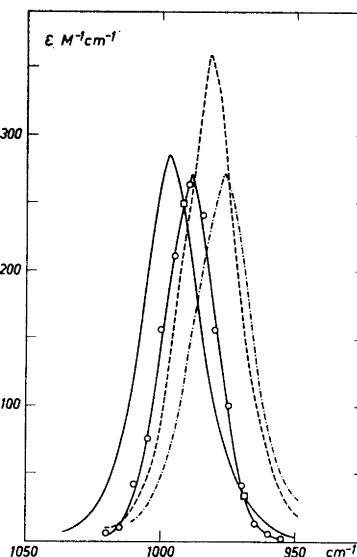


Fig. 5. The resulting absorption curves of the complexes  $\text{VO}^{2+}$  (—),  $\text{VOL}^+$  (—○—○—),  $\text{VOL}_2$  (---) and  $\text{VOL}_3^-$  (-.-.-.-). The symbol  $\square$  represents the two isosbestic points of the  $\text{VO}^{2+}$ — $\text{VOL}^+$  system (cf. the text). The values of  $\varepsilon$  of the  $\text{VOL}^+$  complex that was obtained from eqn. (4) are depicted by  $\circ$ .

$$d\mu/dr = \pm 8.7 \times 10^{-10} \text{ e.s.u.} \quad (7)$$

Here the positive sign must hold as the dipole moment of the  $\text{V}=\text{O}$  bond by necessity increases, when the bond length increases. If one chooses to express the value of  $d\mu/dr$  by using the electronic charge,  $4.8 \times 10^{-10} \text{ e.s.u.}$ , as the unit one obtains

$$d\mu/dr = 1.8 \text{ a.u.} \quad (7a)$$

The meaning of this relation will be discussed below.

Even if one considers the  $\text{V}(\text{OH}_2)_5$  unit as completely rigid and thus introduces the combined atomic masses of this unit in the expression for  $\mu_{\text{red}}$  the value of  $d\mu/dr$  is changed by less than 10% ( $d\mu/dr = 9.4 \times 10^{-10} \text{ e.s.u.}$ ).

Before using the relation (6) one should in principle correct the liquid phase value of  $A$  to one corresponding to gas phase conditions. It was found in the previous work,<sup>6</sup> however, from a comparison of the intensities in gas phase and aqueous solution of  $\text{SO}_2$  that such a correction, in this frequency range, was of the order of experimental accuracy. Because of this and because of the lack of reliable theoretical correction formulae we have accepted the observed value of  $A$  as the basis of calculation.

## DISCUSSION

*The thiocyanate complex system.* Quantitative studies on the complexes formed between the  $\text{VO}^{2+}$  and  $\text{SCN}^-$  ions have been performed earlier by Furman and Garner<sup>15</sup> and by Golub and Kostrova.<sup>16</sup> The former authors report  $\beta_1 = 8.3 \pm 0.6 \text{ M}^{-1}$  at an ionic strength = 2.6 M and 25°C, whereas the latter ones give  $\beta_1 = 18 \text{ M}^{-1}$  (spectrophotometry, varying ionic medium) and  $\beta_1 = 53 \text{ M}^{-1}$  (potentiometry, varying medium). These latter values are really not useful in a comparison with the value of  $\beta_1 = 24 \text{ M}^{-1}$  that we report, as the ionic strength has not been kept constant. They are of the same order of magnitude as ours, though. On the other hand, it is rather surprising that the value of  $\beta_1$  reported by Furman and Garner<sup>15</sup> is three times lower than ours for almost exactly the same value of the ionic strength. However, several factors may possibly account for this: the different temperature, the method of calculation used by Furman and Garner,<sup>15</sup> usually giving too low values<sup>17,18</sup> of the first stability constant, if more than one complex can be formed in the system. Furthermore, the difference in the composition of the media is considerable ( $\text{NaClO}_4 + \text{HClO}_4$  was used by Furman and Garner and  $\text{NaCl}$  in this work. Actually, because of the chloride complexity, one should expect a smaller value of  $\beta_1$  in the chloride than in the perchlorate medium. Activity coefficients of the ionic species can however differ considerably, even if the formal ionic strength is almost the same in both cases.

