Magnetic Properties and Structure of Hexakisureavanadium Tri-iodide

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The magnetic susceptibility and magnetic anisotropy of $V(urea)_6I_3$ was measured in the temperature range 80—300 K. The results were interpreted in terms of the $^3T_{1g}$ ground term with the set of parameters $\lambda = 45$ cm^{-1}, $\Delta = 450$ cm^{-1}, $k = 0{\cdot}5$. The structure of the salt was determined by *X*-ray means at room temperature and at *ca.* 90 K. It changes only by a small anisotropic contraction of bond lengths. There is an appreciable distortion of the VO_6 octahedron by a 'twist' about a three-fold axis, which is not changed by temperature. There is also a very slight distortion of the octahedron along this axis, which changes from zero or a very slight compression at room temperature to a slight elongation at the low temperature.

THE magnetic properties of tervalent vanadium complexes have been comparatively little studied. There are few reports of measurements over a range of temperature and almost none seem available on the magnetic anisotropy, apart from the system of V^{3+} in dilute solid solution in Al_2O_3.[1,2] It is important that these data be available, since the ion in octahedral co-ordination does not give an e.s.r. spectrum. Rapid spin–lattice relaxation and the difficulties often encountered with systems of integral spin quantum number in that technique are responsible. As part of our programme of studying the magnetic properties of transition-metal ions in close-to-cubic stereochemical environments, we report the behaviour of the magnetic susceptibility and anisotropy of $V(urea)_6I_3$ from 80 to 300 K. There is also measurement of the susceptibility at the single temperature 4·2 K. The variation of the susceptibility of the perchlorate salt has been given in the same higher temperature range by Machin and Murray.[3]

In order to make the most use of single-crystal magnetic susceptibility measurements it is essential to know the structural details of the compound under study. In particular, it is desirable to know whether the structure changes appreciably with temperature in the range of study. Without this knowledge, the interpretation of the temperature-dependence of the magnetic susceptibilities may be open to some doubt. Very few *X*-ray diffraction investigations of tervalent vanadium compounds have been made, and none seems available at low temperature. We report the crystal structure of $V(urea)_6I_3$ at room temperature and at *ca.* 90 K.

RESULTS

The averaged principal molar susceptibilities of the V^{3+} ion in $V(urea)_6I_3$ at a series of temperatures between 80 and 300 K are listed in Table 1. The molar magnetic anisotropy, $\chi_{cV} - \chi_{aV}$, is given as a function of temperature, for the three single crystals studied, in Figure 1. The magnetic moments corresponding to the principal and average magnetic susceptibilities are compared with the theory for the $^3T_{1g}$ term in Figure 2. The lists of F_{obs} and F_{calc} for the structure determination are available in

TABLE 1

The principal molar susceptibilities and the magnetic anisotropy of the V^{3+} ion in $V(urea)_6I_3$ at seven temperatures. The results were obtained by averaging the susceptibility for two sets of powder data, each involving measurement of 15 temperatures, and the anisotropy data for three crystals, involving measurement at respectively 18, 15, and 6 temperatures. Values are in units of 10^{-9} SI mol^{-1}

T/K	300	250	200	150
$\chi_{1V} = \chi_{cV} = \chi_{\parallel V}$	41·2	48·7	59·7	77·8
$\chi_{3V} = \chi_{aV} = \chi_{\perp V}$	41·0	49·15	61·15	80·5
$\Delta\chi_V = \chi_{aV} - \chi_{cV}$	−0·252	0·504	1·445	2·72

T/K	120	100	80
$\chi_{1V} = \chi_{cV} = \chi_{\parallel V}$	95·5	113·3	140·0
$\chi_{3V} = \chi_{aV} = \chi_{\perp V}$	99·3	117·8	145·3
$\Delta\chi_V = \chi_{aV} - \chi_{cV}$	3·73	4·49	5·30

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[1] W. H. Brumage, C. R. Quade, and C. C. Lin, *Phys. Rev.*, 1963, **131**, 949.

[2] W. H. Brumage, E. C. Seagraves, and C. C. Lin, *J. Chem. Phys.*, 1965, **42**, 3326.

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The co-ordination geometry of the V^{3+} ion in the VO_6 octahedron is illustrated in Figure 4. The positional parameters and bond length and angle data for the salt are given in Table 2 and the thermal parameters in Table 3.

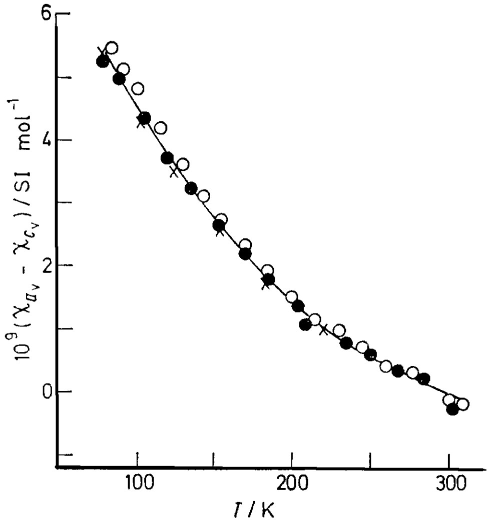

FIGURE 1 The molar magnetic anisotropy of three single crystals of $V(urea)_6I_3$ as a function of temperature

