

IONS OF THE *d*-GROUPS IN STRONG LIGAND FIELDS

8.1. The ions and their compounds

THE palladium ($4d$) and platinum ($5d$) groups are transition groups of the same general type as the $3d$ group, but on which very much less experimentation has been carried out, mainly because their compounds are less easy to prepare. The ions take up a number of valencies, corresponding to varying numbers of electrons in the partly-filled d -shells that lie 'outside' a core of closed shells. For the $4d$ group the core is like that of the krypton atom with configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4d^6 \text{ (36 electrons).}$$

Thus, for the $4d$ group the position resembles that of the $3d$ group, where the open $3d$ shell lies outside an argon core, $1s^2 2s^2 2p^6 3s^2 3p^6$ (18 electrons), but for the $5d$ group the position is more complicated. The core is xenon-like, with configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 \text{ (54 electrons)}$$

only for the ion La^{2+} for which, like the neutral atom La, it is energetically favourable for the odd electron to enter the $5d$ shell rather than the $4f$ shell. The main group of $5d$ ions have a core corresponding to Lu^{3+} , Hf^{4+} , Ta^{5+} , or W^{6+} , with configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 \text{ (68 electrons)}$$

in which the lanthanide $4f$ shell is also filled.

The stable isotopes of the main $4d$, $5d$ groups (together with the long lived isotope 99 of technetium, which has no stable isotopes) are listed in Tables 8.1 and 8.2, together with their nuclear spins and moments. The ionic species principally studied in magnetic resonance are given in Table 8.3, together with a number of $3d$ ions which form 'strong ligand field' compounds in octahedral coordination. The ionic size for $4d$ ions, and more so for $5d$ ions, tends to be somewhat larger than that of comparable $3d$ ions in the same charge state, but it will be seen from Table 8.3 that the stable ions tend to carry a rather larger positive charge, so that their size is comparable with that of $3d$ ions with the same number of electrons in the d -shell.

TABLE 8.1

Atoms of the 4d group, and nuclear properties of the stable isotopes that have nuclear spin not equal to zero. Technetium has no stable isotopes, and the one radioactive isotope quoted is that for which magnetic resonance has been observed. The nuclear moments are quoted to four significant figures (where justified from nuclear magnetic resonance), and include the diamagnetic correction

<i>Z</i>		Mass number	Abundance (%)	Nuclear spin <i>I</i>	Nuclear magnetic moment (n.m.)	Nuclear electric quadrupole moment <i>Q</i> (barns)
39	Y	89	100	$\frac{1}{2}$	-0.1373	
40	Zr	91	11.23	$\frac{5}{2}$	-1.303	
41	Nb	93	100	$\frac{9}{2}$	+6.167	-0.2
42	Mo	95	15.72	$\frac{5}{2}$	-0.9135	0.12
		97	9.46	$\frac{5}{2}$	-0.9327	1.1
43	Tc	99	(radioactive)	$\frac{9}{2}$	+5.680	+0.3
44	Ru	99	12.7	$\frac{5}{2}$	-0.63	
		101	17.1	$\frac{5}{2}$	-0.69	
45	Rh	103	100	$\frac{1}{2}$	-0.0883	
46	Pd	105	22.2	$\frac{5}{2}$	-0.6015	
47	Ag	107	51.35	$\frac{1}{2}$	-0.1136	
		109	48.65	$\frac{1}{2}$	-0.1305	

TABLE 8.2

Atoms of the 5d group, and nuclear properties of the stable isotopes that have nuclear spin not equal to zero. The nuclear moments are quoted to four significant figures (where justified from nuclear magnetic resonance), and include the diamagnetic correction, except for the two iridium isotopes

<i>Z</i>		Mass number	Abundance (%)	Nuclear spin, <i>I</i>	Nuclear magnetic moment (n.m.)	Nuclear electric quadrupole moment <i>Q</i> (barns)
74	W	183	14.4	$\frac{1}{2}$	+0.117	
75	Re	185	37.1	$\frac{5}{2}$	+3.172	+2.6
		187	62.9	$\frac{5}{2}$	+3.204	+2.6
76	Os	187	1.64	$\frac{1}{2}$	+0.067	
		189	16.1	$\frac{3}{2}$	+0.6566	+0.8
77	Ir	191	37.3	$\frac{3}{2}$	+0.1440	+1.5
		193	62.7	$\frac{3}{2}$	+0.1568	+1.5
78	Pt	195	33.8	$\frac{1}{2}$	+0.6060	
79	Au	197	100	$\frac{3}{2}$	+0.1449	+0.58

TABLE 8.3

Ions of the 4d and 5d groups, together with ions of the 3d group known to occur in 'strong crystal field' octahedral coordination

	<i>d</i> ¹	<i>d</i> ²	<i>d</i> ³	<i>d</i> ⁴	<i>d</i> ⁵	<i>d</i> ⁶	<i>d</i> ⁷	<i>d</i> ⁸	<i>d</i> ⁹
Ions of the 3d group			Mn ⁴⁺ Cr ³⁺ V ²⁺	Mn ³⁺	Fe ³⁺ Mn ²⁺	Co ³⁺ Fe ²⁺	Ni ³⁺	Cu ³⁺	
Ions of the 4d group	Mo ⁵⁺ Nb ⁴⁺ Zr ³⁺ Y ²⁺	Mo ⁴⁺ Nb ³⁺ Zr ²⁺	Te ⁴⁺ Mo ³⁺ Nb ²⁺	Ru ⁴⁺ Te ³⁺ Mo ²⁺	Rh ⁴⁺ Ru ³⁺ Te ²⁺ Mo ⁺	Rh ³⁺ Ru ²⁺	Pd ³⁺ Rh ²⁺	Ag ³⁺ Pd ²⁺ Rh ⁺	Ag ²⁺ Rh ⁰
Ions of the 5d group			Re ⁴⁺	Os ⁴⁺	Ir ⁴⁺	Pt ⁴⁺ Ir ³⁺	Pt ³⁺		
	La ²⁺								

