Three-co-ordinated Transition-metal Compounds. Part III.[1] Electron Spin Resonance Studies on Tris(bistrimethylsilylamido)derivatives of Titanium, Chromium, and Iron

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The e.s.r. spectra of the complexes $M[N(SiMe_3)_2]_3$ (M = Ti, Cr, and Fe) are reported and interpreted in terms of the effect of a large trigonal crystal field on the d^n configurations. The ordering of the Kramers doublets for the chromium and iron compounds has been determined by depopulation experiments and substantiated with theoretical calculations.

We have reported[1] the electronic spectra, magnetic susceptibilities, and preliminary e.s.r. data for the trigonal compounds $M[N(SiMe_3)_2]_3$ (M = Sc, Ti, V, Cr, and Fe). The *d–d* transitions were discussed in terms of crystal field calculations for the appropriate d^n electronic configurations in D_{3h} symmetry; the assignments of the ground states were confirmed by the e.s.r. results. The crystal field calculations showed considerable perturbation of the *d*-orbital energies indicating the presence of a strong trigonal field. We now describe details of the e.s.r. spectra of the Ti, Cr, and Fe compounds, showing the effect of such a field on the ground states ^2A, ^4A, and ^6A respectively.

Titanium.—A solution of the titanium compound in toluene gave a strong, symmetrical e.s.r. signal at room temperature corresponding to an average *g*-value of 1·911. The spectrum of the same sample frozen at −140 °C showed considerable anisotropy with two principal components, indicating axial symmetry in the compound and *g*-values of $g_{\parallel} = 1{\cdot}993$ and $g_{\perp} = 1{\cdot}869$. A similar spectrum was observed for a polycrystalline sample, except that there was now some evidence of hyperfine splittings presumably arising from the nuclei ^{47}Ti and ^{49}Ti, which both have nuclear spins and occur in natural abundances of a few per cent.

Titanium(III) complexes which give rise to e.s.r. signals at room temperature with *g*-values close to 2 and which have D_3 symmetry are quite common and include, for instance, $Ti(acac)_3$,[2] $KTi(C_2O_4)_2,2H_2O$,[3] $Ti(en)_3Cl_3$, and $Ti(pn)_3Cl_3$.[4] The interpretation of the *g*-values for these compounds[4] is complicated because the D_3 symmetry arises from a distorted octahedral arrangement of ligands and, even though the ground state orbital is d_{z^2}, the excited states are mixtures of the remaining *d*-orbitals. In the present case the situation is simpler. With a crystal field of D_{3h} symmetry the *d*-orbitals split according to: $d_{z^2}(a_1')$; $d_{xz}, d_{yz}(e'')$; $d_{x^2-y^2}, d_{xy}(e')$. The observed e.s.r. spectrum indicates a $^2A_1'$ ground state (from d_{z^2}),

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[1] Part II, E. C. Alyea, D. C. Bradley, R. G. Copperthwaite, and K. D. Sales, preceding paper.

[2] B. R. McGarvey, *J. Chem. Phys.*, 1961, **38**, 388.

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

[4] R. J. H. Clark and M. L. Greenfield, *J. Chem. Soc.* (*A*), 1967, 409.

when the usual theory for the g-values [5] gives the expressions $g_{\parallel} = 2$ and $g_{\perp} = 2(1—3\zeta/\Delta)$, where ζ is the spin–orbit coupling parameter and Δ is the energy difference between the ground state and the excited $^2E''$ state. With the free-ion value for ζ (154 cm^{-1}) and Δ derived from the observed electronic spectrum of the compound,[1] $g_{\perp}$ turns out to be 1·808, in reasonable agreement with the experimental value. Complete agreement can be obtained if ζ is reduced to 70% of its free-ion value.