DISCUSSION

Magnetism.—The magnetic anisotropy of $V(urea)_6I_3$ is small at room temperature and falls as temperature is lowered until it is zero at 292 K. It then changes sign and rises rapidly in magnitude as temperature falls. The temperature of zero anisotropy is an aid in the fitting of the data to the theory for the $^3T_{1g}$ term. Even at 80 K the anisotropy is only *ca.* 5% of the susceptibility. The magnetic moment is quite near the spin-only value of 2·83 B.M. at room temperature and only falls slightly as the temperature is reduced to 80 K. The moment at 4·2 K, however, shows a quite considerable decrease, to 2·32 B.M. A cursory examination of this behaviour in relation to the theory for the $^3T_{1g}$ term shows that it is consistent provided that the ratio of the splitting of the orbital degeneracy of the term (Δ) to the spin–orbit coupling parameter (λ) is large.[4-7]

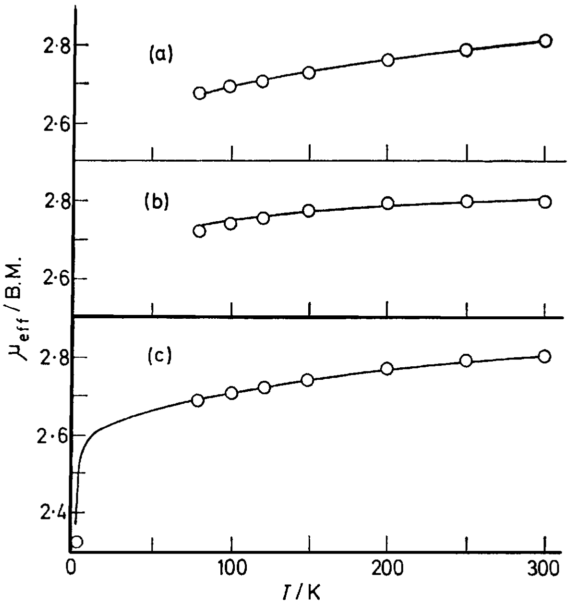

FIGURE 2 The magnetic moments of $V(urea)_6I_3$ (a) parallel to and (b) perpendicular to, the crystal *c* axis, and (c) the average moment, as a function of temperature. The solid lines represent the theory for the $^3T_{1g}$ term with the parameters $\Delta = 450$ cm^{-1}, $\lambda = 45$ cm^{-1}, $k = 0{\cdot}5$

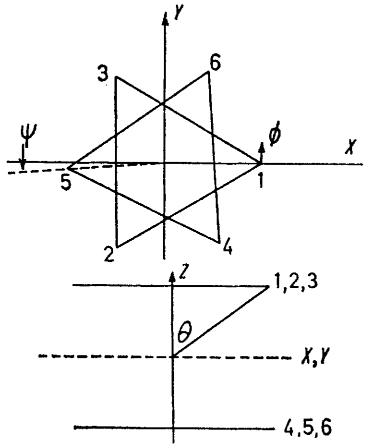

FIGURE 3 The definitions of the angles ψ and θ which specify the distortion from regular octahedral stereochemistry in the VO_6 octahedron

The theory for the behavour of the $^3T_{1g}$ term of the d^2 configuration under the influence of a low-symmetry ligand-field component which lifts the orbital degeneracy, of spin–orbit coupling, and of a reduction in the effective angular momentum (k) has been given.[4] The programme was adapted to print values of $\mu_{eff,\parallel}$ and $\mu_{eff,\perp}$, and data at very low temperatures were processed. Copies of the programme or of the data are available on application to Professor Figgis. The theory also includes, by means of a parameter A, the interaction between the

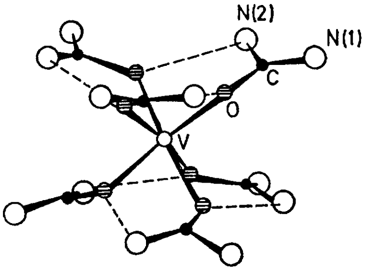

FIGURE 4 The atomic arrangement in the $V(urea)_6^{3+}$ units. Broken lines indicate the intra-unit hydrogen bonding

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[4] B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc.* (*A*), 1966, 1411.

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ground $^3T_{1g}(F)$ term and the higher term of the same symmetry classification originating from the ^3P free-ion term, $^3T_{1g}(P)$. A can be deduced[4] from a knowledge of the values of the cubic ligand-field parameter, Dq, and the Racah interelectronic repulsion parameter, B. These quantities are available from an interpretation of the optical absorption spectrum. The spectra of solutions of $V(urea)_6{}^{3+}$ salts[8] and of single crystals of the present compound[9] have been reported. A is 1·26, consequent upon a ratio $Dq : B = 3{\cdot}0$.

