501. *The Magnetic Properties of Vanadium*(III) *Complexes.*

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The magnetic susceptibilities of four vanadium(III) complexes in which there are six equivalent ligand atoms surrounding the central vanadium ion have been measured over the temperature range 80—300° K. The complexes were ammonium vanadium alum, trisacetylacetonatovanadium(III), potassium trisoxalatovanadium(III) trihydrate, and potassium trismalonatovanadium(III). Their susceptibilities obey a Curie law quite closely. The values of the Curie constants and, for the alum, the magnetic data available at lower temperatures from other authors are discussed with reference to the theory of the V^{3+} ion in a ligand field of cubic symmetry but with a small component of axial symmetry superimposed.

THE V^{3+} ion in co-ordination complexes is well known to exhibit a magnetic moment of about 2·7 B.M., *i.e.*, slightly below the spin-only moment of 2·83 B.M. for two unpaired electrons. In particular, the magnetic properties of ammonium vanadium alum have been studied previously.[1] It has been pointed out [2] that a magnetic moment of 2·7 B.M. at room temperature is to be expected for the V^{3+} ion in a ligand field of cubic symmetry, when the relation between the spin–orbit coupling constant and thermal energy is taken into account. However, the moment of the V^{3+} ion in a cubic ligand field would be expected to fall as the temperature is lowered, whereas, for the alum at least, the moment observed at room temperature is constant down to quite low temperatures. The distribution of the six ligand water molecules surrounding the tervalent metal ion in an alum departs from that of a regular octahedron,[3] corresponding to an extension or compression of the octahedron along a trigonal axis. The magnetic behaviour of this alum has been fairly satisfactorily accounted for in terms of a ligand field of trigonal symmetry, superimposed on the main cubic field and arising from the distortion of the octahedron.[4]

We now report careful measurements of the magnetic suceptibility of ammonium vanadium alum and several other tervalent vanadium complexes in which the vanadium ion is surrounded by six equivalent ligand atoms. We compare the results with the theory developed for the magnetic behaviour of V^{3+} in ligand fields of symmetry lower than cubic.

van der Handel and Siegert [1] measured the magnetic susceptibility of ammonium vanadium alum over the range 1—300° K: at very low temperatures the susceptibility was independent of temperature, whereas at fairly high temperatures it obeyed a Curie law. The majority of their measurements were made at temperatures below 20° K, the range above this being represented by only four determinations. Information on the accuracy of the measurements and the purity of the sample employed was not given. Fritz and Pinch [1] measured the susceptibility of this alum from 1° to 10° K and found substantial agreement with the results of van der Handel and Siegert. In this instance it was known that only slight oxidation of the alum took place during the measurements, and accuracy of the measurement of the susceptibility appears to be good. Chakravarty [1] reported the susceptibility of the alum at four temperatures (identical with those of van der Handel and Siegert) between 70° and 300° K; agreement with the results of those authors was very good.

The experimental data on ammonium vanadium alum yield, essentially, four pieces of information: (i) the temperature, δ, below which the susceptibility becomes constant, (ii) the value of this constant susceptibility, (iii) the Curie constant, C, in the higher temperature range, and (iv) the value of a term in the susceptibility, independent of temperature,

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[1] van der Handel and Siegert, *Physica*, 1937, **4**, 871; Fritz and Pinch, *J. Amer. Chem. Soc.*, 1956, **78**, 6223; Chakravarty, *Indian J. Phys.*, 1958, **32**, 447.

[2] Figgis, *Nature*, 1958, **182**, 1568.

[3] Bevers and Lipson, *Proc. Roy. Soc.*, 1934, *A*, **148**, 664; Lipson, *ibid.*, 1935, *A*, **151**, 347.

[4] Siegert, *Physica*, 1937, **4**, 138.

at higher temperatures. The values of these items from the data of van der Handel and Siegert are listed in Table 1.