TABLE 1

Values of $|D|$ and $|E|$ for some chromium(III) complexes

Complex	$\|D\|/cm^{-1}$	$\|E\|/cm^{-1}$	Ref.
$Cr(acac)_3$	0·60	0·009	*a*
trans-$[Cr(en)_2Cl_2]^+Cl^-,HCl,H_2O$	0·504	0·036	*b*
Cr^{3+} in $NH_4[Co(edta)],4H_2O$	1·069	0·202	*c*
$Cr[N(SiMe_3)_2]_3$	1·85	0·006	*d*

[a] B. R. McGarvey, *J. Chem. Phys.*, 1964, **40**, 809. [b] B. R. McGarvey, *J. Chem. Phys.*, 1964, **41**, 3743. [c] R. Aasa, K. E. Falk, and S. A. Reyes, *Arkiv Kemi*, 1966, **25**, 309. [d] This work.

Chromium.—The powder spectra of the chromium(III) compound at X- and Q-band are characterised by effective g-values of $g_{\perp}$ *ca.* 4 and $g_{\parallel}$ *ca.* 2, the $g_{\parallel}$ component being rather weak. At X-band a further transition, which is split into two components, is observed at high field. The line positions, in gauss, of the spectra are: (i) X-band, 1650 (s), 3300 (m), 16,700 (sh), 18,400 (m); (ii) Q-band, 6560 (s), 13,080 (m).

TABLE 2

Non-zero matrix elements of the spin–orbit coupling for chromium(III)

	$^4E'',a_1'e''e',M_s = \frac{1}{2}$	$^2E'',(a_1')^2e'',M_s = \frac{1}{2}$	$^2E'',(e'')^3,M_s = \frac{1}{2}$
$^4A_2',a_1'(e'')^2,M_s = \frac{3}{2}$	$-\zeta/\sqrt{6}$	$\zeta\sqrt{3/2}$	$\zeta\sqrt{3/2}$

	$^4E'',a_1'e''e',M_s = \frac{3}{2}$	$^4E'',a_1'e''e',M_s = -\frac{1}{2}$	$^2E'',(a_1')^2e'',M_s = -\frac{1}{2}$	$^2E'',(e'')^3,M_s = -\frac{1}{2}$	$^2A_1',a_1'(e'')^2,M_s = \frac{1}{2}$
$^4A_2',a_1'(e'')^2,M_s = \frac{1}{2}$	$\zeta/\sqrt{6}$	$-\zeta\sqrt{2/3}$	$\zeta/2$	$\zeta/2$	$\zeta\sqrt{2}/\sqrt{3}$

The magnetic susceptibility data [1,6] and the assignment of the electronic absorption spectrum [1] for this compound indicate that the ground state is $^4A_1'$; the e.s.r. spectrum is interpreted in terms of a $^4A_1'$ state split in zero magnetic field. The spin Hamiltonian used to describe this situation is: [7]

$$\mathscr{H} = g\beta\mathbf{H}\cdot\mathbf{S} + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2)$$

where g is isotropic and *ca.* 2, S is 3/2, and D and E are the zero-field splitting parameters. For axial symmetry, E should be zero. The method used to find solutions for this type of spin Hamiltonian has been described elsewhere.[8] Using a g-value of 1·98, analysis indicates that the effective g-values of four and two require D to be greater than 0·2 cm^{-1} and E to be approximately zero, whilst the position of the high field line leads to an estimated D value of 1·85 ± 0·05 cm^{-1}. This high field line is slightly split indicating that E is not exactly zero; E is estimated to be 0·006 cm^{-1}.

The analysis given above does not enable the sign of D to be determined. This sign may, however, be found by measuring the intensity of the e.s.r. signal at very low temperatures, a procedure which also gives an independent estimate of the magnitude of D. A positive D value means that the Kramers doublets arising from a $^4A_1'$ ground state are such that the $M_s = \pm 1/2$ doublet is lower in energy than the $M_s = \pm 3/2$ doublet, whereas a negative D implies that this order is reversed. The signal at 1650 G is due to a transition between the $M_s = \pm 1/2$ levels; thus at pumped helium temperatures it should be possible to distinguish between the two cases as the intensity of the signal will be proportional to the population of the $M_s = \pm 1/2$ levels.