TABLE 2(*a*)

Positional parameters for $V(urea)_6I_3$ at *ca.* 300 K and *ca.* 90 K. E.s.d. values given in parentheses after each quantity are for the last one or two decimal places

ca. 300 K

Atom	*x*	*y*	*z*
C	0·1578(23)	0·0409(30)	0·1368(37)
O	0·1074(11)	0·0595(12)	0·1714(24)
N(1)	0·2438(18)	0·1022(17)	0·1062(30)
N(2)	0·1399(19)	−0·0393(17)	0·1201(32)
V	0·0000(0)	0·0000(0)	0·0000(0)
I	0·2975(2)	0·3333(0)	0·0833(0)

ca. 90 K

Atom	*x*	*y*	*z*
C	0·1588(5)	0·0379(5)	0·1398(7)
O	0·1070(3)	0·0596(3)	0·1690(4)
N(1)	0·2443(3)	0·1035(3)	0·1031(5)
N(2)	0·1399(3)	−0·0422(3)	0·1256(5)
V	0·0000(0)	0·0000(0)	0·0000(0)
I	0·2993(0)	0·3333(0)	0·0833(0)

TABLE 2(*b*)

Bond lengths/pm and angles/° in $V(urea)_6I_3$ at *ca.* 300 K and *ca.* 90 K. E.s.d. values are given in parentheses after each quantity

(*a*) Directly bonded interactions

	ca. 300 K	*ca.* 90 K
V–O	198(2)	193(1)
O–C	119(4)	117(1)
C–N(1)	141(4)	139(1)
C–N(2)	130(4)	123(1)
∠V–O–C	137·0(2·9)	133·6(0·6)
∠O–C–N(1)	125·1(4·3)	121·0(0·7)
∠O–C–N(2)	124·2(4·4)	124·7(0·8)
∠N(1)–C–N(2)	110·7(4·0)	113·5(0·7)
∠O–V–O	85·2(1·0)	88·0(0·2)
	174·1(1·0)	174·0(0·2)
	93·6(1·2)	96·2(0·2)
	90·7(1·0)	87·8(0·2)
Twist angle	7·0	7·0
∠C(3)–V–O	55·3(0·7)	53·5(0·2)

(*b*) Hydrogen-bonded interactions

	ca. 300 K	*ca.* 90 K
N(2)–O	297	283
N(1)–I	361	349
	368	351

TABLE 3

Anisotropic temperature factors of $V(urea)_6I_3$. E.s.d.s ($\times 10^3$) are given in parentheses; upper line at *ca.* 300 K, lower line at *ca.* 90 K

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C	3·5(1·9)	8·8(2·8)	9·9(4·7)	2·3(2·1)	5·6(2·4)	4·7(3·1)
	2·7(0·4)	2·4(0·4)	1·2(0·9)	1·5(0·3)	0·4(0·4)	0·6(0·4)
O	1·5(0·7)	3·7(0·9)	9·9(2·9)	1·6(0·7)	−1·2(0·4)	−2·8(1·4)
	0·5(0·2)	0·5(0·2)	1·2(0·5)	0·4(0·2)	−0·1(0·0)	−0·2(0·2)
N(1)	5·6(1·6)	5·9(1·7)	9·6(3·8)	3·5(1·3)	1·7(2·0)	−0·3(2·0)
	0·8(0·2)	0·4(0·2)	0·2(0·6)	0·3(0·2)	−0·1(0·2)	−0·2(0·2)
N(2)	4·4(1·5)	2·5(1·3)	11·3(3·7)	1·8(1·2)	0·5(1·9)	2·7(1·8)
	0·9(0·2)	1·1(0·3)	0·6(0·6)	0·6(0·2)	0·3(0·3)	0·5(0·3)
V	4·8(0·4)	4·8(0·4)	3·7(1·7)	2·4(0·4)	0(0)	0(0)
	1·4(0·1)	1·4(0·1)	2·0(0·4)	0·7(1·0)	0(0)	0(0)
I	4·6(0·1)	4·6(0·1)	7·7(0·2)	2·3(0·1)	0(0)	0(0)
	1·1(0·0)	1·1(0·0)	1·6(0·1)	0·5(0·0)	0(0)	0(0)

The theory for the $^3T_{1g}$ term can be refined somewhat, and an extensive discussion of the effects of molecular geometry on the anisotropic magnetic properties of tetragonally distorted tetrahedral bivalent nickel complexes has been advanced.[10,11] In the present case the distortion from cubic symmetry is essentially trigonal in character, and this requires a considerably different approach to extend the theory for the $^3T_{1g}$ ground term, involving much more extensive calculations. The requirement arises because the interaction between the $^3T_{1g}$ ground term and the higher triplet terms of the d^2 configuration caused by the trigonal component in the ligand field takes place through 'off-diagonal' matrix elements in addition to the 'diagonal' elements which are sufficient in tetragonal symmetry. Pryce and Runciman[12] introduced the appropriate interaction in the one-electron system of Ti^{3+} in dilute solid solution in Al_2O_3 in connection with the optical absorption spectrum. They employed the parameter v' as the matrix element [equation (1)] of the trigonal distortion potential, V_{trig}, between the t_{2g} and e_g d-orbital sets in cubic symmetry. For the present purposes it is more convenient

$$v' = \langle t_{2g}|V_{\text{trig}}|e_g\rangle \qquad (1)$$

to define a parameter, Uq, which is related to the matrix element between two of the d wave functions as in equation (2). In a point-charge crystal field model

$$Uq = \frac{\pm 3}{10\sqrt{2}} \langle d_{\pm 2}|V_{\text{trig}}|d_{\mp 1}\rangle \qquad (2)$$

these off-diagonal matrix elements have their origin largely in the 'twist' of the octahedron discussed below in the section on the structure of the salt. Indirectly, they also lift the orbital degeneracy of the $^3T_{1g}$ ground term. The 'diagonal' matrix elements of V_{trig},-$\langle d_{m_l}|V_{\text{trig}}|d_{m_l}\rangle$, lead directly to the splitting of the orbital degeneracy of the term, Δ. They have their origin in the compression or elongation of the octahedron along the three-fold axis. Figure 3 illustrates the definition of the angle of twist, ψ, and the C(3)–V–O angle, θ, which describe the distortion of the O_6 co-ordination octahedron about the V^{3+} ion. The co-ordination geometry about that ion is D_3. From the basis $\psi = 7{\cdot}0°$ and

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[11] M. Gerloch and R. C. Slade, *J. Chem. Soc.* (*A*), 1969, 1022.

