Magnetic Anisotropy and Structure of Hexa(urea)titanium Salts

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The magnetic anisotropy of $Ti(urea)_6(ClO_4)_3$ and $Ti(urea)_6I_3$ has been measured between 80 and 300 K. The behaviour is interpreted in terms of the model of the ^2D term of the d^1 configuration under the influence of a ligand field of cubic symmetry with a trigonal component superimposed, and of spin–orbit coupling. It is found that the orbital angular momentum reduction factor is quite low at *ca.* 0·45, and that the spin–orbit coupling constant is less than one half of the free-ion value. The ground $^2T_{2g}$ term is split by *ca.* 500 cm^{-1}, and the origin of this splitting does not seem to be to any large extent due to the ' twist ' of *ca.* 5° about the C_3 axis observed in the co-ordination octahedron from structural studies.

MAGNETIC susceptibility data on compounds of trivalent titanium are not uncommon, but they pertain mostly to compounds where the co-ordination site symmetry of the Ti^{3+} ion is fairly low. The results correspond to the Ti^{3+} ion in a highly distorted environment. The alum, where the site symmetry appears to be higher, has been the subject of several investigations,[1-4] but the symmetry of the cubic crystal precludes anisotropy studies. It is of some importance that magnetic anisotropy data be available on the Ti^{3+} ion in close-to-octahedral stereochemistry, since e.s.r. data on the system is very difficult to obtain, on account of fast spin–lattice relaxation arising from a set of low lying levels.

The hexa-urea salts of trivalent first-row transition series ions form an extensive isomorphous series. They belong to the space group $R\bar{3}c$. The titanium perchlorate and iodide salts have been the subject of single-crystal *X*-ray studies,[5-9] the former including low temperature results.[9] The Ti^{3+} ion lies at the centre of an octahedron which is essentially regular, within

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experimental error, except for a 5° twist of one pair of opposite faces relative to each other, about a three-fold axis. The site symmetry is D_3. The angle of twist is known to be independent of temperature in the perchlorate salt. The three-fold axis concerned is collinear with the unique *c* axis of the rhombohedral crystal. The main features of the co-ordination geometry of the Ti^{3+} ion in the hexa-urea salts are illustrated in Figure 1.

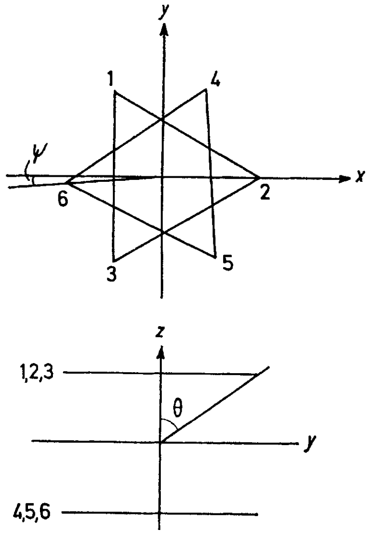

FIGURE 1 Representation of the co-ordination geometry about the Ti^{3+} ion in the $Ti(urea)_6{}^{3+}$ unit. The angles θ and ψ which define the distortion of the TiO_6 octahedron are illustrated

In this work the magnetic anisotropy of single crystals of $Ti(urea)_6(ClO_4)_3$ and $Ti(urea)_6I_3$ have been measured between 80 and 300 K, together with the average magnetic susceptibility. The results appear to be the first available for the anisotropy of the Ti^{3+} ion in an accurately known and close-to-octahedral stereochemistry. The theory of the magnetic properties of the d^1 configuration in a site symmetry corresponding to a twisted octahedron has been developed. The theory for a tetragonal distortion of the octahedron[10] and for a compression or elongation along a three-fold axis[11] has been discussed in detail previously.

RESULTS

Magnetic susceptibility measurements were made on powder specimens of $Ti(urea)_6(ClO_4)_3$ and $Ti(urea)_6I_3$ at a series of temperatures in the range 80—300 K. Magnetic anisotropy measurements were made on single crystals of each of the salts, extending from 80 to 300 K for the perchlorate compound and 90 to 300 K for the iodide. The results are given in the Table as smoothed average values of the principal magnetic moments at a series of temperatures, and are illustrated in Figures 2 and 3, along with the comparison between theory and experiment.