The intensity of the line at 1650 G was measured by comparison with the signal from powdered hydrated copper sulphate contained within a capillary inside the main sample tube. The cupric ion gives a signal which does not interfere with the chromium line and the intensity of which increases with decreasing temperature in the normal way. By assuming a value for D the Boltzmann populations of the various levels can be calculated and a theoretical rate of change of signal intensity with temperature derived. The intensity of the Cr^{III} signal is found to decrease on cooling, which is consistent with a negative D value; D is estimated to be $-1·3$ cm^{-1}. As the experiments at liquid helium temperatures are subject to some difficulties, mainly in temperature measurement, the magnitude of D derived from the solution of the spin Hamiltonian is expected to be the more accurate.

Table 1 shows some of the largest values obtained for the magnitudes of D and E for Cr^{III} complexes. As D for $Cr[N(SiMe_3)_2]_3$ is exceptionally large and would appear to be the largest yet reported for a Cr^{III} compound we have considered the theoretical reasons for this.

The usual interpretation of the origin of the zero-field splitting in this type of complex involves the mixing of excited states with the ground state *via* spin–orbit coupling.[9] As we already have the crystal field wavefunctions and energies of all the states for this compound [1] we have calculated D. The non-zero matrix elements of the spin–orbit coupling between the relevant states are shown in Table 2. Using second-order peturbation

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[5] J. S. Griffith, 'The Theory of Transition-Metal Ions,' Cambridge University Press, 1961, p. 334.

[6] E. C. Alyea, J. S. Basi, D. C. Bradley, and M. H. Chisholm, *Chem. Comm.*, 1968, 495.

[7] Ref. 5, p. 366.

[8] R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.*, 1969, **50**, 294; J. C. Hempel, L. O. Morgan, and W. B. Lewis, *Inorg. Chem.*, 1970, **9**, 2064.

[9] J. S. Griffith, *Mol. Phys.*, 1964, **8**, 213.

theory the energies of the Kramers doublets are (relative to the unperturbed level):

$$^4A_1',\ M_s = 3/2:\ -\zeta^2(1/3\Delta_1 + 3/2\Delta_2 + 3/2\Delta_4)$$

$$^4A_1',\ M_s = 1/2:\ -\zeta^2(7/9\Delta_1 + 1/2\Delta_2 + 2/3\Delta_3 + 1/2\Delta_4)$$

where ζ is the one electron spin–orbit coupling constant, and Δ_i refers to the energy difference between excited state i and the ground state; the index i refers to the excited states in the order $^4E''$, $^2E''[a_1'e''e']$, $^2A_1'$ and $^2E''[(e'')^3]$. The spin Hamiltonian used above predicts a separation of $2D$ between the Kramers doublets so that:

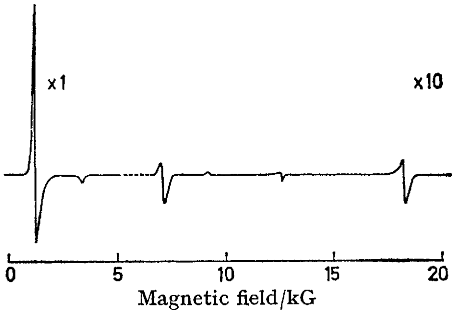

FIGURE 1 X-Band spectrum of $Fe[N(SiMe_3)_2]_3$

$$D = \zeta^2(2/9\Delta_1 - 1/2\Delta_2 + 1/3\Delta_3 - 1/2\Delta_4)$$
$$= 1{\cdot}03 - 2{\cdot}48 + 1{\cdot}24 - 2{\cdot}07$$
$$= -2{\cdot}3\ \text{cm}^{-1}$$

where we have taken ζ to be the free-ion value (273 cm^{-1}) and estimated values for the Δ_i from the crystal-field diagram derived to fit the observed electronic spectrum.[1] The calculated value for D is in good agreement with the experimental value both in respect of sign and magnitude. Apparently the negative sign and large magnitude of D are due to the low lying $^2E''$ states, which in turn are a consequence of the strong crystal field of D_{3h} symmetry. This calculation is a confirmation of the correctness of our assignments of the electronic spectrum.[1]

Iron.—The effective g-values derived from the powder spectra of $Fe[N(SiMe_3)_2]_3$ at X- and Q-band are $g_{\parallel}$ *ca.* 2 and $g_{\perp}$ *ca.* 6, with the $g_{\parallel}$ parallel component being much the weaker of the two. Several absorptions are observed at high field and are listed in Table 3; the complete spectrum at X-band is shown in Figure 1.