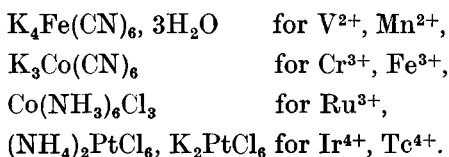
TABLE 8.4

Free ion values of $\langle r^{-3} \rangle$, $\langle r^2 \rangle$, $\langle r^4 \rangle$ for ions of the 4d group, from Freeman and Watson (1965); values of ζ from Blume, Freeman and Watson (1964), with additional values of ζ_{exp} from estimates of Dunn (1961)

		$\langle r^{-3} \rangle$ (a.u.)	$\langle r^2 \rangle$ (a.u.)	$\langle r^4 \rangle$ (a.u.)	ζ (exp) (cm ⁻¹)	ζ (calc) (cm ⁻¹)
4d ¹	Y ²⁺	2.034	5.588	59.00	300	312
	Zr ³⁺	3.160	3.857	25.33	500	507
	Nb ⁴⁺				750	
	Mo ⁵⁺				1030	
4d ²	Zr ²⁺	2.706	4.526	37.86	425	432
	Nb ³⁺	3.913	3.308	18.60	670	644
	Mo ⁴⁺				950	
	Nb ²⁺	3.414	3.829	26.98	555	560
4d ³	Mo ³⁺	4.707	2.905	14.39	800	812
	Te ⁴⁺				(1150)	
	Mo ²⁺	4.175	3.319	20.22	695	717
	Te ³⁺				(990)	
4d ⁴	Ru ⁴⁺				(1350)	
	Mo ⁺	3.662	3.954	32.98	(630)	
	Te ²⁺	5.015	2.903	15.41	(850)	
	Ru ³⁺	6.496	2.313	9.17	(1180)	1197
4d ⁵	Rh ⁴⁺				(1570)	
	Ru ²⁺	5.858	2.628	12.87	1000	1077
	Rh ³⁺	7.447	2.117	7.79	1400	1416
	Rh ²⁺	6.804	2.374	10.60	1220	1291
4d ⁶	Pd ³⁺	8.487	1.939	6.59	1640	1664
	Pd ²⁺	7.814	2.158	8.83	1600	1529
	Ag ³⁺	9.611	1.782	5.61	1930	1940
	Ag ²⁺	8.905	1.972	7.41	1840	1794

The wave-functions for *4d*, *5d* electrons have the same angular dependence as for *3d* electrons, but their radial wave-functions differ in that the *4d* functions have one node, and the *5d* two nodes, while the *3d* have none. Near the nucleus the radial wave-functions have an amplitude which increases rapidly with the atomic number *Z*, so that larger values of the hyperfine interactions, particularly in the *5f* group, are to be expected than for *3d* ions. This can be seen from Table 8.4, by comparing the values of $\langle r^{-3} \rangle$ obtained by Freeman and Watson (1965) by Hartree-Fock calculations for the *4d* group, with the corresponding values for *3d* ions in Table 7.6. Values of the spin-orbit coupling parameter ζ , which is similarly dependent on the amplitude of the wave-functions near the nucleus, are also noticeably larger for *4d* ions, the values given in Table 8.4 being due to Blume, Freeman, and Watson (1964) and Dunn (1961). No detailed calculations have been made for *5d* ions, but values of ζ in the range 2000–3000 cm⁻¹ have been estimated, and correspondingly large values of $\langle r^{-3} \rangle$ for the hyperfine interaction must be expected.

Amongst the host lattices used for electron paramagnetic resonance experiments on these ions are MgO(cubic), Al₂O₃(trigonal), and CaWO₄(tetragonal), which have also been used extensively for other transition ions. For strong ligand field octahedral complexes the configuration (*dε*)⁶ behaves as a 'diamagnetic' ion (though it has a small temperature independent susceptibility) with a closed shell (see § 8.2). Examples of this kind which have been used in host lattices are as follows:



The point symmetry at the magnetic ion in the platinum compounds is exactly octahedral, the Pt⁴⁺ ion being surrounded by a regular octahedron of chlorine ions. In the other host lattices the point symmetry is rhombic or lower, and this is true also of a number of other substances that have been used as host lattices.

We shall discuss the theory and results for the octahedral complexes first, followed by one case of eightfold coordination (*5d*¹, La²⁺ in CaF₂) in § 8.13. Historically the explanation of the magnetic properties of the iron group cyanides in terms of a strong ligand field was first given by Van Vleck (1935). The contributions from the orbital magnetic

moments, including the effects of spin-orbit splitting, were calculated by Kotani (1949) for octahedral symmetry. The theory has been extended by Kamimura (1956), Bleaney and O'Brien (1956), Kotani (1960), Tanabe (1960), and Sugano (1960); and, with particular reference to $4d$, $5d$ compounds, by Kamimura, Koide, Sekiyama, and Sugano (1960).

8.2. The strong ligand field octahedral complex

The strong crystal field approach using single electron states has been outlined in § 7.3, and the effects of bonding in § 7.4. The most important parameter is the octahedral ligand field splitting, which is denoted by $10Dq$ in the crystal field approach or, more generally, by Δ . A number of calculations indicate that the effect of covalent bonding is greatly to increase Δ over the value that is obtained in a purely 'ionic' approach; certainly, the latter gives a value that is only about one-third of that observed experimentally for Ni^{2+} in KNiF_3 . The theoretical situation is outlined by Owen and Thornley (1966), who also quote experimental results showing how Δ increases for different ligand ions for the transition ions Cr^{3+} , $3d^3$ and Ni^{2+} , $3d^8$ (see Table 8.5). In general, the value of Δ appears to be larger by

TABLE 8.5

Variation of the octahedral crystal field splitting Δ (in units of 10^3 cm^{-1}) for various ligands and two different ions of the $3d$ group (quoted by Owen and Thornley (1966) from Jorgensen (1962))

	Ligand	Br^-	Cl^-	F^-	H_2O	NH_3	CN^-
Ion	Cr^{3+} , $3d^3$		13.8	15.2	17.4	21.6	26.7
	Ni^{2+} , $3d^8$	7.0	7.2	7.3	8.5	10.8	

a factor of about 2 for the tripositive ions compared with the dipositive ions (cf. also Cu^{3+} and Ni^{2+} , $3d^8$ in Al_2O_3 , Table 7.20). In the $3d$ group the cyanides have unusually large values of Δ , values over 30000 cm^{-1} being reported for $\text{Fe}^{3+}(\text{CN})_6$ by Naiman (1961) and for $\text{Fe}^{2+}(\text{CN})_6$ by Jorgensen (1962). Since the values of the Racah parameter B are probably less than 1000 cm^{-1} for these ions in the solid state (see Table 7.5), it may be expected that such values of Δ ($= 10Dq$) are sufficient to make the configurations $(d\epsilon)^n$ the ground states (see Figs. 7.13, 7.14).