TABLE 1. *Magnetic properties of ammonium vanadium alum.*

Quantity *	Exptl., other authors	Calc., Siegert	Exptl., this work
δ/k	6·9°	6·9°	—
C	0·85	0·85	0·95 ± 0·02
High-temp. T.I.P. (c.g.s.u. × 10^6) (χ_{CHT})	250	450	≯150
Low-temp. T.I.P. (c.g.s.u.) (χ_{CLT})	0·24	0·17	—

* T.I.P. = Temperature-independent paramagnetism.

Siegert[4] interpreted his results with van der Handel in terms of the splittings of the ground levels of the V^{3+} ion, as given in Fig. 1. The details of this theory have recently been discussed by Chakravarty.[5] Siegert chose to fit δ and C of the experimental data by means of the two parameters involved in his theory, namely Δ, the separation between the orbital singlet and the orbital doublet, and λ', the " effective " value of the spin–orbit coupling constant. He assumed that the cubic ligand field was strong, *i.e.*, that there was complete mixing of ^3P and ^3F of the free ion under the influence of the field. Agreement with the experimental data for the remaining two items, the values of the temperature-independent susceptibilities, was not good (see Table 1). Siegert required $\Delta = 670$ cm.$^{-1}$. The data of Fritz and Pinch and of Chakravarty do nothing to change this interpretation.

FIG. 1. *Splittings of the energy levels of the* V^{3+} *ion. The numbers under a line indicate the degeneracy of the energy level concerned (spin* × *orbital).*

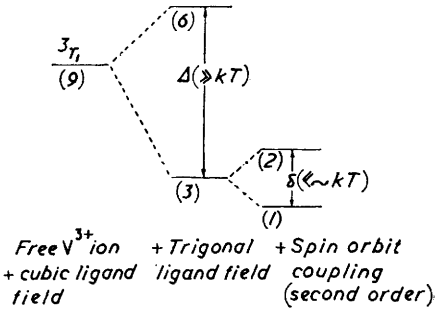
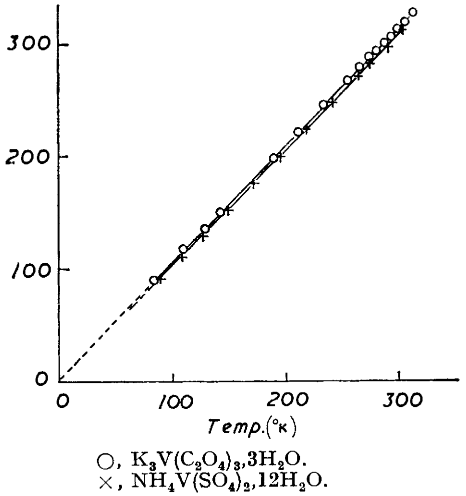


FIG. 2. *Inverse of molar susceptibility* versus *temperature for ammonium vanadium alum and potassium trisoxalatovanadate*(III) *trihydrate.*



Results.—Our measurements on ammonium vanadium alum are summarised in Table 1 and in Figs. 3 and 4. In Table 2 the results of our measurements on the other tervalent vanadium

TABLE 2. *Magnetic properties of the octahedral vanadium*(III) *complexes studied in this work.*

Compound	$\mu_{\text{eff.}}$ (300° K)	Curie constant	θ	High-temp. T.I.P.* (× 10^{-6})
$NH_4V(SO_4)_2,12H_2O$	2·80	0·95	0°	50
V (acetylacetonate)$_3$	2·80	0·97	2	50
$K_3V(C_2O_4)_3,3H_2O$	2·80	0·96	1	50
$K_3V[CH_2(CO_2)_2]_3$	2·78	0·99	14	100

* Estimates only; maximum possible values are ~150.

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[5] Chakravarty, *Proc. Phys. Soc.*, 1959, **74**, 711.