The magnetic susceptibility and anisotropy are very similar in the two salts. The anisotropy is small (*ca.* 8% of $\overline{\chi_{Ti}}$) at 300 K, and is positive in the sense that $\chi_{\parallel} > \chi_{\perp}$. It reverses sign at a temperature of *ca.* 165 K in the perchlorate salt and *ca.* 180 K in the iodide salt. It rises sharply in magnitude as temperature falls.

The principal magnetic moments for the ^2D term of the d^1 configuration parallel to and perpendicular to a unique three-fold axis were calculated from the matrices given in the Appendix. Perturbation of the ^2D term was performed with the operator:

$$V_{oct} + V_{trig} + \lambda L \,.\, S$$

The resulting eigenfunctions were attacked with the magnetic moment operator in the form $(kL_i + 2S_i)$, $i = \parallel$ or $\perp$ to the three-fold axis, and magnetic properties evaluated from the knowledge of the eigenvalues in the usual way, employing a computer programme.

The behaviour of the principal magnetic moments as functions of the parameters k, Δ, λ and Uq which characterise the model was examined in the way described for the $^2T_{2g}$ term previously,[12] k is the orbital angular momentum reduction factor and it appears in the magnetic moment operator $\mu = (kL_i + 2S_i)$; Δ is the splitting of the $^3T_{1g}$ term, positive if the orbital singlet is lowest; Uq is defined below. It was found that the effect of the parameter Uq decreased as Δ increased. Increasingly large values of Uq decreased the calculated anisotropy of the system

The magnetic properties of $Ti(urea)_6(ClO_4)_3$ and $Ti(urea)_6I_3$ at various temperatures. Susceptibility values are in units of 10^{-9} SI mol^{-1}

T/K	300	280	260	240	220	200	180	160	140	120	100	90	80
$Ti(urea)_6(ClO_4)_3$													
$\overline{\chi_{Ti}}$	16·86	17·85	19·01	20·34	21·91	23·75	26·02	28·74	32·15	36·72	42·8	46·8	51·6
$\overline{\mu_{eff}}$	1·793	1·783	1·773	1·762	1·751	1·738	1·726	1·710	1·692	1·674	1·650	1·636	1·620
$\Delta\chi_{Ti}$	1·47	1·42	1·33	1·16	0·98	0·75	0·38	−0·21	−1·09	−2·17	−3·58	−4·56	−6·16
$K_{\parallel}$	17·84	18·79	19·89	21·12	22·57	24·25	26·28	28·60	31·43	35·28	40·4	43·8	47·5
$K_{\perp}$	16·37	17·38	18·57	19·95	21·58	23·50	25·89	28·81	32·51	37·44	44·0	48·3	53·6
$\mu_{eff\parallel}$	1·847	1·829	1·814	1·791	1·774	1·755	1·735	1·707	1·673	1·641	1·603	1·583	1·555
$\mu_{eff\perp}$	1·767	1·759	1·752	1·745	1·739	1·727	1·722	1·711	1·701	1·691	1·673	1·661	1·652
$Ti(urea)_6I_3$													
$\overline{\chi_{Ti}}$	16·05	16·94	17·97	19·17	20·58	22·22	24·19	26·59	29·62	33·67	39·40	43·2	
$\overline{\mu_{eff}}$	1·750	1·737	1·724	1·711	1·697	1·681	1·664	1·645	1·624	1·603	1·583	1·572	
$\Delta\chi_{Ti}$	1·21	1·16	1·09	0·97	0·74	0·45	0·00	−0·64	−1·62	−2·94	−4·90	−6·22	
$K_{\parallel}$	16·86	17·71	18·70	19·82	21·07	22·52	24·19	26·16	28·54	31·71	36·13	39·1	
$K_{\perp}$	15·65	16·55	17·61	18·85	20·33	22·07	24·19	26·80	30·16	34·65	41·03	45·3	
$\mu_{eff\parallel}$	1·791	1·773	1·758	1·739	1·718	1·692	1·663	1·633	1·595	1·555	1·515	1·496	
$\mu_{eff\perp}$	1·727	1·715	1·707	1·696	1·687	1·673	1·663	1·652	1·640	1·626	1·614	1·611	

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Some of the effects are illustrated in Figure 4 for $k = 1\cdot0$. For values of Δ greater than *ca.* 300 cm^{-1} the effect of Uq is not appreciable below *ca.* 50 cm^{-1}.