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$Dq = 1700$ cm$^{-1,8,9}$ we calculate $Uq = 70$ cm^{-1} in the crystal-field model. A more detailed account of the relationship of the parameters to the molecular geometry will be presented elsewhere.[13] Employing the preceding formalism, we can construct the matrix for the appropriate operator within the enlarged basis set of all the triplet term wave functions of the d^2 configuration. The operator is (3), corresponding to a cubic ligand field

$$V = V_{\text{oct}} + V_{\text{trig}} + \lambda L \, . \, S \qquad (3)$$

with a superimposed trigonal component and spin-orbit coupling. The elements of the matrix are listed in the Appendix.

The basis set for the four triplet terms of the d^2 configuration in cubic stereochemistry, $^3T_{1g}(F)$, $^3T_{1g}(P)$, $^3T_{2g}(F)$, and $^3A_{2g}(F)$, involves 30 wave functions. With the free-ion wave function set employed the resultant 30×30 matrix factorises into three 10×10 matrices, of which two are identical but for the signs of some of the off-diagonal matrix elements of $V_{\text{oct}} + V_{\text{trig}}$.

If proper linear combinations of the free-ion wave functions appropriate to the D_3 symmetry were taken, factorisation into two 10×10, one 6×6, and one 4×4 matrices would follow. However, that factorisation would be of little or no help in the calculation of the magnetic properties of the system. The evaluation of the magnetic susceptibility resulting from this system follows along the lines set out for the $^3T_{1g}$ ground term alone, but is tedious. It has not been attempted on a large scale at this stage. No improvement in the reproduction of the anisotropic magnetic properties of $V(\text{urea})_6I_3$ relative to the theory for the $^3T_{1g}$ ground term alone is available from it since that is already available within the experimental error. Preliminary calculations indicate that no marked change in the parameters k and λ from that theory seem likely to result if Uq has the fairly small magnitude (<50 cm^{-1}) which has been observed in $Ti(\text{urea})_6{}^{3+}$ salts.[13-15]. The significance of the parameter Δ is likely to be rather different in the extended treatment, and this aspect is discussed below.

Our results were fitted to the theory for the $^3T_{1g}$ term[4] by employing a grid display of the inverse of the sum of the squares of the deviations between μ_{eff}(obs) and μ_{eff}(calc) at seven temperatures, as detailed.[16] The criterion used was that the fit between the theory and experiment should be equally good for $\mu_{\text{eff},\parallel}$ and $\mu_{\text{eff},\perp}$. Since the co-ordination geometry about the V^{3+} ion is so close to regular octahedral, we required that λ and k be isotropic. These restrictions placed much closer limits on the ranges of the parameters derived than had been obtained from the average susceptibility data.[3] The region of best fit was $\Delta = 450$ cm^{-1}, $\lambda = 45$ cm^{-1}, and $k = 0{\cdot}50$. The parameters reproduce the value of μ_{eff} at 4·2 K fairly well (2·38 B.M.).

These parameters are very similar to values found in previous work for V^{3+} complexes.[1-3,15,17-21] For example, Machin and Murray[3] reported values of Δ in the range 160—880 cm^{-1} for some octahedrally co-ordinated tervalent vanadium compounds, with 840 cm^{-1} for $V(\text{urea})_6(ClO_4)_3$. Bose *et al.*[21] found it necessary to introduce a variation of Δ with temperature covering the range 540—890 cm^{-1}. The free-ion value for λ in V^{3+} is 105 cm^{-1}, so that there is a very considerable reduction on incorporation of the ion into the complex. This reduction is greater than in most, but not all, of the previous studies. Likewise, k is lower than in the majority of the other studies. The simple relationship $\lambda = k\lambda_0$ appears to be maintained. No obvious reason for the low values observed for λ and k in this and other octahedral tervalent vanadium complexes is obvious. They are not unique, however, for data for $Ti(\text{urea})_6{}^{3+}$ salts[13-15] and other octahedral tervalent titanium compounds have often been interpreted with these parameters similarly reduced. In the case of k, it has been pointed out that there is little point in searching for the reason for the reduction, since its origin is obscure.[22]