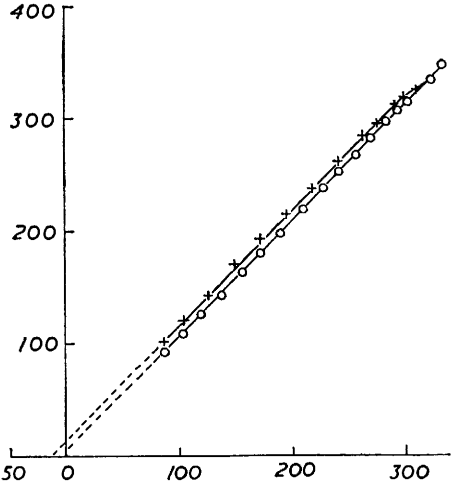
complexes studied are listed; they are also set out in Figs. 2 and 3, which give plots $1/\chi_V$ *versus* temperature. In the particular case of the alum, Fig. 4 is a plot of $\frac{1}{8}\mu_{\text{eff.}}^2$ against $T^{\frac{1}{2}}$; this is done to facilitate the comparison of data from all observers over the entire range of temperature. The solid line of Fig. 4 is a plot of the expression:

$$\tfrac{1}{8}\mu_{\text{eff.}}^2 = 0{\cdot}935\ (\delta/2kT)\frac{\{1-(1-\delta/2kT)\exp(-\delta/kT)\}}{1+2\exp(-\delta/kT)} + 10^{-4}T \quad . \quad . \quad (1)$$

0·935 is the best fit for the Curie constant to accord with our results and the theory; δ is taken as 6·9°.

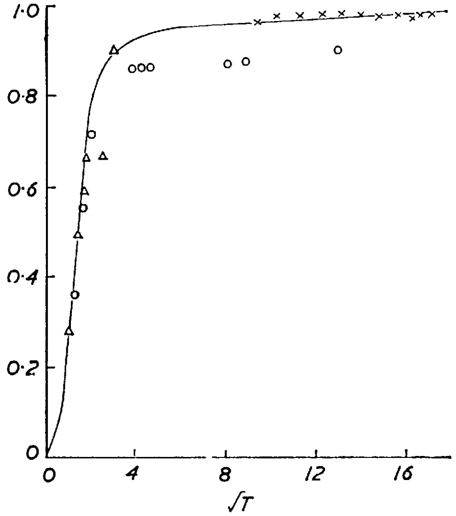
For $kT \gg \delta$ this expression reduces to: $\frac{1}{8}\mu_{\text{eff.}}^2 = 0{\cdot}935 + 10^{-4}T$. The molar susceptibility for the V^{3+} ion in ammonium vanadium alum in dilute sulphuric acid solution was found to be 3360×10^{-6} c.g.s.u., independent of the concentration of the solution, for 0·1M- and 1·0M-vanadium. This value of the susceptibility corresponds to a Curie constant of 0·955.

FIG. 3. *Inverse of molar susceptibility* versus *temperature for potassium trismalonatovanadium*(III) *and trisacetylacetonatovanadium*(III).



×, $K_3V(C_3H_2O_4)_3$. ○, $V(C_5H_7O_2)_3$.

FIG. 4. $\frac{1}{8}\mu_{\text{eff.}}^2$ versus $\sqrt{T}$ *for ammonium vanadium alum, experimental for various authors and calculated according to* (1).



Exptl.: ×, *This work*; ○, *van der Handel and Siegert*; △, *Fritz and Pinch.* —, *Calc. from* (1).

DISCUSSION

Ammonium Vanadium Alum.—Our measurements of the magnetic susceptibility of this alum over the temperature range 80—300° *K*, as set out in Table 1 and Fig. 2, confirm the main features of the earlier measurements but differ in important details. We have found that the susceptibility is some 7% higher than that given by van der Handel and Siegert or Chakravarty.[1] Since we measured the absolute susceptibilities with an accuracy of ±2% and analysed the compound before and after the measurement, we are confident that the earlier measurements were not sufficiently precise or that some of the V^{3+} ion had been oxidised. As discussed below, the interpretation of the magnetic properties of the V^{3+} ion in a cubic ligand field depends critically on the departure of the moment from the spin-only value for two unpaired electrons, *viz.*, 2·83 B.M., and, therewith, of the Curie constant from 1·00. Consequently, we find that, although the interpretation of the susceptibility of ammonium vanadium alum given by Siegert and based on his results with van der Handel serves to account for our measurements, the choice of the parameters which occur in the interpretation is different.

