454. *The Magnetic Properties of Some Tervalent Titanium Compounds.*

By B. N. FIGGIS, J. LEWIS, and F. MABBS.

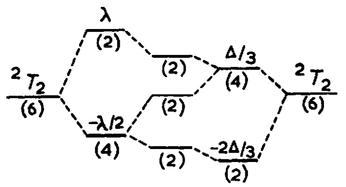
The magnetic susceptibilities of $CsTi(SO_4)_2,12H_2O$, Ti(acetylacetone)$_3$, and Ti(benzoylacetone)$_3$ have been measured between 80° and 300°K. The results for the alum have been interpreted in terms of the theory for a $^2T_2$ term perturbed by spin–orbit coupling and an axial ligand field component, and appear to be more reasonable than those already available. It is not possible to understand the behaviour of the magnetic susceptibilities of the other two compounds in detail.

THE magnetic properties of the d^1-configuration have not been investigated in detail; this is largely because very few compounds giving rise to this configuration are readily available. The theory of spin–orbit coupling operating within the $^2T_2$ term, which is the ground term of the d^1-configuration in an octahedral ligand field, leads to the conclusion that the magnetic moment should fall with temperature, to zero at zero temperature.[1] If departure of the ligand field from octahedral symmetry is considered, by the introduction of an axial component in the field, it is found that the magnetic moment still falls with temperature but in a less marked manner.[2] The only first-row transition element ions which lead to the d^1-configuration and of which octahedral compounds are at all readily synthesised are titanium(III) and vanadium(IV). By far the best known compound is the cæsium alum of tervalent titanium, $CsTi(SO_4)_2,12H_2O$, and this is the only one which has been the subject of any detailed magnetic study. This paper presents new magnetic susceptibility results obtained on this alum, and on two other tervalent titanium compounds, between 80° and 300°K.

FIG. 1. The splitting at the $^2T_2$ term by spin–orbit coupling and an axial ligand field.

I	II	III	IV	I
cubic ligand field	I + λ**L.S**	I + λ**L.S** + axial ligand field	I + axial ligand field	cubic ligand field

The numbers in parentheses indicate the degeneracy of the level immediately above.



The magnetic susceptibility of $CsTi(SO_4)_2,12H_2O$ has been studied at liquid-helium temperatures and up to room temperature.[3] Recent work at very low temperatures [4] (1·0—4·2°K) and at higher temperatures [5,6] (80—300°K) has not agreed well with the earlier work, probably because of the difficulty of preventing oxidation of Ti^{3+} to diamagnetic Ti^{4+}. The magnetic susceptibility in the helium range may be interpreted [4] on the splitting of the $^2T_2$ term illustrated in Fig. 1, III, with the separation between the ground level and the next highest level of the order of 100 cm.$^{-1}$. The low-temperature magnetic susceptibility results can be correlated with electron-spin resonance measured at the same temperature.[7,8] In interpreting the low-temperature information it was

---

[1] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.
[2] Figgis, *Trans. Faraday Soc.*, 1961, **57**, 198.
[3] Van der Handel, Thesis, Leiden, 1940.
[4] Benzie and Cooke, *Proc. Roy. Soc.*, 1951, *A*, **209**, 269.
[5] Bose, Chakravarty, and Chatterjee, *Indian J. Phys.*, 1959, **33**, 325.
[6] Dutta-Roy, Chakravarty, and Bose, *Indian J. Phys.*, 1959, **33**, 483.
[7] Bijl, *Proc. Phys. Soc.*, 1950, **63**, *A*, 405.
[8] Bleaney, Bogle, Cooke, Duffus, O'Brien, and Stevens, *Proc. Phys. Soc.*, 1955, **68**, *A*, 57.

found necessary to assume an electron delocalisation from the t_{2g}-orbitals of the titanium ion which reduced the effective orbital angular momentum by the factor k. k was estimated to be less than 0·95, and the separation, Δ, between the orbital singlet and the orbital doublet of the $^2T_2$ term in the axial ligand field (trigonal symmetry was assumed) was deduced to be of the order of 100 cm.$^{-1}$. The spin–orbit coupling parameter, ζ, was assumed to be close to the free-ion value, 154 cm.$^{-1}$. Between 100° and 300°K the magnetic moment of $CsTi(SO_4)_2,12H_2O$ has been reported [5,6] to fall from 1·69 to 1·65 B.M.