A recent investigation by Schlund and Wendt<sup>19</sup> yields a set of values of  $K_1$  and  $K_2$  at various temperatures and valid at low ionic strengths. Although not directly comparable with our results, only the values of  $K_1$  seem to be reliable (*e.g.*,  $\beta_1 = K_1 = 210 \text{ M}^{-1}$  at  $I = 0$  and 25°C).

The fact that the stability constants seem to agree as well as can be expected with the results of other available determinations, shows that the frequency decrease is really caused by the formation of distinct chemical species and not by any nonspecific medium effect. As before<sup>6</sup> we can use this as a criterion that also the intensity changes that are observed can be ascribed to the same chemical causes.

The stability constants reported here correspond to the following formation constants  $K_1 = 24 \text{ M}^{-1}$ ,  $K_2 = 7 \text{ M}^{-1}$ , and  $K_3 = 7 \text{ M}^{-1}$ . The ratio  $K_1/K_2 = 3.3$  is of the order usually found for monodentate ligands, but the ratio  $K_2/K_3$  is surprisingly small. This can either imply that the third complex is unusually strong or that the difficulty of reading correct  $\bar{n}$ -values at high  $C_L$  in Fig. 2 results in an overestimation of the third stability constant and that a fourth complex also exists to some extent in the solutions investigated.

We thus believe that the two first constants are given with good accuracy, whereas we do not feel completely sure about the third one. This, of course, will be reflected also by the values reported for  $A_n$ , the  $\nu_{\text{VO}}$  absorption intensity of the  $n$ :th complex. Thus the value of  $A_3$  must be regarded with some caution, whereas the values of  $A_1$  and  $A_2$  are probably much more trustworthy.

In order to get a more quantitative estimation of the influence of an error in  $\beta_1$  on the value of  $A_1$ , let us consider the simplified case when only the first complex is formed, *i.e.* for small values of  $[\text{L}]$  and consequently close to the condition for which  $\varepsilon_1$  is determined. In such a case eqn. (4) approximates to



$$\varepsilon_1 = \frac{\varepsilon - \varepsilon_0 \alpha_0}{\alpha_1} \approx \frac{\varepsilon - \varepsilon_0 + \beta_1 C_M (\varepsilon - \varepsilon_0) + \varepsilon \beta_1 C_L}{\beta_1 C_L} \quad (8)$$

It is then obvious that for those frequencies, where  $\varepsilon = \varepsilon_0$ , it should hold that  $\varepsilon_1 = \varepsilon_0$  independent of the value of  $\beta_1$ . This means that at the isosbestic points we will automatically obtain the correct value of  $\varepsilon_1$ . Furthermore, from eqn. (8) it follows that the error of  $\varepsilon_1$  will be largest, when  $|\varepsilon - \varepsilon_0|$  is large, *i.e.* on both sides of the isosbestic point (points). However, it can be seen from Fig. 5 that all points over the entire frequency range 1020—950  $\text{cm}^{-1}$  fall on a smooth curve, which has all the characteristics of a wellshaped absorption curve.

In order to make a further test to find out if the variation of  $A_n$  in the sequence  $A_0 > A_1 < A_2$  is more than can be ascribed to the combined influence of errors in stability constants and errors of the intensities of the composite bands, we have plotted  $\varepsilon_{\text{max}}$  of the latter bands (Table 1) against  $[L]$  (Fig. 6).

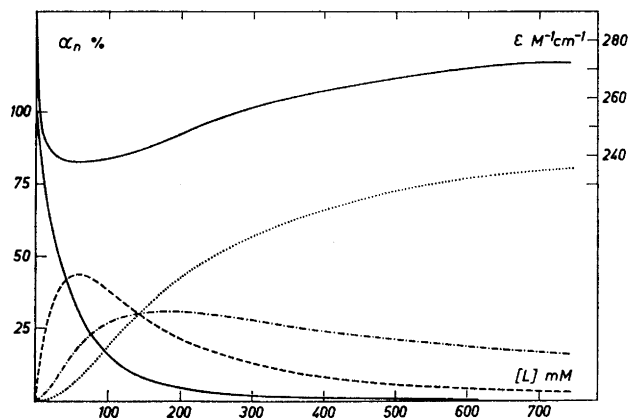


Fig. 6.  $\varepsilon_{\text{max}}$  of each of the absorption bands originally recorded plotted against the value of  $[L]$  that relates to the  $C_M$ ,  $C_L$ -values and the stability constants. Upper, fulldrawn curve.