Siegert's theory yields the following expressions:

$$
\begin{aligned}
C &= 1 - 4D^2\lambda/3\Delta \\
\delta &= (D^2\lambda^2/\Delta)(1 - 2D\lambda/\Delta) \\
\chi_{\text{CLT}} &= (16N\beta^2/3\delta)(1 - 2D^2\lambda/\Delta) \\
\chi_{\text{CHT}} &= 4N\beta^2D^2/3
\end{aligned}
$$

Here it has been assumed that $\lambda \ll \Delta$, so that λ^2/Δ^2 may be neglected relative to 1; the justification for this is discussed by Siegert. D is the equivalent of the quantity $|B|\lambda$ in Siegert's nomenclature, and is a measure of the degree to which the cubic ligand field mixes the ^3P term of the free ion into the $^3T_1$ term of the ^3F ground term. With no mixing (weak field), $D = 3/2$; with complete mixing (strong field), $D = 1$.

Rather than employ λ as a parameter, as done by Siegert, we have chosen to retain it as a known quantity at the free-ion value of 105 cm.$^{-1}$ and to introduce, instead, the parameter k which allows for the loss of orbital angular momentum associated with the T_1 term when delocalisation of the t_{2g} electrons in π-bonding occurs.[6] * The introduction of k is accomplished by employing $k\mathbf{L}$ for the orbital angular momentum operator wherever it appears; the spin–orbit coupling operator then becomes $\lambda k\mathbf{L}\cdot\mathbf{S}$ and the magnetic moment operator $(k\mathbf{L} + 2\mathbf{S})\beta$. Then it is found that $D = k|\mathrm{B}|/\lambda$. Also, instead of dealing with the case of a strong ligand field, we have evaluated the mixing coefficient of ^3P into the $^3T_1(^3F)$ ground term under the assumption that the cubic ligand field is the same as that found in aqueous solutions containing the V^{3+} ion, *viz.*, $10Dq = 19{,}000$ cm.$^{-1}$.[9] The centre-of-gravity separation ^3P–^3F *in the complex* was taken as 9300 cm.$^{-1}$.[7,8] This gives:

$$\psi(^3T_1) = [\psi(T_1)^3F - 0{\cdot}35\ \psi(T_1)^3P]/1{\cdot}06$$

and $D = 1{\cdot}2k$.

As set out in Table 3, our experimental results on ammonium vanadium alum in the range 80—300° K, as well as those obtained by other workers at lower temperatures, can be quite satisfactorily accounted for on the re-interpreted theory of Siegert. The main points are that, provided t_{2g} electron delocalisation is allowed for, the free-ion value of the spin–orbit coupling may be employed, and that a considerably larger axial field splitting

TABLE 3. *Quantities specifying the magnetic behaviour of ammonium vanadium alum, as calculated in Siegert's theory.*

		Calculated											
	Best exptl.	$D = 1{\cdot}2$ (complex) $k =$				$D = 1$ (strong field) $k =$				$D = 1{\cdot}5$ (weak field) $k =$			
Quantity	value	1·0	0·9	0·8	0·7	1·0	0·9	0·8	0·7	1·0	0·9	0·8	0·7
C	0·95	0·935	0·935	0·935	0·935	0·93	0·93	0·93	0·93	0·935	0·935	0·935	0·935
δ/k	6·9°	7·1°	7·0°	6·9°	6·8°	7·1°	7·0°	6·9°	6·8°	7·1°	7·0°	6·9°	6·9°
χ_{CLT}	0·24	0·26	0·26	0·26	0·26	0·25	0·25	0·25	0·25	0·26	0·26	0·26	0·26
$10^6\chi_{\text{CHT}}$ ...	$\not>$150	210	210	210	210	220	220	220	220	210	210	210	210
Δ *		3000	2400	1900	1450	2000	1600	1300	1000	5250	4250	3400	2600

* Δ is chosen to give the best fit for C and δ/k simultaneously.