Calculations of Δ for the $4d$, $5d$ groups will obviously be much more

difficult than for the $3d$ group. However, the values of $\langle r^4 \rangle$ for the $4d$ group in Table 8.4 are very much larger than for analogous ions of the $3d$ group (Table 7.6), so that a larger ionic contribution to Δ would be expected. It is not surprising that, experimentally, all ions studied in both the $4d$, $5d$ groups are found to belong to the 'strong ligand field' configurations.

Whatever the origin of Δ , its magnitude relative to the Racah parameter B determines the order in which the d -orbitals are filled. As can be seen from a comparison of Fig. 7.7 (applicable to small Δ) and Fig. 7.8 (applicable to large Δ), the configurations are the same for d^1 , d^2 , d^3 , d^8 , and d^9 , and we shall expect only rather small differences between the results of paramagnetic resonance experiments for these ions in weak and strong ligand fields. The main differences occur for the ions d^4 to d^7 ; in a strong ligand field it is energetically preferable for the electrons first to occupy the $d\epsilon$ or t_2 shell, so that filling of this shell continues subject to the restraints imposed by the Pauli principle. This gives a closed $(d\epsilon)^6$ or $(t_2)^6$ sub-shell at d^6 , and such ions have singlet ground states, both for orbit and spin, giving only a small temperature independent susceptibility. This makes it possible to use them as diluents in a number of strong ligand field complexes containing other paramagnetic ions in electron paramagnetic resonance experiments. The ion $(d\epsilon)^5$ resembles $(d\epsilon)^1$, except that it has one 'hole' instead of one electron in the $(d\epsilon)$ shell; similarly, $(d\epsilon)^4$ resembles $(d\epsilon)^2$, with two holes instead of two electrons. The remaining ion $(d\epsilon)^3$ has an orbital singlet state, with $S = \frac{3}{2}$ which is the maximum spin-multiplicity allowed in the $(d\epsilon)$ shell; its magnetic properties are virtually 'spin-only', as for the half-filled shell d^5 in a weak ligand field complex.

The four ions $(d\epsilon)^1$, $(d\epsilon)^2$, $(d\epsilon)^4$, and $(d\epsilon)^5$ all have triplet orbital ground states that can be regarded as manifolds with $\tilde{l} = 1$ and $\tilde{g}_l = -1$, though the latter may be reduced by a factor k to allow for bonding effects. The effective spin-orbit coupling is reversed in sign for the 'hole' configurations $(d\epsilon)^4$, $(d\epsilon)^5$ from that for the 'electron' configurations $(d\epsilon)^1$, $(d\epsilon)^2$, and in an exactly octahedral field the states \tilde{J} into which the (\tilde{l}, S) manifold splits are shown in Fig. 8.1. Again, the value of the spin-orbit coupling is likely to be lower than the free ion value, because of bonding effects. Within the $(d\epsilon)$ manifold, only π -bonding orbitals can be formed, so that the value of k above should be just $k_{\pi\pi}$, as given by eqn (7.7).

For d^7 in a strong octahedral field we have just one electron in a

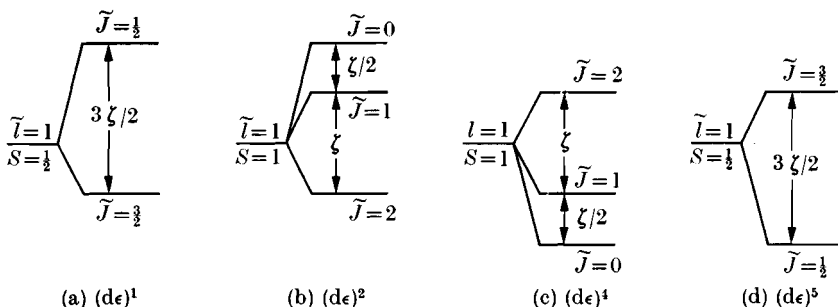


FIG. 8.1. Splittings of the $(\tilde{l} = 1, S)$ manifolds under spin-orbit coupling $\zeta(\mathbf{l} \cdot \mathbf{s})$ for the strong octahedral configurations $(d\epsilon)^1$, $(d\epsilon)^2$, $(d\epsilon)^4$, and $(d\epsilon)^5$, all of which have a triplet orbital ground state $\tilde{l} = 1$. The effective spin-orbit coupling is $\tilde{\lambda}(\tilde{\mathbf{l}} \cdot \mathbf{S})$, with $\tilde{\lambda} = -\zeta$ for $(d\epsilon)^1$ and $+\zeta$ for $(d\epsilon)^5$, and $\tilde{\lambda} = \pm\zeta/2S$ is $-\zeta/2$ for $(d\epsilon)^2$ and $+\zeta/2$ for $(d\epsilon)^4$. The splittings shown for $(d\epsilon)^2$, $(d\epsilon)^4$ assume that ζ is small compared with the electrostatic repulsion between the electrons, measured by the Racah parameter $(3B+C)$; exact formulae are given by Kamimura, Koide, Sekiyama, and Sugano (1960).

$d\gamma$ orbital 'outside' the closed sub-shell $(d\epsilon)^6$, and the behaviour of this ion (with $S = \frac{1}{2}$) is more akin to that of d^9 , with one hole in the $(d\gamma)$ shell, than to that of d^7 in a weak octahedral field.