In the present treatment, since the site symmetry is so close to octahedral, the parameters λ and k were restricted to be isotropic. This restriction greatly reduces the facility with which the experimental data may be reproduced by the theory, but seems likely to produce a physically more meaningful result. Dq was fixed at 1700 cm^{-1}, the value reported on the basis of the optical absorption spectrum.[13] The interpretation of the data took the form of a search for a set of parameters, k, Δ, λ, and Uq, which would reproduce the magnetic moments parallel and perpendicular to the three-fold axis as a function of temperature approximately equally well. Taken individually, each of the two sets of data could have been reproduced very well by the theory, but the two sets of parameters which did this differed appreciably. It is felt that the set which reproduces both sets of data fairly well is the more meaningful.

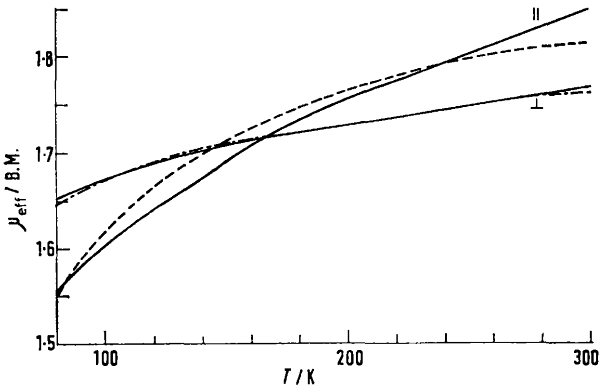

FIGURE 2 The principal magnetic moments of Ti(urea)$_6$(ClO$_4$)$_3$ as a function of temperature. The solid lines are the smoothed experimental data, — — —, calculated for $\mu_{\text{eff}\parallel}$, — · — · —, calculated for $\mu_{\text{eff}\perp}$, from the theory for the ^2D term with $Dq = 1700$ cm^{-1}, $\Delta = -400$ cm^{-1}, $k = 0\cdot46$, $\lambda = 53$ cm^{-1}, $Uq < 50$ cm^{-1}

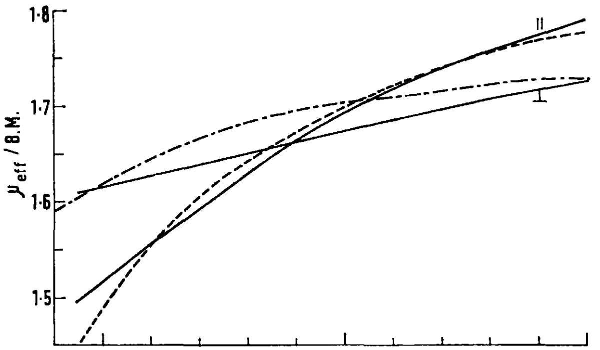

FIGURE 3 The principal magnetic moments of Ti(urea)$_6$I$_3$ as a function of temperature. The solid curves are the smoothed experimental data. — — —, calculated for $\mu_{\text{eff}\parallel}$, — · — · —, calculated for $\mu_{\text{eff}\perp}$, from the theory for the ^2D term with $Dq = 1700$ cm^{-1}, $\Delta = -600$ cm^{-1}, $k = 0\cdot45$, $\lambda = 75$ cm^{-1}, $Uq < 50$ cm^{-1}

The set of parameters derived for each salt is not unique, as is usual in this field,[11,14,15] but is representative. In particular, the data require that both k and λ be much reduced from their free-ion values, respectively 1·0 and 154 cm^{-1}. The net fits for the two sets of data for each compound are acceptable, although not as good as is commonly experienced in reproducing average susceptibility data. The sets of parameters deduced are

Ti(urea)$_6$(ClO$_4$)$_3$: $k = 0\cdot46$, $\lambda = 53$ cm^{-1}, $\Delta = -400$ cm^{-1}, $Uq < 50$ cm^{-1}; Ti(urea)$_6$I$_3$: $k = 0\cdot45$, $\lambda = 75$ cm^{-1}, $\Delta = -600$ cm^{-1}, $Uq < 50$ cm^{-1}.