In this figure are also included curves representing  $\alpha_n$  ( $n=0-3$ ). It is interesting to note that the minimum of the  $\varepsilon_{\text{max}}$ -curve appears at the position of the maximum of  $\alpha_1$ .

As has been pointed out, the value of  $\beta_3$ , and consequently  $\alpha_3$ , is somewhat uncertain, so no perfect relationship can be expected between  $\varepsilon_{\text{max}}$  and the higher  $\alpha_n$ -curves.

*The bond dipole moment derivative.* The simplest way to consider the variation of the dipole moment of a two-atomic molecule with the interatomic distance ( $r$ ) is to apply the fixed charge model. Here one assumes that the charge distribution is not dependent on  $r$ , so if the charge on the atoms are  $+\delta$  and  $-\delta$  (atomic units), the dipole moment is

$$\mu = r \times \delta \quad (9)$$

and

$$d\mu/dr = \delta \quad (10)$$

This approach is most unsatisfactory as has been pointed out, *e.g.* by Barrow (Ref. 14, p. 79), and this situation is clearly illustrated by our findings. A fixed charge model would place almost all electrons possible on the oxygen atom in the VO group, thus approaching the formula  $V^{4+}-O^{2-}$ . This follows from eqn. (7a). Such a formulation is in contradiction not only to chemical common sense but also to the quantitative results of Ballhausen and Gray<sup>2</sup> and Vanquickenborne and McGlynn.<sup>3</sup> The first-mentioned authors obtain a value of the charge on the oxygen atom of about 0.6 a.u. (atomic units), the latter ones an even lower value of about 0.2 a.u. (*cf.* Table 1 of Ref. 3). A more realistic view is, of course, to introduce the variation of charge on the oxygen atom with the interatomic distance. If this charge is still denoted by  $\delta$  eqn. (9) is unchanged but one now has the relation.

$$\frac{d\mu}{dr} = \delta + r \frac{d\delta}{dr} \quad (11)$$

If one introduces into this equation, *e.g.*, the mean value of the alternative estimations<sup>2,3</sup> of  $\delta$ , *i.e.* 0.4 a.u., and the V=O distance in  $VO(H_2O)_5SO_4$  for  $r$ , *i.e.* 1.67 Å,<sup>20</sup> it is possible to estimate  $d\delta/dr$  from the relation

$$\begin{aligned} 1.8 &= 0.4 + r d\delta/dr \\ d\delta/dr &= 0.8 \text{ a.u./\AA} \end{aligned} \quad (12)$$

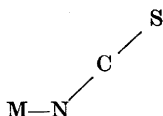
or, expressing also  $r$  in atomic units

$$d\delta/dr = 0.4 \text{ a.u.} \quad (13)$$

This calculation illustrates the drastic redistribution of charge that appears when stretching of the V=O bond diminishes the possibilities of orbital overlap. For very large interatomic distances it is reasonable that the "bond" will approach the  $V^{4+}-O^{2-}$  formulation, giving a limiting value of  $d\mu/dr$  as 2 a.u. From this relation it is then possible to present a rough sketch of the  $\mu$  versus  $r$  diagram (Fig. 7). Of course, the placing of the inflexion point (if any) is rather arbitrary. From the form of the curve chosen here, it follows that the purely ionic bonding  $V^{4+}-O^{2-}$  should appear at about 5–6 Å interatomic distance, *i.e.* when the overlap of orbitals must be quite negligible.

