Studies in Eight-co-ordination. Part I. Crystal-field Energies in the D_{2d} Point-group

By **C. D. Garner** and **F. E. Mabbs,**[*] Department of Chemistry, University of Manchester, Manchester, M13 9PL

The relative energies of the d orbitals of transition-metal ions in eight-co-ordinate complexes with D_{2d} symmetry have been calculated using a point-charge model. These energies have been shown to be sensitive to the detailed geometry assumed and also to the crystal-field parameters Dq and Cp.

RECENTLY an increasing number of eight-co-ordinate complexes of known structure have been reported,[1] many of which approximate closely to the D_{2d} point-group. There have also been a number of investigations into their electronic spectra, magnetic susceptibilities, and electron spin resonance behaviour. This has prompted several authors [2-10] to use crystal-field theory to arrive at orbital splitting patterns for this geometry. The situation is unsatisfactory since not all these orbital splitting patterns agree. Furthermore, apart from an investigation [10] of the variation of the energies of the d orbitals for a small range of ligand angles, and an investigation [7] which took account of the two different Cr–O distances in $[Cr(O_2)_4]^{3-}$, there have been no attempts to determine the sensitivity of the orbital energies to variations in geometry and crystal-field parameters in this type of system.

We have extended the work of ref. 7 and we now report, in general terms, the effects of variations in geometry and crystal-field parameters on the d orbital splitting patterns under the point-group D_{2d}, confining ourselves to a point-charge model. The results of magnetic and spectral measurements on particular complexes and their interpretation in terms of the crystal-field model will be reported subsequently.

Crystal Field Calculation.—Eight-co-ordination within the point-group D_{2d} may be considered as consisting of two interpenetrating tetrahedra designated by ligand atoms of type A and B (Figure 1). Ligands of type A belong to the elongated tetrahedron whilst type B belong to the flattened tetrahedron. The total crystal-field potential exerted by these eight ligands, considered as point charges, may readily be obtained as the sum of the potentials due to the individual tetrahedra.[11] The matrix elements between the single electron d functions under the action of this potential have been evaluated [12] in terms of the parameters $Dq = Ze^2\bar{r}^4/6R^5$. and $Cp = 2Ze^2\bar{r}^2/7R^3$, where R is the metal ligand distance, and the polar angles θ_A and θ_B. In order that our calculations may be relevant to a number of structures in which the two sets of ligands are not equidistant from the central metal ion we have taken Dq and Cp of the most distant ligands to be given by:

$$(Dq)' = Dq \times a^5$$
$$(Cp)' = Cp \times a^3$$

where $a = R_A/R_B$ if $R_A \leqslant R_B$ or $a = R_B/R_A$ if $R_B \leqslant R_A$.

The eigenvalues and eigenfunctions resulting from the perturbation by the crystal field were calculated numerically for various values of Dq, Cp, and a by

[1] R. V. Parish, *Co-ord. Chem. Rev.*, 1966, **1**, 439; S. J. Lippard, *Progr. Inorg. Chem.*, 1967, **8**, 109.

[2] J. H. E. Griffiths, J. Owen, and J. M. Ward, *Proc. Roy. Soc.*, 1953, *A*, **219**, 526.

[3] B. N. Figgis and J. Lewis in 'Modern Co-ordination Chemistry,' ed. J. Lewis and R. J. Wilkins, Interscience, New York, 1960.

[4] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 1958.

[5] M. Randic, *J. Chem. Phys.*, 1961, **36**, 2094.

[6] R. M. Golding and A. Carrington, *Mol. Phys.*, 1962, **5**, 377.

[7] J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, 1962, **37**, 17.

[8] G. Glieman, *Theoret. Chim. Acta*, 1962, **1**, 14.

[9] B. R. McGarvey, *Inorg. Chem.*, 1966, **5**, 476.

[10] R. V. Parish and P. G. Perkins, *J. Chem. Soc. (A)*, 1967, 345.

[11] M. Gerloch and R. C. Slade, *J. Chem. Soc. (A)*, 1969, 1012.

[12] B. N. Figgis, 'Introduction to Ligand Fields,' Interscience, New York, 1966.

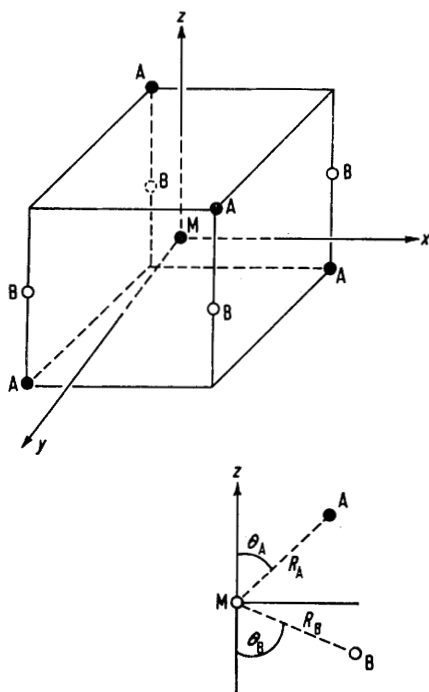diagonalising the energy matrix using the Atlas Computer at the University of Manchester.