This high-temperature value of the magnetic susceptibility cannot be interpreted with the same values of the parameters for axial field splitting and electron delocalisation as are used at low temperatures. Electron spin resonance cannot be determined on the system at higher temperatures. It has been estimated that the parameters at high temperatures are $\Delta = 800$ cm.$^{-1}$, ζ close to 150 cm.$^{-1}$, and k, which was taken to be anisotropic, has the mean value of 0·65.[9] It has been suggested that some change takes place between 100° and 4°K which drastically alters the axial ligand field component to which the titanium ion is subject.

The electron spin resonance spectrum of $Ti(acac)_3$ has also been studied; the g values are close to 2·0 and the resonance is visible at room temperature.[10] It has been suggested that the primary ligand field is large and there is a trigonal distortion component of 4300 cm.$^{-1}$.

Results and Discussion

We have measured the magnetic susceptibility of $CsTi(SO_4)_2,12H_2O$, $Ti(acetylacetone)_3$, and $Ti(benzoylacetone)_3$ between 80° and 300°K on equipment described previously.[11] For the first two compounds, measurements were made on two separate preparations which were analysed before and after the measurement. The results for magnetic susceptibilities are set out in the Table, and plots of μ_{eff} against temperature are given in

Magnetic susceptibilities (10^{-6} c.g.s./mole).

$CsTi(SO_4)_2,12H_2O$ (1)		$CsTi(SO_4)_2,12H_2O$ (2)		$Ti(acac)_3$ *	
Temp. (K)	χ_{Ti}	Temp. (K)	χ_{Ti}	Temp. (K)	χ_{Ti}
298·1°	1347	304·4°	1385	293·1°	1020
279·6	1429	280·0	1490	284·6	1060
254·4	1544	255·0	1594	259·5	1245
230·0	1667	231·0	1744	235·8	1219
206·5	1822	207·2	1905	211·8	1391
182·5	2003	183·8	2074	188·3	1471
159·9	2221	161·2	2300	165·7	1669
137·7	2504	137·6	2595	142·0	1986
119·9	2783	119·2	2918	118·9	2357
103·5	3107	100·3	3313	97·8	2767
80·0	3796	80·5	3958	83·4	3190

$Ti(acac)_3$ *		$Ti(benzoylacetone)_3$	
Temp. (K)	χ_{Ti}	Temp. (K)	χ_{Ti}
296·0°	885	304·6°	1014
245·7	1066	280·2	1095
197·0	1320	255·2	1194
173·5	1487	231·1	1326
151·1	1683	207·4	1465
127·2	2009	183·9	1637
105·0	2429	160·4	1867
79·8	3154	138·6	2183
		119·1	2526
		98·7	3020
		86·0	3434

* acac = Acetylacetone; two preparations were used and are recorded.

---

[9] Bose, Chakravarty, and Chatterjee, *Proc. Roy. Soc.*, 1960, *A*, **255**, 145.
[10] Jarrett, *J. Chem. Phys.*, 1957, **27**, 1298.
[11] Figgis and Nyholm, *J.*, 1959, 331.

Fig. 2. The mean of the susceptibilities obtained for different specimens was employed for the evaluation of μ_{eff}. A correction of 25×10^{-6} c.g.s./mole was subtracted from the χ_{Ti} values before plotting μ_{eff} in order to allow for the second-order Zeeman effect from the higher lying ^2E term of $2N\beta^2/10Dq$.