8.3. Hyperfine interaction

The hyperfine interaction must also be calculated using one-electron wave-functions, as in eqns (7.37), (7.45), or (7.47), and (7.55) for the magnetic interaction. Values for $\langle r^{-3} \rangle$ computed for the free $4d$ ions are given in Table 8.4, but smaller values are probably required for the ion in a magnetic complex owing to bonding effects. Values of χ (see eqn (7.66)) have been computed (see Watson and Freeman 1967a) for a number of $4d$ ions; they are found to lie in the range -8 to -9 a.u., which is about three times as large as for the $3d$ ions, but again smaller values are likely to hold for the complexes. For the nuclear electric quadrupole interaction an appropriate form is found by combining eqns (17.10) and (17.12), with

$$\langle l \| \alpha \| l \rangle = -\frac{2}{(2l-1)(2l+3)} = -\frac{2}{21}$$

for a d -electron (see Table 18).

8.4. d^1 in a strong octahedral field; $(d\epsilon)^1$, (t_2) , $S = \frac{1}{2}$

The theory for this ion is essentially similar to that for d^1 in an intermediate ligand field, discussed in § 7.8.

Measurements have been reported on $4d^1$, Mo^{5+} in $\text{K}_3(\text{InCl}_6) \cdot 3\text{H}_2\text{O}$

by Owen and Ward (1956); in TiO_2 by Kyi (1962) and Chang (1964); and in K_2SnCl_6 by Low (1967). Ignoring small departures from axial symmetry, we can summarize the results by saying that g_{\parallel} lies between 1.9 and 2, with g_{\perp} somewhat lower. This indicates that distortions of the octahedron give an axial field that splits the orbital triplet by an amount large compared with the spin-orbit coupling, making the ground state a Kramers doublet that is mainly $|\tilde{0}\pm\rangle$ in the nomenclature of § 7.8 (see Tables 7.9, 7.10). We can then expand the formulae (7.80) for the g -values in the limit of small δ , giving

$$\begin{aligned} g_{\parallel} &= 2 - 2\delta^2(2+k), \\ g_{\perp} &= 2 - \sqrt{8}k\delta - 2\delta^2, \end{aligned} \quad (8.1)$$

which shows that we would expect a larger departure of g_{\perp} than of g_{\parallel} from the free spin value, since the former depends on δ and the latter only on δ^2 . The same result is also clearly to be expected from Fig. 7.23, since we are near the top of the ellipse where g_{\parallel} has its maximum value.

8.5. d^2 in a strong octahedral field; $(d\epsilon)^2$, $(t_2)^2$, $S = 1$

The theory for the ground state of this ion is similar to that for d^2 in intermediate octahedral ligand fields. In exact octahedral symmetry the splitting of the (L, S) manifold by the spin-orbit coupling is shown in Fig. 8.1(b). However, for the $5d$ group the spin-orbit coupling may be so large that it competes with the electrostatic repulsion between the two electrons; in putting the two electrons into different $(d\epsilon)$ orbitals with parallel spin we have assumed the latter is overwhelming, giving a modified form of Hund's rule. Explicit formulae for the energy levels including both electrostatic repulsion and spin-orbit coupling can be written down in terms of the two parameters ζ and $(3B+C)$, where B , C are the Racah parameters (see Kamimura, Koide, Sekiyama, and Sugano 1960).

8.6. d^3 in a strong octahedral field; $(d\epsilon)^3$, $(t_2)^3$, $S = \frac{3}{2}$

The ground state is an orbital singlet with fourfold spin degeneracy, the same as for d^3 in intermediate octahedral fields (cf. Fig. 7.11). Typical g -values are 1.992 for V^{2+} , Cr^{3+} ($3d^3$) in the complex cyanides (Baker, Bleaney, and Bowers 1956); 1.9896(5) for Tc^{4+} ($4d^3$) in K_2PtCl_6 (Low and Llewellyn 1957). These are closer to the free spin value than the corresponding g -value for $3d^3$ ions in hydrated salts because the orbital contribution is more effectively quenched by the stronger

cubic field. The magnetic hyperfine constants are almost isotropic, and arise mainly from the core polarization effect. For V^{2+} , Cr^{3+} the value of A is about 80 per cent of that observed in hydrated salts, the reduction being attributed to the effect of covalent bonding. In Tc^{4+} the large hyperfine constant $|A| = 0.0135 \text{ cm}^{-1}$ for the isotope ^{99}Tc , $I = \frac{9}{2}$, leads to a value of about -5 a.u. for the core polarization parameter χ , rather smaller than the values of 8 to 9 a.u. calculated by Watson and Freeman (1967a).

The resonance spectrum of Re^{4+} , $5d^3$ has been observed in K_2PtCl_6 by Rahn and Dorain (1964). Only the $M = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition was visible, but assuming exact cubic symmetry they deduced the values $g = 1.815(1)$, $|A| = 389(1) \times 10^{-4} \text{ cm}^{-1}$ (unresolved value for isotopes 185, 187, each with $I = \frac{5}{2}$), together with appreciable higher-order terms of the form given in eqn (18.21) for a Γ_8 quartet. However the observed anisotropy may be due to small distortions from octahedral symmetry (see Dorain and Wheeler (1966)). The low value of g illustrates the considerable role played by intermediate coupling in the $5d$ group.

8.7. d^4 in a strong octahedral field; $(d\epsilon)^4$, $(t_2)^4$, $S = 1$

This ion resembles $(d\epsilon)^2$, except that with two holes instead of two electrons in the $d\epsilon$ shell the effective sign of the spin-orbit coupling is reversed. In the rather low symmetry of the Mn^{3+} ion in the $K_3Mn(CN)_6$ complex the energy levels are split into a number of singlets, but the susceptibility (Cooke and Duffus 1955) follows roughly the variation with temperature predicted for octahedral symmetry. The latter gives a ground orbital triplet state $\bar{l} = 1$ with $\bar{g}_l = -1$, which combines with the spin $S = 1$ through the spin-orbit coupling to give states $\bar{J} = 0, 1$, and 2 , the singlet state $\bar{J} = 0$ being lowest as shown in Fig. 8.1. A rather better fit to the temperature variation of the susceptibility is obtained using a value of ζ somewhat smaller (60 to 80 per cent) than the free ion value. At very low temperatures only a temperature independent susceptibility due to the $\bar{J} = 0$ state is observed, and the salt has been used as a diluent for $K_3Co(CN)_6$ by Baker, Bleaney, and Bowers (1956).