In the salt we have studied, the co-ordination geometry of the V^{3+} ion shows a slight compression at *ca.* 90 K, but not at room temperature. The angle between the V–O bond and the three-fold axis is θ. Gerloch *et al.*[23] have examined in detail the effect of a trigonal point-charge crystal-field potential corresponding to an octahedron elongated (or compressed) along a three-fold axis on the magnetic behaviour of the Fe^{3+} ion in $FeSiF_6,6H_2O$. They show that the splitting of the $^5T_{2g}$ ground term can be put in the form (4). The quantity Cp

$$\Delta = \frac{-10}{7} Dq \, . \, f_1(\theta) - 200^{\frac{1}{2}} Dq \, . \, f_2(\theta) - \tfrac{9}{2}\, Cp \, . \, f(\theta) \qquad (4)$$

involves radial integrals with the spherical harmonic in $V_{\text{trig}}, Y_2{}^0$. It is suggested to be rather larger in magnitude than Dq. $f(\theta)$, $f_1(\theta)$, and $f_2(\theta)$ Depend only on θ. For values of θ near 54·75°, which holds for a regular octahedron, particularly the smaller ones, the terms in the expression in Dq are large compared with that in Cp, but of opposite sign. Consequently, Δ can be very critically dependent upon θ in this region. Applied qualitatively to $V(\text{urea})_6I_3$, it might be expected that Δ could have changed markedly with temperature, since θ does. We found no difficulty in fitting our data over the entire temperature range to one set of parameters.

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This does not necessarily mean that Δ does not change with temperature, since certain changes could be incorporated in the fitting procedure. Bose *et al.*,[21] however, found it necessary to allow Δ to vary within a comparatively narrow range in order to reproduce their data for the ammonium alum.

The development of an analytical expression for Δ in the $^3T_{1g}$ term of the d^2 configuration is possible, but the result is rather cumbersome. The complication arises partly because the matrix elements for the ligand field involve two-electron integrals, but more particularly because of the configurational interaction between the ground term and the $^3T_{1g}(P)$ term. Indeed, there is a splitting of the $^3T_{1g}$ ground term in the absence of 'diagonal' matrix elements of the crystal field. We have investigated this effect empirically, by diagonalising the matrices given in the appendix for various values of the parameters Uq and Dq/B with $\theta = 54{\cdot}75°$, $\lambda = 0$. The splitting of the term is *ca.* $7Uq$, depending somewhat on the value of Dq/B. It can be seen that the effects of the 'twist' of the octahedron are capable of producing a splitting of the orbital degeneracy of the $^3T_{1g}$ term of a magnitude comparable with the experimental value. Effects from this origin would not be expected to depend on temperature.

It seems likely that in the present salt at any rate, and perhaps also in V^{3+} in Al_2O_3, because the distortion from a regular octahedron is trigonal and involves a twist of opposite faces, the contribution to Δ arises more through the parameter Uq of the off-diagonal matrix elements of the potential than through the diagonal elements and the function of θ. This observation helps to account for the rather surprisingly large values of Δ deduced for many Ti^{3+} and V^{3+} compounds.

Structure.—The salts of the cations $M(urea)_6{}^{3+}$ are known for the ions Al^{3+}—Fe^{3+} and have been studied in some depth from the spectral and magnetic points of view. The structures of $Ti(urea)_6I_3$ and $Ti(urea)_6(ClO_4)_3$ have been reported,[14,15,24-26] including the latter salt at *ca.* 90 K. With the perchlorate salt the position is somewhat confused by a disorder phenomenon, and large single crystals suitable for the anisotropy measurements are difficult to grow. Consequently, we chose to study the iodide salt in connection with the vanadium system, inspite of the disadvantages of the heavy iodine atoms from the structural point of view. The salt is isomorphous with the titanium analogue and belongs to the space group $R_{\bar{3}c}$.

The structure of $V(urea)_6I_3$ is almost identical with that of $Ti(urea)_6I_3$ at room temperature. At *ca.* 90 K there is no change apart from a small anisotropic thermal contraction. Detailed descriptions of the structure are available [14,25] and only an outline is given here. The structure consists of $V(urea)_6{}^{3+}$ units which stack into a hexagonal array of columns, and iodide ions which lie in interstices between the columns. The columns lie along the *c* axis of the crystal.

Each $V(urea)_6$ unit is composed of two sets of three urea molecules, with strong hydrogen bonding within each set. The oxygen atoms of the urea molecules lie at the corners of an equilateral triangle at the inside of the set. One set lies on each side of the V^{3+} ion, and there are only van der Waals contacts between the sets. A set of three urea molecules forms a roughly saucer-shaped disc whose axis is along the crystal *c* axis. The two sets are nearly, but not quite out of phase with each other, so that the co-ordination geometry of the V^{3+} ion is a regular octahedron of oxygen atoms, slightly distorted by a 'twist' about a three-fold axis, which is the crystal *c* axis. The angle of twist is 7° at both the temperatures studied. Also, the octahedron is slightly distorted along this axis because the angle between the C_3 axis and any oxygen atom, subtended at the vanadium atom, differs from the ideal value (54·75°). This distortion changes from zero or a very slight compression at room temperature ($\theta = 55{\cdot}3 \pm 0{\cdot}7°$) to a slight but definite elongation at *ca.* 90 K ($\theta = 53{\cdot}5 \pm 0{\cdot}2°$).

The iodide ions fit between the columns and serve to bind them together by hydrogen bonding to four amine residues of the urea molecules of the $V(urea)_6$ units. The N(1) nitrogen atom of each urea molecule is involved in hydrogen bonding to two iodide ions, while the N(2) nitrogen atom is involved strongly in the intramolecular hydrogen bonding of the disc. The N(1)–I hydrogen bond length is 360—370 pm. It is notable that the C–N(1) bond length is 10 pm longer than the C–N(2) bond length, and the difference may indicate that the electron density in the C–N bond is depleted by the hydrogen bonding to the iodide ions more than by that to the oxygen atoms of the urea molecules.