Now, turning to the question of the influence on the  $\nu_{VO}$  intensity following upon ligand substitution in the remaining five coordination sites, the fact that both  $\delta$  and  $d\delta/dr$  can be affected makes any interpretations quite difficult. If, as we believe, the  $A_1/A_0=0.85$  and  $A_2/A_0=1.15$  ratios are significant, the only thing one can say is that the two parameters  $\delta$  and  $d\delta/dr$  are affected differently in the complexes  $VO(NCS)^+$  and  $VO(NCS)_2$ . Possibly this effect is related to the possibility of the ligands being in axial or equatorial positions. Even if only equatorial positions are considered, it must be remembered that Vanquickenborne and McGlynn<sup>3</sup> point out that the angle  $\alpha$  between the V=O bond and the equatorial plane affects the energy levels of the complex quite considerably. Although this effect is most pronounced for the antibonding

orbitals, some small changes also occur for the bonding ones. It thus could happen that one thiocyanate ion forming a somewhat angular bond



would tilt the  $V=O$  bond, whereas a second ligand in *trans*-position to the first one would cancel out this effect, thus giving rise to increase of intensity. Such an increase is really what one expects from the observed decrease in  $\nu_{\max}$  of the absorption bands. From Badgers rule<sup>21</sup> this should imply an increase of the interatomic distance and thus, from Fig. 7, an increase of  $d\mu/dr$ .

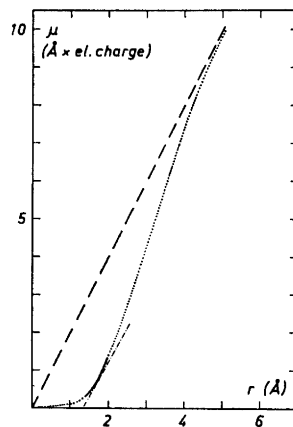


Fig. 7. An estimation of the form of the  $\mu$  versus  $r$  function from the value of  $d\mu/dr$  at the equilibrium value of  $r$ . The straight line (---) depicts the situation for a  $V^{4+}-O^{2-}$  bond.

This work is part of a project financially supported by *Statens Naturvetenskapliga Forskningsråd* (The Swedish Natural Science Research Council).

#### REFERENCES

- Selbin, J. *Coord. Chem. Rev.* **1** (1966) 293.
- Ballhausen, C. J. and Gray, H. B. *Inorg. Chem.* **1** (1962) 111.
- Vanquickenborne, L. G. and McGlynn, S. P. *Theoret. Chim. Acta* **9** (1968) 390.
- Evans, J. C. *Inorg. Chem.* **2** (1963) 372.
- Selbin, J., Holmes, L. H. and McGlynn, S. P. *J. Inorg. Nucl. Chem.* **25** (1963) 1359.
- Larsson, R. *Acta Chem. Scand.* **22** (1968) 983.
- Rossotti, F. J. C. and Rossotti, H. S. *Acta Chem. Scand.* **9** (1955) 1177.
- Fronæus, S. In Jonassen, H. B. and Weissberger, A. *Techniques of Inorg. Chem.* Interscience, New York, London 1963, Vol. 1, Chapt. 1.
- Ahrland, S. and Norén, B. *Acta Chem. Scand.* **12** (1958) 1595.
- Instruction Manual PE 521, Perkin Elmer Corp. 1963.
- Ramsay, D. A. *J. Am. Chem. Soc.* **74** (1952) 72.
- Zugaza, A. and Hidalgo, A. *Mem. Real Acad. Ciencias Madrid* **4** (1996) 1.

13. Furman, N. H. *J. Am. Chem. Soc.* **50** (1928) 1675.
14. Barrow, G. *Introduction to Molecular Spectroscopy*, McGraw, New York 1962.
15. Furman, S. C. and Garner, C. S. *J. Am. Chem. Soc.* **73** (1951) 4528.
16. Golub, A. M. and Kostrova, R. A. *Ukrain. Khim. Zh.* **29** (1963) 128.
17. Olerup, H. *Järnkloridernas komplexitet*, (Diss.), Lund 1944.
18. Kruh, R. *J. Am. Chem. Soc.* **76** (1954) 4865.
19. Schlund, A. and Wendt, H. *Ber. Bunsenges.* **72** (1968) 652.
20. Lundgren, G. *Rec. Trav. Chim.* **75** (1956) 585.
21. Badger, R. M. *J. Chem. Phys.* **2** (1934) 128.

Received May 27, 1969.