For an ion such as Os^{4+} , $5d^4$, the spin-orbit coupling is so large that only the singlet ground state is occupied at room temperature. The effect of its temperature independent susceptibility in shifting the nuclear magnetic resonance of ^{19}F in K_2OsF_6 through the formation of bonds has been studied theoretically, and compared with experiment,

by Greenslade and Stevens (1967). The temperature variation of the susceptibility of K_2RuCl_6 and K_2OsCl_6 has been fitted theoretically by Kamimura, Koide, Sekiyama, and Sugano (1960).

8.8. d^5 in a strong octahedral field; $(d\epsilon)^5$, $(t_{2g})^5$, $S = \frac{1}{2}$

This ion can be regarded as having just one hole in the $(d\epsilon)$ shell, so that the spin $S = \frac{1}{2}$; this corresponds in Fig. 7.13 to a cubic field so strong ($Dq/B > 2.9$) that a doublet state attains a lower energy than the sextet state ${}^6S_{\frac{5}{2}}$, which is the ground state in weak and intermediate cubic fields. For one hole in the $(d\epsilon)$ shell we have again a triplet orbital ground state $\bar{l} = 1$, with an effective $\bar{g}_l = -1$; however the effective spin-orbit coupling constant will be reversed in sign to that for $(d\epsilon)^1$, so that within the triplet we have just $\zeta(\bar{l}, S)$. It has been shown by Bleaney and O'Brien (1956) that if all matrix elements to $(d\gamma)$ states are neglected, an energy matrix can be obtained somewhat similar to (7.77), irrespective of the symmetry of any distortion of the octahedron, by a suitable choice of axes. In general a set of three Kramers doublets is then obtained under the combined effect of the distortion and the spin-orbit coupling. In the nomenclature of Bleaney and O'Brien the three orbital states are $|b_+\rangle$, $|a\rangle$, and $|b_-\rangle$; the ground doublet can be written (with superscripts for the spin orientation) as

$$\left. \begin{aligned} |+\rangle &= \cos \theta [\sin \alpha |a^+\rangle + \cos \alpha |b_+^-\rangle] + \sin \theta |b_-^-\rangle \\ |-\rangle &= -\cos \theta [\sin \alpha |a^-\rangle - \cos \alpha |b_-^+\rangle] + \sin \theta |b_+^+\rangle \end{aligned} \right\} \quad (8.2)$$

and the principal g -values, using an orbital reduction factor k that is of course $k_{\pi\pi}$ in the nomenclature of § 7.4, are given by

$$\left. \begin{aligned} g_z &= \cos^2 \theta \{g_s \sin^2 \alpha - (g_s + 2k) \cos^2 \alpha\} + \sin^2 \theta (2k - g_s), \\ \frac{1}{2}(g_x + g_y) &= -\cos^2 \theta \{g_s \sin^2 \alpha + 2\sqrt{(2)}k \cos \alpha \sin \alpha\}, \\ \frac{1}{2}(g_x - g_y) &= \sin 2\theta \{g_s \cos \alpha + \sqrt{(2)}k \sin \alpha\}. \end{aligned} \right\} \quad (8.3)$$

Here the identification of the states $|+\rangle$, $|-\rangle$ has been chosen to make g_x , g_y have the same sign; for a given value of α this fixes the sign of g_z , since the sign of $(g_x g_y g_z)$ is invariant (see § 15.6).

Corresponding formulae for the magnetic hyperfine structure are more complicated because they are not independent of the symmetry of the distortion away from octahedral symmetry. Formulae are given by Bleaney and O'Brien (1956) for two cases, one in which the z -axis is along a fourfold axis of the octahedron and the other in which it is along a threefold axis; even so the magnetic hyperfine term ($\tilde{S} \cdot \mathbf{A} \cdot \mathbf{I}$)

with $\tilde{S} = \frac{1}{2}$ for the ground doublet is one in which **A** is not necessarily a 'symmetric tensor' (see the discussion in §§ 15.6 to 15.8).

3d⁵ ions, Mn²⁺, Fe³⁺, in the complex cyanides

Paramagnetic resonance measurements have been made by Baker, Bleaney, and Bowers (1956) on the *3d⁵* ions, Mn²⁺ in K₄Fe(CN)₆, 3H₂O and Fe³⁺ in K₃Co(CN)₆. The results are summarized in Table 8.6. These results are characteristically different from those for *3d⁵* in the weak field state ${}^6S_{\frac{5}{2}}$ (see Table 7.17) in that there is no sign of any fine structure (i.e. $\tilde{S} = \frac{1}{2}$), and the *g*-values are markedly anisotropic, diverging widely from the free spin value. If we take $g_s = 2$, $k = 1$, we obtain from (8.3) the following simple relationship between the principal *g*-values,

$$\frac{(g_x - g_y)}{2\sqrt{(2)}\tan \theta} = \frac{(g_x + g_y)}{-2 \sin \alpha} = \frac{g_z}{\sin \alpha - \sqrt{(2)}\cos \alpha}, \quad (8.4)$$

showing that both the unknown constants θ and α can then be found just from the ratios of the *g*-values. However, if this procedure is followed for K₃Fe(CN)₆ (diluted), one obtains values for the constants which give *g*-values in the correct proportions but whose actual values are about 8 per cent too high. This is a simple demonstration of the fact that the strong crystal field model cannot be used without making allowance for a reduction in the orbital moment because of bonding. If all the *g*-values are assumed to be negative, they can be fitted using $\cot \alpha = 1.01$, $\tan \theta = -0.028$, $k = 0.87_5$, and a reasonable fit can then be obtained for the temperature variation of the susceptibility of a single crystal of K₃Fe(CN)₆ using a value of about 280 cm⁻¹ for $|\zeta|$, which is a good deal smaller than the free ion value of about 486 cm⁻¹ (see Table 7.4).

An alternative set of parameters is obtained if we assume that g_z is positive, and g_x, g_y both negative, but these require a very low value of $k = 0.56$ and give a less good fit to the susceptibility.