We have evaluated the parameters involved in the description of the magnetic properties of $CaTi(SO_4)_2,12H_2O$; they were assessed by comparison with the data published earlier for the magnetic moment of the $^2T_2$ term under simultaneous perturbation by spin-orbit coupling and an axial ligand field.[2] The best fit for our results is shown as the solid line in Fig. 2. This line corresponds to the set

$$k = 0{\cdot}7,\ \Delta = 350\ \text{cm.}^{-1},\ \lambda = \zeta = 93\ \text{cm.}^{-1},\ \zeta/\zeta_0 = 0{\cdot}65.$$

(ζ_0 is the free-ion spin-orbit coupling parameter, 154 cm.$^{-1}$.) Our results for the susceptibility of $CsTi(SO_4)_2,12H_2O$ are quite appreciably above those reported previously;[5,6] they show a larger change in the magnetic moment with temperature, and this is why the set of parameters we have obtained is distinctly different from that suggested previously.

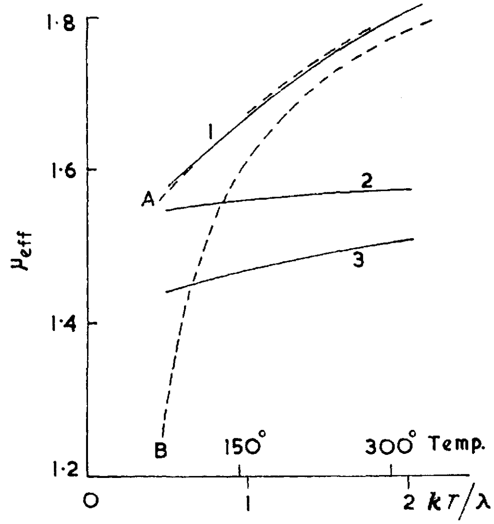


FIG. 2. Plots of μ_{eff} against temperature (T) (°K) and kT/λ.
(A) $k = 0{\cdot}7$, $\lambda/\lambda_0 = 0{\cdot}65$, $v = 3{\cdot}6$, $\Delta = 350$ cm.$^{-1}$.
(B) $k = 0{\cdot}6$, $\lambda/\lambda_0 = 0{\cdot}65$, $v = 1$.
1, $CsTi(SO_4)_2,12H_2O$. 2, Ti(benzoylacetone)$_3$. 3. Ti(acetylacetone)$_3$.

In our treatment of the theory of the splitting of the $^2T_2$ term, it is assumed that k is isotropic; an anisotropy in k as large as that previously postulated must be regarded as somewhat unlikely.

The electron spin resonance g values are $|g_{\parallel}| = 1{\cdot}25$ and $|g_{\perp}| = 1{\cdot}14$.[7] These may be expressed in terms of the theory of the $^2T_2$ term under the action of spin-orbit coupling and an axial ligand field component as follows:

$$g_{\parallel} = 2[1 - (1 + k_{\parallel}{}^2]y/(1 + y^2); \qquad g_{\perp} = 2(1 + 2^{\frac{1}{2}}k_{\perp}y)/(1 + y^2);$$

with $$y = 2^{-\frac{1}{2}}[v + \tfrac{1}{2} \pm (v^2 + v + 2{\cdot}25)^{\frac{1}{2}}] \text{ and } v = \Delta/\zeta.$$

If it is assumed that k is isotropic the two equations involving $g_{\parallel}$ and $g_{\perp}$ have one reasonable solution. Both $g_{\parallel}$ and $g_{\perp}$ must be positive, $k = k_{\parallel} = k_{\perp} = 0{\cdot}6$, and $y = -0{\cdot}41$. This value of y gives $v = 1$, *i.e.*, $\Delta = \lambda$. From the g values alone it is not possible to deduce anything about the absolute magnitude of Δ or ζ. It is to be expected that ζ will be the free-ion value, 154 cm.$^{-1}$, or less.