TABLE 3

Absorptions in the e.s.r. spectra of powdered $Fe[N(SiMe_3)_2]_3$ (line positions in G)

X-Band	Q-Band
1120 (s)	4700(s)
3380 (w)	13,000 (m)
7125 (m)	13,900 (m)
9170 (w)	18,620 (m)
12,650 (w)	
18,200 (m)	

The information derived from the magnetic susceptibility results,[1,10] the electronic spectrum,[1] and the Mössbauer studies [10] suggests a $^6A_1'$ ground state for the compound. The interpretation of the e.s.r. results is similar to that for chromium except that S in the spin Hamiltonian is 5/2 which, with zero-field splitting, gives rise to three Kramers doublets. With a g-value of 2·00 the closeness of the effective g-values to 6 and 2 suggests that D is greater than 0·2 cm^{-1} and that E is zero (or nearly so), whilst the detailed solutions of the spin Hamiltonian enable D to be determined as 1·00 cm^{-1}. As the medium strength lines at 7125 and 18,200 G show no signs of structure, E is taken to be zero. The weak lines at 9170 and 12,650 G are predicted by the theory but with zero intensity; they might be found to be weakly allowed if quartic terms had been included in the spin Hamiltonian.[8]

The above findings were checked by carrying out single-crystal studies on $Fe[N(SiMe_3)_2]_3$. With the needle axis of the crystal aligned in the direction of the magnetic field the signal was extremely broad and centred near $g = 2$. At other orientations defined by rotations of the crystal about an axis perpendicular to the needle axis the observed g-values varied with θ, the angle between the needle axis and the magnetic field direction, as shown in Figure 2. For axial symmetry the g-value at an angle θ is given by

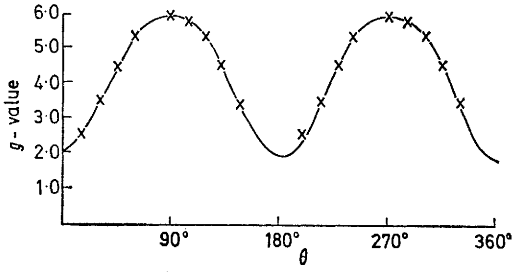

FIGURE 2 Variation of the effective g-value for a single crystal of $Fe[N(SiMe_3)_2]_3$ with θ, the angle between the field direction and the needle axis of the crystal

$$g_\theta^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta$$

which, for $g_{\parallel} = 2$ and $g_{\perp} = 6$, simplifies to

$$g_\theta = 2(1 + 8\sin^2\theta)^{\frac{1}{2}}$$

Thus the results given in Figure 2 confirm the axial symmetry of the compound and show that the crystal axes coincide with the axes of the effective g-tensor.

Depopulation experiments [11] were conducted to determine the sign of, and to provide an independent estimate of, D. The intensity of the $g = 6$ signal (for the powdered sample) was found to decrease with decrease in the temperature, and D is deduced to have the value $-0{\cdot}80$ cm^{-1}. As for chromium, the magnitude of D derived from the solutions of the spin Hamiltonian is to be preferred.

Some typical magnitudes of D and E for Fe$^{\text{III}}$ complexes are shown in Table 4; the D value for

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[10] E. C. Alyea, D. C. Bradley, R. G. Copperthwaite, K. D. Sales, B. W. Fitzsimmons, and C. E. Johnson, *Chem. Comm.*, 1970, 1715.

[11] J. Peisach, W. E. Blumberg, E. T. Lode, and M. J. Coon, *J. Biol. Chem.*, 1971, **246**, 5877.

$Fe[N(SiMe_3)_2]_3$ is seen to be representative of Fe^{III} in an axial field.