4d⁵ ions, Ru³⁺

Not many results are available for *4d⁵*, a typical set being shown in Table 8.6. These are for Ru³⁺ in Co(NH₃)₆Cl₃, which is monoclinic and shows three pairs of magnetically inequivalent complexes (Griffiths, Owen, and Ward 1953; Griffiths, O'Brien, Owen, and Ward 1955). The results resemble those for the *3d⁵* ions in the same table. The hyperfine constants are an average for the two isotopes 99,101, which each

TABLE 8.6

Representative values of g and A (signs undetermined) for a number of ions in $(d\epsilon)^5$ or $(t_2)^5$ configurations. The hyperfine constants given for Ru and Ir are from the unresolved structures due to the pairs of odd isotopes ^{99}Ru , ^{101}Ru and ^{191}Ir , ^{193}Ir respectively. In each case the spins of the pair are the same, and the nuclear magnetic moments differ by less than 10 per cent. The results for Ir^{4+} are from Thornley (1968), where further values are given

	Ion and host lattice	$ g_x $	$ g_y $	$ g_z $	$ A_x $ (in units of 10^{-4} cm^{-1})	$ A_y $	$ A_z $
$3d^5$	Mn^{2+}	2.624(8)	2.182(8)	0.63(10)	84.5(5)	46.5(5)	104(20)
	$\text{K}_4\text{Fe}(\text{CN})_6, 3\text{H}_2\text{O}$						
	Fe^{3+}	2.35(2)	2.10(2)	0.915(10)			
$4d^5$	$\text{K}_3\text{Co}(\text{CN})_6$						
	Ru^{3+}	2.06(1)	2.02(1)	1.72(1)	48(2)	48(2)	49(2)
	$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	1.80(1)	1.90(1)	2.06(1)	48(2)	48(2)	50(2)
		1.15(1)	1.84(1)	2.66(1)	45(2)	41(2)	54(2)
$5d^5$	Ir^{4+}	2.168(5)	2.078(5)	1.050(3)	25.5(10)	25.5(10)	24.9(5)
	$\text{Na}_2\text{PtCl}_6, 6\text{H}_2\text{O}$						
	Ir^{4+} (cubic) $(\text{NH}_4)_2\text{PtCl}_6$	(—)1.786(4), isotropic			26.3(6), isotropic		

have $I = \frac{5}{2}$ and whose nuclear magnetic moments differ only by about 9 per cent (see Table 8.1). The rather small variation in the hyperfine constants suggests the main contribution comes from core polarization, though even the latter does not give an isotropic contribution because of the varying way in which spin and orbit are admixed in different directions. Although the hyperfine constants appear to be of the same order as those for ^{55}Mn in the same table, the nuclear moments of the two ruthenium isotopes are only about $\frac{1}{2}$ of that of ^{55}Mn (for which also $I = \frac{5}{2}$), so that the electronic parameters in the hyperfine structure for $4d^5$ are considerably larger than those for $3d^5$, as would be expected.

The spectrum of Ru^{3+} in Al_2O_3 has been observed by Geschwind and Remeika (1962), who find

$$g_{\parallel} < 0.06, |g_{\perp}| = 2.430, \quad |^{101}A_{\perp}| = 0.0043 \text{ cm}^{-1}.$$

The g -values can be fitted with $k = 0.837$ in eqns (8.3).

$5d^5$ ions, Ir^{4+}

Octahedral complexes of the type $[\text{IrCl}_6]^{2-}$, $[\text{IrBr}_6]^{2-}$ containing the ion $5d^5$, Ir^{4+} have been studied extensively by Griffiths and Owen, following the early discovery of complex hyperfine structure due to the ligand ions (Owen and Stevens 1953). Some representative results are included in Table 8.6, those for the complex in $\text{Na}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$ which is not exactly octahedral being again rather similar to the results discussed above for the $3d^5$, $4d^5$ ions. The g -values for a number of salts (taking g_{\perp} as an average of the values of g_x , g_y) can be fitted onto an ellipse similar to that in Fig. 7.23, but with a reduced value of $k = 0.83$, as shown in Fig. 8.2.

The case of cubic symmetry is of particular interest. If in eqns (8.3) we put $\theta = 0$, $\sin \alpha = (\frac{1}{3})^{\frac{1}{2}}$, $\cos \alpha = (\frac{2}{3})^{\frac{1}{2}}$ we obtain

$$g_x = g_y = g_z = g = -\frac{1}{2}g_s - \frac{4}{3}k. \quad (8.5)$$

The same result follows from Table 7.10 on putting $\cos 2\delta = \frac{1}{3}$ and taking g_{\perp} to be negative for the doublet A , which is always the lowest doublet for $(d\epsilon)^5$ because of the change of sign in the spin-orbit coupling; see Fig. 7.22. Here we have again identified the spin contribution by writing g_s and not just 2. If $k = 1$ we obtain $g = -2$, where the negative sign again emphasizes the fact that there is a large orbital contribution, and that this is not a spin-only value. If $k < 1$, we can fit the measured value of $|g| = 1.786$ for Ir^{4+} in the exact octahedral symmetry of $(\text{NH}_4)_2\text{PtCl}_6$ by again taking $k = 0.84$, and this point is also included in Fig. 8.2.

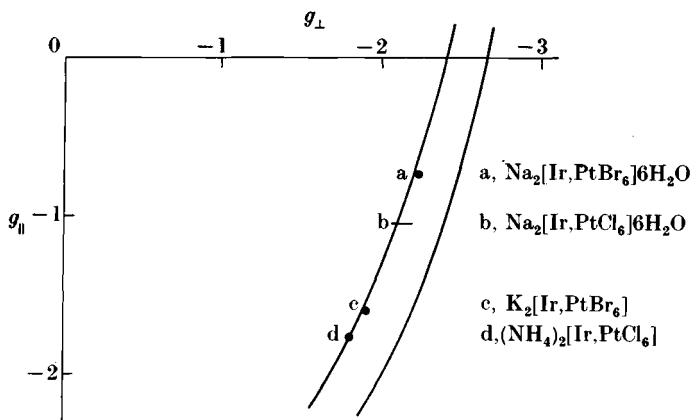


FIG. 8.2. Plot of g_{\parallel} against g_{\perp} for a number of iridium ($5d^5$), ($d\epsilon$)⁵ compounds. The curves correspond to eqns (8.3) with $g_{\perp} = \frac{1}{2}(g_x + g_y)$, (i.e. $\theta = 0$). The outer curve is drawn for $k = 1$, and is the same as that in Fig. 7.23 for a range of values between $\delta = \pi/2$ and π . The inner curve is drawn using a value of $k = 0.83$. (After Griffiths and Owen 1954).