Our results on the magnetic susceptibility of $CsTi(SO_4)_2,12H_2O$, namely, $\Delta = 350$ cm.$^{-1}$, $\lambda = 93$ cm.$^{-1}$, $k = 0{\cdot}7$, seem more compatible with the very-low-temperature data than do those put forward previously; they do not indicate that there is an order of magnitude change in the distortion parameter, Δ, between low temperatures and 80—300°K. However, it is not possible to fit both our data and the g values with exactly the same set of parameters. The set of parameters we suggest is more consistent in so far as we find that the spin–orbit coupling constant is reduced in the complex in much the same way as is k, whereas previously it has been assumed that the free-ion value held in the complex in spite of the reduction in k.

Our results on the compounds Ti(acetylacetone)$_3$ and Ti(benzoylacetone)$_3$ cannot be fitted to any reasonable combination of the parameters specifying the magnetic behaviour of the $^2T_2$ term: if ζ is increased above the free-ion value a fit can be obtained, but this is not a reasonable solution to the problem. The magnetic moment of these compounds is substantially lower than that to which the $^2T_2$ term can lead for $\boldsymbol{k}T/\lambda$ in the range of interest, say 0·3—2. It is tempting to ascribe such low results to oxidation of the Ti^{3+}; we have taken every precaution to prevent such oxidation and have analysed the specimens after measurement to try to check that it has not taken place.

The g values of Ti(acac)$_3$ are $g_{\parallel} = 2{\cdot}00$, $g_{\perp} = 1{\cdot}93$. These, together with the fact that the resonances can be observed at room temperature, indicate that the primary cubic field and the distortion from cubic symmetry must both be large. The values quoted in the introduction are reasonable in the light of a knowledge of the usual range of these quantities in metal complex ions. Given that these quantities are large, the more detailed theory for the $^2T_2$ term gives $g_{\parallel} = 2(1 - 2k\lambda/10Dq)$, $g_{\perp} = 2(1 - 2k\lambda/10Dq - k\lambda/\Delta)$, and $\mu_{\text{eff}} = \frac{3}{4}g^2 + 8k^2\boldsymbol{k}T/\Delta$. For $10Dq = 20{,}000$ cm.$^{-1}$, as for the $Ti(H_2O)_6{}^{3+}$ ion, and $\Delta = 3000$ cm.$^{-1}$ of the order of the distortion in some V^{3+} complexes with oxygen ligands,[12] and with k and λ/λ_0 about 0·7, as in the alum, one may calculate that $g_{\parallel} = 1{\cdot}99$ and $g_{\perp} = 1{\cdot}93$. Thus a very reasonable amount of distortion from cubic symmetry can account satisfactorily for the g values of Ti(acac)$_3$. However, from the g values and with an inclusion of about 100×10^{-6} c.g.s./mole from the second-order Zeeman effect it may be deduced that the magnetic moment should be 1·80 B.M., and almost independent of temperature.

The moments we have found for Ti(acac)$_3$ and Ti(benzoylacetone)$_3$ are substantially independent of temperature. The best explanation of this fact, together with a moment somewhat below the spin-only value, seems to be that the distortion parameter is large—the 3000 cm.$^{-1}$ suggested by the electron spin resonance results would be suitable—and that, in spite of our care, some oxidation to diamagnetic Ti^{4+} has taken place.

EXPERIMENTAL

The compounds were prepared and analysed by standard methods. The authors are indebted to Dr. M. Cox for the loan of the complexes. The accuracy of the measurement of the absolute magnetic susceptibilities was 2—3% on any given sample; that of the relative susceptibility on the same sample at different temperatures was about 0·5%. The measurements were carried out on apparatus previously described.[11]

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER ST.,
LONDON, W.C.1.

[*Received, August* 9*th*, 1962.]

---

[12] Figgis, Lewis, and Mabbs, *J.*, 1961, 3138.