TABLE 4

Values of $|D|$ and $|E|$ for some iron(III) complexes

Complex	$\|D\|/cm^{-1}$	$\|E\|/cm^{-1}$	Ref.
$Fe(acac)_3$	0·11		*a*
$[Fe(Ph_3AsO)_4](ClO_4)_3$	1·05	0·00	*b*
$[Fe(Ph_3AsO)_4Br_2]^+$	*ca.* 1·50	0·00	*b*
Fe^{3+} in $NH_4[Co(edta)]4H_2O$	0·769	0·238	*c*
$Fe(S_2CN[CH_2]_4)_3$	1·68	*ca.* 0·56	*d*
met-myoglobin	4·4	*ca.* 0·0	*e*
$Fe[N(SiMe_3)_2]_3$	1·00	0·00	*f*

[a] M. Gerloch, J. Lewis, and R. C. Slade, *J. Chem. Soc.* (*A*), 1969, 1422. [b] S. A. Cotton and J. F. Gibson, *J. Chem. Soc.* (*A*), 1971, 859. [c] W. E. Blumberg in 'Magnetic Resonance in Biological Systems,' eds. A. Ehrenberg, B. G. Mälmstrom, and T. Wänngard, Pergamon, 1967. [d] J. Peisach, W. E. Blumberg, E. T. Lode, and M. J. Coon, *J. Biol. Chem.*, 1971, **246**, 5877. [e] E. F. Slade and D. J. E. Ingram, *Proc. Roy. Soc.*, 1969, **A312**, 85. [f] This work.

TABLE 5

Non-zero matrix elements of the spin–orbit coupling for iron(III)

The wavefunctions are abbreviated with the symbols $|\psi_i,M_s\rangle$; the ψ_i refer to the states in the order: ${}^6A_1'[(e'')^2a_1'(e')^2]$, ${}^4E''[(e'')^3a_1'e']$, ${}^4E''[(e'')^3(e')^2]$, ${}^4E''[e''(a_1')^2(e_1')^2]$, ${}^4E''[e''a_1'(e')^3]$, ${}^4A_2'[e'')^2a_1'(e')^2]$ and the second symbol in the ket gives the M_s component. The ${}^4A_2'$ state arises from the ${}^4P$ term of the free-ion; that from ${}^4F$ has a zero matrix element

	$\|\psi_2,3/2\rangle$	$\|\psi_3,3/2\rangle$	$\|\psi_4,3/2\rangle$	$\|\psi_5,3/2\rangle$
$\|\psi_1,5/2\rangle$	$\zeta/\sqrt{2}$	$\zeta\sqrt{3/2}$	$\zeta\sqrt{3/2}$	$\zeta/\sqrt{2}$

	$\|\psi_2,1/2\rangle$	$\|\psi_3,1/2\rangle$	$\|\psi_4,1/2\rangle$	$\|\psi_5,1/2\rangle$	$\|\psi_6,3/2\rangle$
$\|\psi_1,3/2\rangle$	$\zeta\sqrt{3}/\sqrt{10}$	$\zeta 3/2\sqrt{5}$	$\zeta 3/2\sqrt{5}$	$\zeta\sqrt{3}/\sqrt{10}$	$\zeta\sqrt{2}$

	$\|\psi_2,3/2\rangle$	$\|\psi_3,3/2\rangle$	$\|\psi_4,3/2\rangle$	$\|\psi_5,3/2\rangle$	$\|\psi_2,-1/2\rangle$	$\|\psi_3,-1/2\rangle$	$\|\psi_4,-1/2\rangle$	$\|\psi_5,-1/2\rangle$	$\|\psi_6,1/2\rangle$
$\|\psi_1,1/2\rangle$	$\zeta/2\sqrt{5}$	$\zeta\sqrt{3}/2\sqrt{10}$	$\zeta\sqrt{3}/2\sqrt{10}$	$\zeta/2\sqrt{5}$	$\zeta\sqrt{3}/2\sqrt{5}$	$\zeta 3/2\sqrt{10}$	$\zeta 3/2\sqrt{10}$	$\zeta\sqrt{3}/2\sqrt{5}$	$\zeta\sqrt{3}$