The thermal parameters for the vanadium and iodine atoms in the room temperature structure correspond quite closely with the values reported [14] for the titanium and iodine atoms in $Ti(urea)_6I_3$. Of course, the limits of accuracy of the present photographic data are much poorer. The thermal parameters for the other atoms agree semiquantitatively. In particular, the feature that β_{33} is larger than the other components of the thermal tensor, corresponding to relative freedom for vibration along the *c* axis because the restraints of the hydrogen bonding arrangement are less, is reproduced. The same remarks pertain to the relationship with the structure of $Ti(urea)_6(ClO_4)_3$.[25]

The structure at *ca.* 90 K is the same as at room temperature, except for a general anisotropic contraction of bond lengths and the slight change in the C(3)–V–O angle. The contraction is analogous to that which occurs in crystalline urea, and emphasises the relationship between the structure of $M(urea)_6X_3$ salts and the structure of urea itself and its clathrate compounds.[25] Of course, there is the expected large decrease in the

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thermal parameters relative to the room-temperature structure. The decrease is the largest for the coefficients β_{33}.

EXPERIMENTAL

$V(urea)_6I_3$ was prepared by an adaptation of the method of Barbieri.[27] Vanadyl sulphate (100 g) in 2M-sulphuric acid solution (250 ml) was reduced electrolytically as described by Palmer,[28] until the blue solution turned to the deep green of the tervalent ion. The electrolysis was stopped when traces of the violet colour of the bivalent ion commenced to appear. This solution was filtered and stored under nitrogen. To a portion of the solution (15 ml) urea (10 g) was added followed by oxygen-free solution of potassium iodide (16 g) in water (13 ml). The resultant solution was warmed, filtered, and allowed to evaporate in a desiccator under nitrogen. Both large *crystals* for magnetic anisotropy measurements and small crystals for *X*-ray studies were deposited (Found: C, 9·4; H, 3·1; I, 48·2; N, 21·0; V 6·4. $C_6H_{24}I_3N_{12}O_6V$ requires C, 9·1; H, 3·05; I, 48·1; N, 21·2; V, 6·4%.

Magnetic susceptibility was measured at room temperature and between 80 and 300 K on equipment previously described.[29,30] The absolute accuracy of susceptibility determination was within ±2%, and relative values at different temperatures within ±1%. Diamagnetic corrections were made from a standard compilation.[31] Magnetic anisotropy was measured by the critical torque method of Krishnan and Banerjee [32] with equipment similar to that described by Gordon [33] and by Fleischmann and Turner.[34] The main differences were that the crystal was surrounded by an all-metal cryostat similar to the one employed for the measurement of the magnetic susceptibility over the range of temperature. The magnetic field of *ca.* 700 mT was supplied by a 100 mm electromagnet in which the pole pieces tapered to plane faces 65 mm in diameter and 30 mm apart. The crystal was glued to a glass fibre of *ca.* 0·2 mm diameter. The glass fibre reached *ca.* 30 mm above the top of the cryostat and carried the mirror. The quartz fibre was attached to the top of the glass fibre and led to the torsion head. Quartz fibres were *ca.* 200 mm long and 20 μm diameter. They were calibrated with reference to triphenylbenzene.[32] The accuracy of the measurement of relative anisotropy at various temperatures is better than 0·5%, but the absolute values are no better than *ca.* ±2% mainly because of uncertainty in the value for the calibration crystal. We thank Mr. D. J. Martin for the measurement of the magnetic susceptibility at 4·2 K, and Dr. R. A. Anderson for access to the equipment. The value was 2014×10^{-9} SI mol^{-1}, corresponding to $\mu_{eff} = 2{\cdot}32 \pm 0{\cdot}06$ B.M.

The *X*-ray data for the hexagonal unit cell were obtained from Weissenberg and oscillation photographs by use of Cu-K_α radiation. The space group is $R\bar{3}c$, No. 167.[35] At *ca.* 300 K: $a = 1{\cdot}749 \pm 0{\cdot}002$ nm, $c = 1{\cdot}438 \pm 0{\cdot}002$ nm. At *ca.* 90 K: $a = 1{\cdot}674 \pm 0{\cdot}003$ nm, $c = 1{\cdot}422 \pm 0{\cdot}003$ nm. The density at room temperature is 2·04 kg l^{-1}: the value calculated from the cell constants and the molecular weight of $V(urea)_6I_3$, with six molecules per hexagonal unit cell, is 2·07 kg l^{-1}. The reflections observed were : $hkil$; $-h + k + l = 3n$; $h\bar{h}0l$, $l = 2n$.