Such large reductions in k and λ, and the fairly large value of Δ have been foreshadowed by earlier studies of the average susceptibilities of these and other Ti$^{\text{III}}$ compounds of near octahedral stereochemistry.[1-4,16-19]

DISCUSSION

As is to be expected from the fact that the structures are almost identical, the two parameter sets derived for the two salts are quite similar. The value for k is very similar to that observed in the isomorphous V^{3+} salt, V(urea)$_6$I$_3$.[20] Δ is of about the same magnitude, although of opposite sign. The values of k and Δ reported for that salt are 0·50 and 450 cm^{-1} respectively. The free-ion spin–orbit coupling constant, λ_0, is 154 cm^{-1} for the Ti^{3+} ion, and the ratio λ/λ_0 is reduced as far or even further than that for the vanadium salt (0·50), and indeed to an extent rarely reported. There seems to be little point in discussing k, since its origin is obscure.[21] The ratio λ/λ_0 has been equated to k in a simple minded way that often is sufficient, and seems roughly successful here.

The theory for the ^2D term of the d^1 configuration in trigonally distorted octahedral symmetry differs appreciably from that for tetragonally distorted stereochemistry[10] because the ground $^2T_{2g}$ term is connected with the higher-lying ^2E_g term by 'off-diagonal' rather than 'diagonal' matrix elements. The theory for an octahedron which is compressed or elongated along a three-fold axis has been given[11] for the ^5D term of the d^6 configuration, and is relevant here because of the correspondence between the configurations in the high spin arrangement, in that $d^6 \equiv d^1 + d^5$ (half-filled d shell). The effects of the twist of the octahedron may be added fairly simply. Pryce and Runicman[22] recognized the presence of the off-diagonal matrix element in con-

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nection with the optical absorption spectrum of the Ti^{3+} ion in corundum and Gladney and Swalen[23] in connection with the e.s.r. spectrum. These workers employed a parameter v' which connects certain of the t_{2g} wave functions of cubic symmetry with the e_g wave functions.

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

However, the interpretation of this parameter in details of the co-ordination geometry may not be straightforward. It includes a contribution from the splitting of the ground $^2T_{2g}$ term. It is more convenient for our purposes to introduce a parameter Uq, which is proportional to the matrix element between two of the free-ion wave functions, and is related to the cubic ligand field parameter Dq:

$$Uq = \pm(3/200^{\frac{1}{2}}) < d_{\pm 2}V_{\text{trig}}d_{\mp 1}>$$

It is a positive quantity. Then the off-diagonal matrix element can be put in the form $\frac{10\sqrt{2}}{3} \cdot (D - U)q$.

Uq, in general, contains a contribution from any elongation or compression of the octahedron along the three-fold axis, specified by the angle θ, as well as from any twist, specified by the angle ψ. The structural data on the salts show that θ has the value for a regular octahedron, $\theta_0 = 54{\cdot}75°$, within the experimental error of *ca.* 0·7°. The rate of change of the off-diagonal matrix element of the crystal field with regard to θ is *ca.* 1% per degree at θ_0. Consequently, on the point charge crystal field model the contribution to Uq from this cause should be rather less than 0·01 Dq. The matrix element is also effectively proportional to the quantity $(1 + \cos 3\psi)^{\frac{1}{2}}$, as discussed in the Appendix. For $\psi = 5{\cdot}0°$, as observed in the salts, this quantity is 0·99 of the regular octahedral value. Consequently, on the point charge crystal field model, the larger contribution to Uq is expected to come from the twist mechanism. It would however, be only *ca.* 0·01 Dq, or *ca.* 17 cm^{-1}.

The effect of the value of the angle θ on the splitting of the ground $^2T_{2g}$ term has been examined by Gerloch and others[11] in the ^5D term of the d^6 configuration. The splitting is given by

$$\Delta = -\frac{10}{7}Dq \cdot f_1(\theta) - 200^{\frac{1}{2}}Dq \cdot f_2(\theta) - \frac{9}{2}Cp \cdot f(\theta)$$

where $f(\theta)$, $f_1(\theta)$, and $f_2(\theta)$ are defined in the Appendix. Cp involves radial integrals with the spherical harmonic Y_2^0 in V_{trig}, and is suggested to be rather larger in magnitude than Dq. If θ is near θ_0, and particularly if it is somewhat smaller, the parts of the expression due to Dq are large compared to that in Cp, but are of opposite sign. Δ can be critically dependent on θ in this region. A departure of θ from θ_0 within the experimental error of the structure determinations could create a value of Δ of 1000 cm^{-1} or more. Applied quantitatively to the Ti(urea)$_6^{3+}$ salts, it might be expected that Δ could differ a good deal from salt to salt, and could change appreciably with temperature. The theory does not reproduce the experimental data particularly well, and it is possible that this reflects some appreciable change in Δ with temperature. In the region of parameter space for which acceptable fits to the data occur, $\mu_{\text{eff}\parallel}$ is rather more sensitive to the value of Δ than is $\mu_{\text{eff}\perp}$, particularly at the lower temperatures and it is notable that $\mu_{\text{eff}\parallel}$ differs more between the two salts studied than does $\mu_{\text{eff}\perp}$.