The theoretical interpretation of D follows similar lines to that for chromium except that for the d^5 case we do not have the wavefunctions for the doublet states. The effect of omitting these states will be considered below. The non-zero matrix elements of the spin–orbit coupling between the ground state and the quartet states are given in Table 5. If we assume that the strong field wavefunctions are good descriptions of the ${}^4E''$ states, then the energies (relative to the unperturbed level) of the Kramers doublets are given to second-order in perturbation theory by the expressions:

$$
\begin{aligned}
&{}^6A_1',\ M_s = 5/2:\ -\zeta^2(1/\Delta_2 + 3/2\Delta_3 + 3/2\Delta_4 + 1/\Delta_5)\\
&{}^6A_1',\ M_s = 3/2:\ -\zeta^2(3/5\Delta_2 + 9/10\Delta_3 + 9/10\Delta_4 + \\
&\qquad 3/5\Delta_5 + 2/\Delta_6)\\
&{}^6A_1',\ M_s = 1/2:\ -\zeta^2(2/5\Delta_2 + 3/5\Delta_3 + 3/5\Delta_4 + \\
&\qquad 2/5\Delta_5 + 3/\Delta_6)
\end{aligned}
$$

where ζ is the one electron spin–orbit coupling constant, and Δ_i are the differences in energy between the ψ_i (see Table 5) and the ground state. Thus D is found to be given by:

$$
\begin{aligned}
D &= \zeta^2(-1/10\Delta_2 - 3/20\Delta_3 - 3/20\Delta_4 - 1/10\Delta_5 + 1/2\Delta_6)\\
&= -1{\cdot}40 - 1{\cdot}06 - 0{\cdot}82 - 0{\cdot}34 + 3{\cdot}20\\
&= -0{\cdot}4\ \mathrm{cm}^{-1}
\end{aligned}
$$

where we have taken ζ to be the free-ion value of 460 cm^{-1} and have estimated the Δ_i from the crystal field diagram.[1] The shortcomings of this calculation, besides the use of perturbation theory, are that the ${}^4E''$ states are not exactly given by the strong field wavefunctions, and that the doublet states have been omitted. Allowance for the interaction between the strong field wavefunctions of ${}^4E''$ will probably make D more negative because the matrix elements of the two states ψ_3 and ψ_4 (see Table 5) are larger than that for ψ_1, thus making the first term in the expression for D more negative. On the other hand, as the doublet states cannot interact with the $M_s = 5/2$ component of ${}^6A_1'$, inclusion of these states can only make D more positive. The overall effect is not easy to assess. However, it is encouraging that our simple calculation gives the correct sign and a reasonable magnitude for D. We can conclude that the negative value arises because of the low lying ${}^4E''$ states, in close analogy to the chromium case.

EXPERIMENTAL

The compounds were prepared as described in Part I.[12] Polycrystalline specimens were sealed under vacuum in quartz or Pyrex tubes. Room-temperature spectra on polycrystalline samples were obtained using a Decca X-3 spectrometer at *X*-band (9·3 GHz) and a Varian V4502-15 spectrometer at *Q*-band (36·0 GHz).

For the anisotropy studies a well formed crystal (dark green needle) of the iron complex *ca.* 4 mm in length was mounted in a Lindemann tube in a dry-box with the aid of a microscope and sealed under vacuum. Using a trace of grease this was fixed to the base of a cylindrical Perspex rod forming part of a goniometer placed in the rectangular cavity of the spectrometer. The orientation of the crystal axis, and thus that of the trigonal axis, with respect to the magnetic field was known.

For the depopulation experiments spectra were recorded at *X*-band using a Varian E 12 spectrometer coupled to a 100 kHz modulated cylindrical cavity housed in a metal helium cavity with pumping port. Samples were inserted through an evacuable air-lock system. Temperature measurement was by means of a carbon resistor calibrated against a germanium resistor.

We thank the S.R.C. for the e.s.r. equipment (Decca X-3) and financial support (to S. A. C.), and Queen Mary College for a studentship (to R. G. C.).

[2/1825 *Received, 2nd August,* 1972]

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[12] E. C. Alyea, D. C. Bradley, and R. G. Copperthwaite, *J.C.S. Dalton*, 1972, 1580.