Intensity data were collected at each temperature from two ranges of inclined-beam oscillation photographs, with oscillation about the *c* axis. The angle of inclination was 20°, and each range covered 24°. Ni-filtered Cu-K_α radiation was employed. The data were recorded on multipack sets of film. For the low-temperature structure a Nonius nitrogen-flow low-temperature accessory, modified to prevent frost deposition on the crystal and the film and to permit a more reliable measurement of the temperature at the crystal position, was employed. Intensities were measured visually by comparison with a standard scale of spots, of which the linearity was verified by use of a Joyce–Loebel microdensitometer. The data were indexed, scaled to a zero-layer Weissenberg photograph set, and L.P. corrected by use of programmes adapted from versions loaned by Towl and Robertson.[36] The crystals were in the form of hexagonal rods, *ca.* 0·07 mm across the faces and 0·15 mm long. 738 non-zero reflections were indexed and processed for the room-temperature structure. For the structure at *ca.* 90 K the number was 680. Since μR was less than 0·15, a correction for absorption was not considered worthwhile. Neutral atom scattering factors, absorption coefficients, and the anomalous dispersion correction for iodine were taken from a standard compilation.[37] Hydrogen atoms were not considered.

Since the crystals are isomorphous with the titanium analogue, a trial set of parameters based upon that model[14,24] was employed. Least-squares refinement proceeded by block-diagonal and then full matrix methods, as described in connection with $Ti(urea)_6(ClO_4)_3$.[25] 43 positional, scale, and thermal parameters were involved. The weighting scheme of Cruickshank *et al.*[38] with $a = 20$ and $b = 0{\cdot}013$ was used. Unobserved reflections were not considered. The introduction of anisotropic thermal parameters was highly significant by statistical tests.[39] The refinement progressed to weighted residuals of $R = 0{\cdot}121$ and $R = 0{\cdot}120$ at room temperature and at *ca.* 90 K respectively.

APPENDIX

The matrix elements for the triplet wave functions of the d^2 configuration under the potential (5) are given here. The wave functions are specified in the

$$V = V_{oct} + V_{trig} + \lambda L \,.\, S \qquad (5)$$

$\langle L,M_L,S,M_S|$ quantisation scheme. $S = 1$ and is omitted. The phase convention of Condon and Shortely

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is used.[40] The ligand-field portion of the potential may be put in the form [20,41] (6). a, b and c are determined

$$V_{\mathrm{oct}} + V_{\mathrm{trig}} = aY_2^{\,0} + bY_4^{\,0} + c(Y_4^{\,3} - Y_4^{\,-3}) \qquad (6)$$

by the details of the point charge model. For a regular octahedron, referred to the C_3 axis, $a = 0$, $b = -(98/81)^{\frac{1}{2}}(2\pi)^{\frac{1}{2}}(zer^4/a^5)$, $c = (140/81)^{\frac{1}{2}}(2\pi)^{\frac{1}{2}}(zer^4/a^5)$. In the present model of a twisted and compressed octahedron we have equations (7)—(11).

$$a = (2/5)^{\frac{1}{2}}(2\pi)^{\frac{1}{2}}(zer^2/a^3)\,.\,f(\theta) \qquad (7)$$

$$b = 8^{-\frac{1}{2}}(2\pi)^{\frac{1}{2}}(zer^4/a^5)\,.\,f_1(\theta) \qquad (8)$$

$$c = (35/2)^{\frac{1}{2}}(2\pi)^{\frac{1}{2}}(zer^4/a^5)\,.\,f_2(\theta)\mathrm{e}^{\pm 3\mathrm{i}\psi} \qquad (9)$$

$$f(\theta) = 3\cos^2\theta - 1, f_1(\theta) = 35\cos^4\theta - 30\cos^2\theta + 3 \qquad (10)$$

$$f_2(\theta) = \sin^3\theta\cos\theta \qquad (11)$$

$$Cp = (2/7)(ze^2r^2/a^3)$$

We have $\langle \mathbf{a}|V|\mathbf{b}\rangle = \langle \mathbf{b}|V|\mathbf{a}\rangle^*$. Any elements not listed are zero. $a = 9Dqf_1(\theta)/28$, $b = Cpf(\theta)$, $c_+ = Dqf_2(\theta)\mathrm{e}^{3\mathrm{i}\psi}$, $c_- = Dqf_2(\theta)\mathrm{e}^{-3\mathrm{i}\psi}$, $d = -8Dqf_1(\theta)/3$, $e = (8/3)^{\frac{1}{2}}Dqf_1(\theta)$, $f = -384^{\frac{1}{2}}f(\theta)Cp/5$, $g = -24f(\theta)Cp/5$.