In exact octahedral symmetry the magnetic hyperfine constant A is of course also isotropic, and from the formulae of Bleaney and O'Brien (1956) it is given by

$$A = 2g_n\beta\beta_n\langle r^{-3} \rangle \left(-\frac{8}{7} + \frac{1}{3}\kappa \right). \quad (8.6)$$

In exact octahedral symmetry the spin-dipolar contribution vanishes, and the first term in (8.6) is the orbital contribution and the second that from core-polarization plus other effects that may contribute to a term of the form $A_s(\mathbf{S} \cdot \mathbf{I})$. In terms of the parameter $\chi = -\frac{3}{2}\kappa\langle r^{-3} \rangle$ of eqn (7.66), and using a mean value of $g_n = 0.10$ for the two odd iridium isotopes 191, 193, for both of which $I = \frac{3}{2}$ and whose moments differ by less than 10 per cent (see Table 8.2), so that the hyperfine parameter in Table 8.6 is the mean for the unresolved structure, we find

$$|\chi + \frac{3}{7}\langle r^{-3} \rangle| = 37 \text{ a.u.} \quad (8.7)$$

Since both χ and $\langle r^{-3} \rangle$ are likely to be fairly large for ions in the $5d$ group, it is difficult to find a reasonable hypothesis about the relative sizes of the two contributions with which to extract further information.

Analysis of the complex hyperfine structure (cf. Fig. 1.16) due to both chlorine and bromine ligands has been attempted by Griffiths and Owen (1954). The t_2 orbitals on the central ion can bond only to p_{π} electrons on the ligand ions, so that eqn (7.10) reduces to

$$A_{\parallel}^L = 2A_d + (A_p)_{\parallel}, \quad A_{\perp}^L = -A_d + (A_p)_{\perp}. \quad (8.8)$$

In cubic symmetry the ligand hyperfine parameter A_p is isotropic, its value being

$$A_p = -2g_n^L \beta \beta_n \langle r_L^{-3} \rangle^{-\frac{1}{2}} f_t \quad (8.9)$$

where, from eqns (7.7), (7.11), $f_t = \frac{1}{4} \lambda_t^2 N_t^{-1} = \frac{1}{2}(1-k)$ is a measure of the strength of the π -bonding (in octahedral symmetry it is the probability of finding the magnetic electron on one particular ligand ion if the region where overlap of a ligand p -orbital onto a central ion d -orbital is assumed to be small). The isotropic ligand hyperfine structure $|A^L| = 26(1)$ MHz measured by Griffiths and Owen (1954) for Ir^{4+} in $(\text{NH}_4)_2[\text{PtC}_6]$ suggests that A_d can be neglected, and gives a value of $f_t = 0.066$ in reasonable agreement with the value of 0.080 obtained from the measured g -value. For bromine ligands the value of A^L is about 5 times larger, consistent with the increased value of $\langle r^{-3} \rangle$ for $4p$ orbits on a bromine ion and the larger nuclear magnetic moment.

The theory of the $(\text{IrX}_6)^{3-}$ complexes has been extended by Thornley (1968), who finds that the inclusion of admixtures from excited states appreciably affects the analysis given above of the experimental results, leading to a larger covalent character than previously assumed.

8.9. d^6 in a strong octahedral field; $(d\epsilon)^6$, $(t_2)^6$, $S = 0$

At this point the $(d\epsilon)$ shell is filled, giving as ground state an orbital and spin singlet when the octahedral ligand field strength is large enough to outweigh the effects of the electronic electrostatic repulsion (see Fig. 7.14). Under these conditions only a small temperature-independent susceptibility is observed for the ground state, and $(d\epsilon)^6$ ions have been used as diluents for other paramagnetic ions in strong octahedral field complexes.

8.10. d^7 in a strong octahedral field; $(d\epsilon)^6(d\gamma)$, $(t_2)^6e$, $S = \frac{1}{2}$

With one electron more than can be accommodated in the $(d\epsilon)$ shell, the extra electron must enter the $(d\gamma)$ or e -shell, giving a net spin $S = \frac{1}{2}$. Since matrix elements of the spin-orbit coupling vanish within the e -manifold, the configurations $(d\epsilon)^6(d\gamma)$ or $(t_2)^6e$ with one electron in the e -shell and $(d\epsilon)^6(d\gamma)^3$ or $(t_2)^6e^3$ with one hole in the e -shell have similar ground states and are experimentally difficult to distinguish. The g -values are close to the free spin value, lying above it only through spin-orbit coupling to excited $(d\epsilon)^5(d\gamma)^2$ states. As can be seen from the experimental results in Table 8.7, a Jahn-Teller effect is to be expected

TABLE 8.7

Experimental results for d^7 , $(d\epsilon)^6(d\gamma)$ or $(t_2)^6e$, in strong octahedral coordination. In two cases all three g -values are unequal, and an average is given for g_{\perp} . Values of \bar{g} are for the isotropic spectrum observed at higher temperatures in cubic or trigonal symmetry. The resonance values given here for Ni^{3+} in MgO , CaO were attributed in the references quoted to Ni^{2+} , $3d^8$, but are ascribed to Ni^{3+} by Höchli, Müller, and Wysling (1965)

Ion	Host lattice	$ g_{\parallel} $	$ g_{\perp} $	$ \bar{g} $	Reference
$3d^7$, Ni^{3+}	MgO			2.1693(5)	Orton, Auzins, Griffiths, and Wertz (1961).
	CaO			2.282(2)	Low and Suss (1963).
	Al_2O_3	2.045(5) (powder)	2.146(2)		Lacroix, Höchli, and Müller (1964).
$4d^7$, Pd^{3+}	Al_2O_3			2.163(1)	Lacroix, Höchli, and Müller (1964).
$4d^7$, Rh^{2+}	ZnWO_4	2.375(2)	2.12 (average)		Whiffin and Orton (1965).
$5d^7$, Pt^{3+}	Al_2O_3	2.011(6)	2.328(4)	2.220(1)	Geschwind and Remeika (1962).
	Yttrium	1.962	2.39		Hodges, Serway, and Marshall (1966).
	Aluminium		(average)		
	Garnet BaTiO_3	1.950(5)	2.459(3)		Simanek, Sroubek, Zdansky, Kaczer, and Novak (1966).

in cubic or trigonal symmetry, giving a change from an isotropic to an anisotropic spectrum as the temperature is lowered.