Gerloch and others[11] employed θ as a variable parameter in the study of $FeSiF_6,6H_2O$ and related compounds where there is no twist of the octahedron, rather than taking the crystallographically determined value.

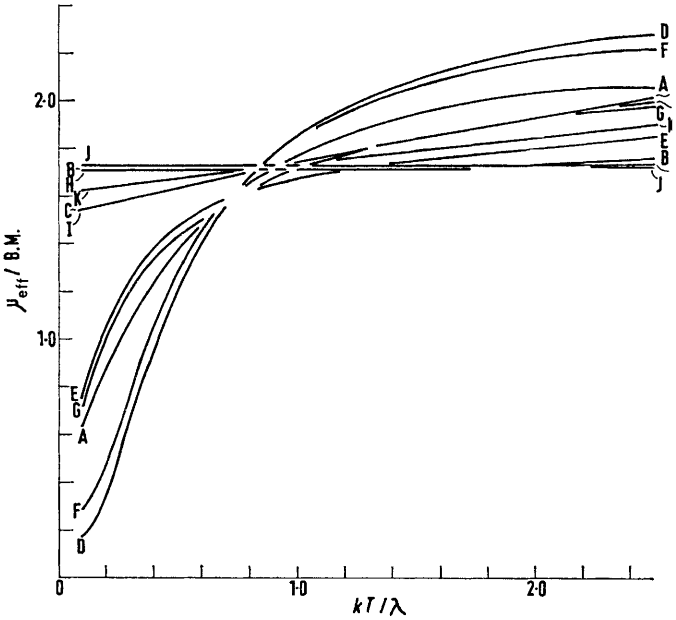

FIGURE 4 The magnetic moments parallel to and perpendicular to the C_3 axis for the ^2D term under a trigonal distortion; $\lambda = 100$ cm^{-1}, $k = 1{\cdot}0$, values in cm^{-1}; A, ∥ and ⊥, $\Delta = 0$, $Uq = 0$; B and C, ∥ and ⊥ $\Delta = 0$, $Uq = 200$; D and E, ∥ and ⊥ $\Delta = 1000$, $Uq = 0$; F and G, ∥ and ⊥, $\Delta = 1000$, $Uq = 200$; H and I, ∥ and ⊥, $\Delta = -1000$, $Uq = 0$; J and K, ∥ and ⊥, $\Delta = -1000$, $Uq = 200$

In the present circumstances, where 0 is more accurately known, and where its effects are intimately connected to those of the twist of the octahedron, it seems that little would be gained from that approach.

It is not necessary for θ to depart from θ_0 in order for an effective splitting of the $^2T_{2g}$ ground term to occur. A contribution to Δ of $\frac{40}{9}$ Uq arises from variation of the off-diagonal crystal field matrix element. On the basis of a contribution to Uq of 17 cm^{-1} from the twist of the octahedron, splitting of some 75 cm^{-1} is deduced. Splitting of this origin does not seem likely to be the major contribution to the observed value of Δ: rather

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[23] H. M. Gladney and J. D. Swalen, *J. Chem. Phys.*, 1965, **42**, 1999.

one must involve a crystallographically undetected compression or elongation of the octahedron along the three-fold axis.

The sign of Δ is negative, so that we conclude that the $^2T_{2g}$ ground term is split to give the orbitally degenerate ^2E component in D_3 symmetry lowest. This result supports the similar deduction made on the basis of the optical absorption spectrum of the iodide salt studied to low temperatures.[13] With the ^2E term lowest, the ion is formally subject to the Jahn–Teller theorem and a further splitting of smaller magnitude may be present. Such a splitting could provide some of the reason that the experimental data is not particularly well reproduced by the theory.

EXPERIMENTAL

The salts were prepared by the method of Barbieri,[24] and crystals grown to the size necessary for magnetic anisotropy measurements by moderately slow cooling of warm solutions. Seeding of fresh solutions was employed in the case of the perchlorate salt. Magnetic susceptibility and magnetic anisotropy was measured at ambient temperature and as a function of temperature on equipment described previously.[25–27] Diamagnetic corrections were made according to a standard compilation.[28]

The measurement of the absolute value of the average susceptibility is estimated to be accurate to ±2%, and of its relative values at different temperatures to ±1%. The measurement of the absolute value of the anisotropy is estimated to be accurate to ±2% and its relative values at different temperatures to ±0·5%.