For the first and second matrices

$\langle 3, \pm 3, \pm 1|V|3, \pm 3, \pm 1\rangle = 2a + 3\lambda - 2b$, $\langle 3, \pm 3, \pm 1|V|3, 0, \pm 1\rangle = \mp 40^{\frac{1}{2}}c_{\pm}$, $\langle 3, \pm 3, \pm 1|V|1, 0, \pm 1\rangle = \mp 40^{\frac{1}{2}}c_{\pm}/3$,| $\langle 3, 0, \pm 1|V|3, 0, \pm 1\rangle = 4a + 8b/5$, $\langle 3, 0, \pm 1|V|3, \mp 3, \pm 1\rangle = \pm 40^{\frac{1}{2}}c_{\pm}$, $\langle 3, 0, \pm 1|V|3, \pm 1, 0\rangle = 6^{\frac{1}{2}}\lambda$, $\langle 3, 0, \pm 1|V|1, 0, \pm 1\rangle = d + g$, $\langle 3, \mp 3, \pm 1|V|3, \mp 3, \pm 1\rangle = 2a - 3\lambda - 2b$, $\langle 3, \mp 3, \pm 1|V|3, \mp 2, 0\rangle = 3^{\frac{1}{2}}\lambda$, $\langle 3, \mp 3, \pm 1|V|1, 0, \pm 1\rangle = \pm 40^{\frac{1}{2}}c_{\pm}/3$, $\langle 3, \pm 1, 0|V|3, \pm 1, 0\rangle = 2a/3 + 6b/5$, $\langle 3, \pm 1, 0|V|3, \mp 2, 0\rangle = \pm 80^{\frac{1}{2}}c_{\pm}/3$, $\langle 3, \pm 1, 0|V|3, \pm 2, \mp 1\rangle = 5^{\frac{1}{2}}\lambda$, $\langle 3, \pm 1, 0|V|1, \pm 1, 0\rangle = e + f$, $\langle 3, \mp 2, 0|V|3, \mp 2, 0\rangle = -14a/3$, $\langle 3, \mp 2, 0|V|3, \mp 1, \mp 1\rangle = 5^{\frac{1}{2}}\lambda$, $\langle 3, \mp 2, 0|V|1, \pm 1, 0\rangle = \mp (40/3)^{\frac{1}{2}}c_{\mp}$, $\langle 3, \pm 2, \mp 1|V|3, \pm 2, \mp 1\rangle = -14a/3 - 2\lambda$, $\langle 3, \pm 2, \mp 1|V|3, \mp 1, \mp 1\rangle = \mp 80^{\frac{1}{2}}c_{\pm}/3$, $\langle 3, \pm 2, \mp 1|V|1, \mp 1, \mp 1\rangle = \pm (40/3)^{\frac{1}{2}}c_{\pm}$, $\langle 3, \mp 1, \mp 1|V|3, \mp 1, \mp 1\rangle = 2/a3 + \lambda + 6b/5$, $\langle 3, \mp 1, \mp 1|V|1, \mp 1, \mp 1\rangle = e + f$, $\langle 1, 0, \pm 1|V|1, 0, \pm 1\rangle = 15B - 28b/5$, $\langle 1, 0, \pm 1|V|1, \pm 1, 0\rangle = \lambda$, $\langle 1, \pm 1, 0|V|1, \pm 1, 0\rangle = 15B + 14b/5$, $\langle 1, \mp 1, \mp 1|V|1, \mp 1, \mp 1\rangle = 15B + \lambda + 14b/5$.

For the third matrix

$\langle 3, -3, 0|V|3, -3, 0\rangle = 2a - 2b$, $\langle 3, -3, 0|V|3, -2, -1\rangle = 3^{\frac{1}{2}}\lambda$, $\langle 3, -3, 0|V|3, 0, 0\rangle = 40^{\frac{1}{2}}c_-$ $\langle 3, -3, 0|V|1, 0, 0\rangle = 40^{\frac{1}{2}}c_-/3$, $\langle 3, -2, -1|V|3, -2, -1\rangle = -14a/3 + 2\lambda$, $\langle 3, -2, -1|V|3, 1, -1\rangle = 80^{\frac{1}{2}}c_-/3$, $\langle 3, -2, -1|V|1, 1, -1\rangle = -(40/3)^{\frac{1}{2}}c_-$, $\langle 3, -1, 1|V|3, -1, 1\rangle = 2a/3 - \lambda + 6b/5$, $\langle 3, -1, 1|V|3, 0, 0\rangle = 6^{\frac{1}{2}}\lambda$, $\langle 3, -1, 1|V|3, 2, 1\rangle = -80^{\frac{1}{2}}c_-/3$, $\langle 3, -1, 1|V|1, -1, 1\rangle = e + f$, $\langle 3, 0, 0|V|3, 0, 0\rangle = 4a + 8b/5$, $\langle 3, 0, 0|V|3, 1, -1\rangle = 6^{\frac{1}{2}}\lambda$, $\langle 3, 0, 0|V|3, 3, 0\rangle = -40^{\frac{1}{2}}c_-$, $\langle 3, 0, 0|V|1, 0, 0\rangle = d + g$, $\langle 3, 1, -1|V|3, 1, -1\rangle = 2a/3 - \lambda + 6b/5$, $\langle 3, 1, -1|V|1, 1, -1\rangle = e + f$, $\langle 3, 2, 1|V|3, 2, 1\rangle = -14a/3 + 2\lambda$, $\langle 3, 2, 1|V|3, 3, 0\rangle = 3^{\frac{1}{2}}\lambda$, $\langle 3, 2, 1|V|1, -1, 1\rangle = (40/3)^{\frac{1}{2}}c_+$, $\langle 3, 3, 0|V|3, 3, 0\rangle = 2a - 2b$, $\langle 3, 3, 0|V|1, 0, 0\rangle = -(40/3)^{\frac{1}{2}}c_+$, $\langle 1, 0, 0|V|1, 0, 0\rangle = 15B - 28b/5$, $\langle 1, 0, 0|V|1, 1, -1\rangle = \lambda$, $\langle 1, 0, 0|V|1, -1, 1\rangle = \lambda$, $\langle 1, 1, -1|V|1, 1, -1\rangle = 15B - \lambda + 14b/5$, $\langle 1, -1, 1|V|1, -1, 1\rangle = 15B - \lambda + 14b/5$.

[2/848 *Received*, 18*th April*, 1972]

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