8.11. d^8 in a strong octahedral field; $(d\epsilon)^6(d\gamma)^2$, $(t_2)^6e^2$, $S = 1$

As can be seen from Fig. 7.16, the ground state of this ion is the same in a weak or a strong octahedral field; it is an orbital singlet with spin $S = 1$, for which formulae are given in Table 7.19. The g -value is almost isotropic even in a trigonal environment such as Al_2O_3 , but a strong octahedral splitting Δ reduces the departure of g from the free spin value, and the splitting of the triplet state. This is exemplified in the comparison of results for Cu^{3+} and Ni^{2+} in Al_2O_3 , given in Table 7.20.

8.12. d^9 in a strong octahedral field; $(d\epsilon)^6(d\gamma)^3$, $(t_2)^6e^3$, $S = \frac{1}{2}$

Again, the properties of this ion in the ground state are similar irrespective of the strength of the octahedral field, so that the discussion of § 7.16 is valid.

TABLE 8.8

Resonance parameters for two $4d^9$ ions. The values of A_{\parallel} , A_{\perp} are mean values for the unresolved hyperfine structure of the two isotopes ^{107}Ag , ^{109}Ag (both $I = \frac{1}{2}$; see Table 8.1); no hyperfine parameters for Rh° (^{103}Rh , $I = \frac{1}{2}$) are given

Ion	Host Lattice	$ g_{\parallel} $	$ g_{\perp} $	$ A_{\parallel} $ $ A_{\perp} $ (in units of 10^{-4} cm^{-1})		Reference
$4d^9$ Ag^{2+}	KCl (77°K)	2.193(1)	2.035(1)	40.9(5)	30.3(5)	Delbecq, Hayes, O'Brien, and Yuster (1963); Sierro (1967). Wilkens, de Graag, and Helle (1965).
	(300°K)	2.09(1) (isotropic)				
	Rh $^{\circ}$ AgCl (110°K)	2.015(2)	2.417(2)			
	(180°–350°K)	2.436(5)	2.207(5)			
	(200°–430°K)	2.287(5) (isotropic)				

TABLE 8.9

Resonance parameters for some $4d^1$, $5d^1$ ions in eightfold and fourfold coordination. The nuclear spins are $\frac{5}{2}$ for both Mo isotopes, and $\frac{7}{2}$ for ^{139}La

Ion	Host lattice	Temperature (°K)	$ g_{\parallel} $	$ g_{\perp} $	$ A_{\parallel} $ (in units of 10^{-4} cm^{-1})	$ A_{\perp} $	Isotope
$4d^1$, Y^{2+}	CaF_2	4.2	2.00	1.958			
		20	1.971 (isotropic)				
		20	1.948	1.987			
$4d^1$, Mo^{5+}	CaWO_4	4.2	1.987	1.887	8.39	41.18	(isotope 95)
					8.64	42.52	(isotope 97)
$5d^1$, La^{2+}	CaF_2	4	2.00(1)	1.904(2)	37(9)	62.6(10)	(isotope 139)
		20	1.937(2) (isotropic)		52(1) (isotropic)		

Refs: Y^{2+} , O'Connor and Chen (1964).
 Mo^{5+} , Azarbajejani and Merlo (1965).
 La^{2+} , Hayes and Twidell (1963).

Resonance parameters for Ag^{2+} and Rh^0 (both $4d^9$) ions are given in Table 8.8. These are in sites of cubic symmetry, with static Jahn–Teller distortions at low temperatures; in each case an isotropic g -value resulting from the dynamic Jahn–Teller effect is observed at higher temperatures. Very similar results are obtained for Ag^{2+} in LiCl and NaCl (Sierro 1967).

8.13. d^1 in cubic (eightfold) coordination

The spectrum of the ion La^{2+} , $5d^1$, replacing Ca^{2+} in CaF_2 has been observed by Hayes and Twidell (1963). Because the sign of the cubic field is reversed in eightfold compared with sixfold coordination, the single d -electron is in one of the ($d\gamma$) or e -states that form the ground state, and the behaviour of La^{2+} is similar to that of a d^9 ion in an octahedral field, except that its spin-orbit coupling parameter is positive, so that the g -values are smaller than the free spin value. At 4°K an anisotropic spectrum characteristic of a static Jahn–Teller effect with symmetry about a fourfold axis of the cube is observed; at 20°K this is replaced by an isotropic spectrum characteristic of a dynamic Jahn–Teller effect, whose resonance parameters are equal to the mean values of the previous spectrum. The resonance results are listed in Table 8.9, together with values for $4d^1$, Y^{2+} in CaF_2 . For the latter, one set of results is very similar to those for La^{2+} , where the value of $g_{\parallel} = 2.00$ in the anisotropic spectrum indicates that the orbital $|3z^2 - r^2\rangle$ has the lower energy. However, for Y^{2+} a spectrum with $g_{\parallel} < g_{\perp}$ could also be observed which must be ascribed to the $|x^2 - y^2\rangle$ orbital (cf. Table 7.22(a) and (b)); it is suggested that this is stabilized by a tetragonal distortion caused by an interstitial compensating ion.

The tetragonal spectra of $4d^1$, Mo^{5+} in CaWO_4 observed by Azarbayejani and Merlo (1965) presumably originate from a Mo^{5+} ion replacing a W^{6+} ion in a WO_4 distorted tetrahedron; the g -values again suggest one d -electron in a $|3z^2 - r^2\rangle$ orbital.