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* We do not need to consider the usual reduction of λ arising from delocalisation of the e_g electrons, since we are concerned only with the operation of spin–orbit coupling within the t_{2g} set. However, it is probable that a reduction of λ takes place because the transfer of charge accompanying the bonding to ligand atoms leads to the t_{2g} electrons' moving in a force field different from that of the free ion.[7] Thus it would be better to take as the spin–orbit coupling operator $kC\mathbf{L}\cdot\mathbf{S}$, where C is a number a little less than 1. As we were unable to decide on a suitable value for C, and in order to keep the treatment as simple as possible, we followed the procedure implicit in the early work on the effective reduction of λ and took $C = 1$.[8]

[6] Stephens, *Proc. Roy. Soc.*, 1953, *A*, **219**, 542.

[7] Dunn, *J.*, 1959, 623.

[8] Owen, *Proc. Roy. Soc.*, 1955, *A*, **227**, 183.

[9] Jörgensen, " Quelques Problèmes de Chimie Minérale," Institute Internationale de Chimie Solvay, Bruxelles, 1956, 355.

of the orbital triplet ground levels must be invoked—some 2000 cm.$^{-1}$. Also a much lower value for χ_{CHT} is deduced, although still higher than the experimentally determined value. χ_{CLT} is in satisfactory agreement with experiment.

Other V^{3+} *Complexes.*—From Table 2 it is obvious that the behaviour of the remaining three tervalent vanadium complexes we have studied is very similar to that of the alum as far as the Curie constant and χ_{CHT} are concerned. However, in view of the Weiss constant of 14°, not too much significance can be placed on the result for the malonate. It seems that these complexes also possess a distortion from cubic symmetry of the ligand field, and of much the same magnitude as that observed in the alum. The presence of such a distortion in these complexes is more readily understood than in the alum, for bonding between pairs of C=O groups must result in a departure from strictly cubic symmetry for the arrangement of the six oxygen atoms around the vanadium ion. It seems curious that the distortion necessary to explain the magnetic data is so similar in all the complexes unless, as Van Vleck [10] has suggested, the effective axial field arises from Jahn–Teller effect phenomena rather than from the exigencies of lattice packing, etc. From the splitting of the " third band " of the ligand-field spectrum of V^{3+} as V_2O_3 diluted with Al_2O_3, Ballhausen and Liehr [11] have inferred that a trigonal field of ~850 cm.$^{-1}$ is present.

Solutions of Ammonium Vanadium Alum.—In order to examine the behaviour of the V^{3+} ion in an environment which is not subject to the exigencies of crystal packing, we measured the susceptibility of two solutions, of different concentration, of ammonium vanadium alum in dilute sulphuric acid. If the susceptibility had been that predicted for the V^{3+} ion in an environment of cubic symmetry, the difference between that value and the value found for the ion in the solid complexes would have been well outside experimental error (a value 7% lower is required; a total experimental error between the two measurements of 3% is estimated). The results indicate that the instantaneous ligand field to which a V^{3+} ion is subject in solution is not entirely of cubic symmetry. Although the time average of the ligand field may correspond to high symmetry, the average of the magnetic susceptibilities arising from the instantaneous non-cubic fields is not expected to be the same as that for a steady-state cubic field. The fact that the solution measurement yields exactly the same magnetic susceptibility as is observed for the solid complexes may perhaps be taken to indicate that the Jahn–Teller effect is the mechanism which determines the effective non-cubic ligand field in both circumstances.