APPENDIX

The matrix elements of the d wave functions, d_{m_l}, under the action of the operator

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

are listed here. The detailed form of V in D_3 symmetry has been discussed in connection with the studies on $\text{V(urea)}_6\text{I}_3$.[20] With the definitions:[11] $f(\theta) = 3\cos^2\theta - 1$, $f_1(\theta) = 35\cos^4\theta - 30\cos^2\theta + 3$, $f_2(\theta) = \sin^3\theta\cos\theta$, $Cp = 2ze^2\overline{r^2}/7a^3$; $a = 9Dq\cdot f_1(\theta)/28$, $b = Cp\cdot f(\theta)$, $c_\pm = Dq\cdot f_2(\theta)$-$(1 + e^{\pm 3i\psi})/2$ and wave functions are specified in the form $\langle m_l, m_s|$ we have

$$\langle m_{l_i},m_{s_i}|V|m_{l_j},m_{s_j} >^* = \langle m_{l_j},m_{s_j}|V|m_{l_i},m_{s_i}\rangle$$

Any elements not listed are zero.

There are two 3 × 3 matrices

$\langle\pm2,\pm\frac{1}{2}|V|\pm2,\pm\frac{1}{2}\rangle = -2a/3 - 4b + \lambda, \langle\pm2,\pm\frac{1}{2}|V|$
$\mp1,\pm\frac{1}{2}\rangle = \pm200^{\frac{1}{2}}c_\pm/3$

$\langle\pm1,\mp\frac{1}{2}|V|\pm1,\mp\frac{1}{2}\rangle = 8a/3 + 2b - \lambda/2, \langle\pm1,\mp\frac{1}{2}|V|$
$0\pm\frac{1}{2}\rangle = 1{\cdot}5^{\frac{1}{2}}\lambda, \langle0,\pm\frac{1}{2}|V|0,\pm\frac{1}{2}\rangle = -4a + 4b,$

and a 4 × 4 matrix

$\langle\pm2,\mp\frac{1}{2}|V|\pm2,\mp\frac{1}{2}\rangle = -2a/3 - 4b - \lambda, \langle\pm2,\mp\frac{1}{2}|V|$
$\mp1,\mp\frac{1}{2}\rangle = \pm200^{\frac{1}{2}}c_\pm/3,$

$\langle\pm1,\pm\frac{1}{2}|V|\pm1,\pm\frac{1}{2}\rangle = 8a/3 + 2b + \lambda/2, \langle\pm1,\pm\frac{1}{2}|V|$
$\pm2,\mp\frac{1}{2}\rangle = \lambda.$

These matrices are Hermitian, rather than real and orthogonal. Their diagonalisation is tedious, as efficient computer programmes for the purpose do not seem to be readily available. Diagonalisation may be obtained with sufficient accuracy for the present purposes provided the off-diagonal matrix elements in spin–orbit coupling are small compared to those in the ligand field portion of V. This criterion is met, since λ appears to be *ca.* 70 cm^{-1} while $200^{\frac{1}{2}}a/3$ is *ca.* 8000 cm^{-1}. If λ and Cp are zero, and $\theta = \theta_0$, matrices simplify, and one has only to solve 2 × 2 matrices of the type,

$$\begin{array}{ll} \langle 2,\frac{1}{2}| & |-1,\frac{1}{2}\rangle \\ -2Dq/3 & 200^{\frac{1}{2}}Dqe^{3i\psi}/3 \\ 200^{\frac{1}{2}}Dqe^{-3i\psi}/3 & 8Dq/3 \end{array}$$

and, these are equivalent to the same matrix element with off-diagonal elements $10Dq(1 + \cos 3\psi)^{\frac{1}{2}}/3$, the modulus.

The matrices diagonalised for the present purposes had the elements $\langle\pm2,\pm\frac{1}{2}|V|\mp1,\pm\frac{1}{2}\rangle$ and $\langle\pm2,\mp\frac{1}{2}|V|\mp1,\mp\frac{1}{2}\rangle$ in the above list replaced by $10Dqf_2(\theta)(1 + \cos 3\psi)^{\frac{1}{2}}/3$. The resultant real orthogonal matrices were diagonalised by standard methods.

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