EXPERIMENTAL

Magnetic Measurements.—The measurements of the absolute values of the magnetic susceptibilities of the complexes were made by the Gouy method at room temperature. The magnetic field of 10,000 gauss was provided by an electromagnet, and the force on the specimen was measured on a semimicro-chemical balance. A specimen 10 cm. long and weighing about 0·4 g. was employed. The equipment was calibrated by means of nickel chloride solution.[12] The accuracy of the measurement of the susceptibilities of the complexes was ±2%. The measurement of the relative values of the susceptibility at different temperatures was made on equipment previously described,[13] and was accurate to ±0·5%. The results of three separate preparations were examined for the alum, of two preparations for the other complexes. Measurements were made at several field strengths up to 10,000 gauss. The measurements of the susceptibilities of solutions of ammonium vanadium alum were made by the Gouy method at room temperature at a magnetic field of 10,000 gauss. The sample volume was 15 ml.

Preparations and Analyses.—Ammonium vanadium alum was prepared by Palmer's method [14] [Found (i): V, 10·6, 10·6; SO_4, 40·5, 40·4; NH_4, 3·5; (after measurement) V, 10·7;

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[10] Van Vleck, *Discuss. Faraday Soc.*, 1958, **26**, 97.

[11] Ballhausen and Liehr, *J. Amer. Chem. Soc.*, 1959, **81**, 538.

[12] Nettleton and Sugden, *Proc. Roy. Soc.*, 1941, *A*, **173**, 313.

[13] Figgis and Nyholm, *J.*, 1959, 331.

[14] Palmer, " Experimental Inorganic Chemistry," Cambridge Univ. Press, 1954.

SO_4, 40·1; (ii) V, 10·6, 10·8; SO_4, 40·8, 40·8; (iii) V, 10·7, 10·7. Calc. for $NH_4V(SO_4)_2,12H_2O$: V, 10·7; SO_4, 40·3; NH_4, 3·8%).

Trisacetylacetonatovanadium(III).—Ammonium vanadium alum was heated with acetylacetone on the water-bath. The product was extracted with chloroform, and the chloroform evaporated off under reduced pressure. The substance, recrystallised from dry ether under reduced pressure, formed small brown needles [Found: V, 14·6, 14·7; C, 51·8, 51·4; H, 6·2, 6·1. Calc. for $V(C_5H_7O_2)_3$: V, 14·6; C, 51·7; H, 6·1%].

Potassium Trisoxalatovanadium(III) *Trihydrate*.—Warm saturated aqueous solutions of potassium oxalate and ammonium vanadium alum were mixed. After cooling, sufficient ethanol was added to start precipitation. The solution was kept in an ice-bath until the deposition of dark green crystals of the trihydrate was complete. The compound was recrystallised from water until free from sulphate ion [Found: V, 10·5; K, 24·3; C_2O_4, 54·2. Calc. for $K_3V(C_2O_4)_3,3H_2O$: V, 10·5; K, 24·1; C_2O_4, 54·3%].

Potassium Trismalonatovanadium(III).—This *complex* was prepared as for the oxalate complex, a saturated solution of potassium malonate being used in place of the oxalate solution [Found: V, 10·4, 10·9; K, 24·5, 24·4; C, 22·6, 23·5; H, 2·0, 2·3. $K_3V(C_3H_2O_4)_3$ requires V, 10·7; K, 24·7; C, 22·8; H, 1·3%].

Solutions.—For a 1M-solution of ammonium vanadium alum in 1M-sulphuric acid at 294° K, χ_V was found to be 3360×10^{-6} c.g.s.u.; for a 0·1M-solution in 1M-sulphuric acid, χ_V was 3330×10^{-6} c.g.s.u. The corresponding Curie constants are 0·95 and 0·96, respectively, if an allowance of 100×10^{-6} is made for χ_{CHT}.

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