FIGURE 1   Diagram of the axis system and labelling of the atoms in D_{2d} symmetry

RESULTS AND DISCUSSION

The parameters Dq, Cp, θ_A, θ_B, and a were chosen to have values in regions corresponding to known values in order that the sensitivity of the energy levels to variations in the geometry and crystal-field parameters might be fully investigated. General expressions for the energies of the d orbitals under the action of the crystal-field potential may be obtained by modifying those reported by Parish and Perkins,[10] and are given in the Appendix.

The results of the calculations are most conveniently presented graphically and are split into two sections *viz* those with values of Dq and Cp in the region expected for (i) divalent metal ions of the first-row transition series, and (ii) more highly charged transition-metal ions.

Divalent Metal Ions of the First-row Transition Series.— When considering the variation of the d orbital energies with θ_A and θ_B or with a we have used a fixed ratio of $Cp/Dq = 4$. This is not unreasonable since the data given by Ballhausen [13] indicates that this ratio may vary between approximately two and eight for a wide range of first-row transition-metal ions and metal-ligand distances.

(*a*) *The effect of varying* a. The effects on the d orbital energies of varying a with a number of fixed values of θ_A, θ_B, Dq, and Cp are shown in Figures 2—5.*

* In Figures 2—11 the curves for the various orbitals are:
——— d_{z^2}, — — — — $d_{x^2-y^2}$, · · · · d_{xy}, — · — · — d_{xz}, d_{yz}.

With ligands of type B arranged in a square plane and those of type A at 30° to the z axis, the d orbital splitting pattern for $Dq = 1000$ and $Cp = 4000$ cm.$^{-1}$, is shown in Figure 2. When all the ligands are equidistant then $d_{x^2-y^2}$, is, as may be expected, the most stable orbital followed by the doubly degenerate pair
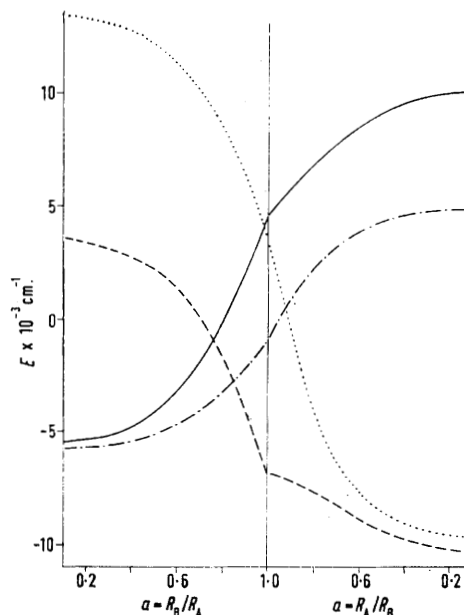

FIGURE 2   The variation of the d orbital energies with a when $\theta_A = 30°$ and $\theta_B = 90°$

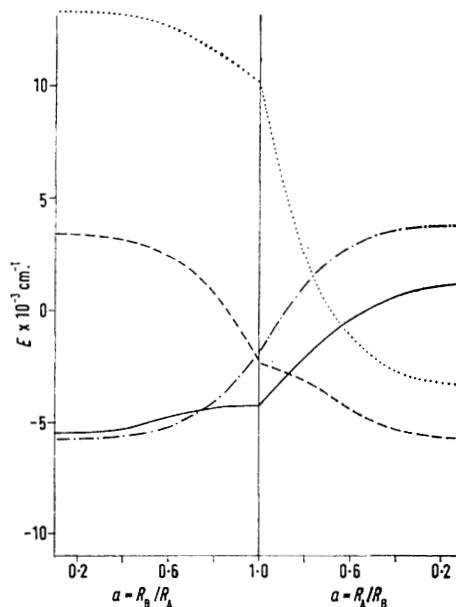FIGURE 3   The variation of the d orbital energies with a when $\theta_A = 45°$ and $\theta_B = 90°$

d_{xz}, d_{yz}. The least stable orbital, however, is d_{z^2} and not d_{xy} as might have been predicted qualitatively. Presumably the combined repulsions from four ligands

[13] C. J. Ballhausen and E. M. Ancon, *Mat. Fys. Medd. Dan. Vid. Selsk.*, 1958, **31**, 3.

close to the z axis, combined with the four in the square plane, is sufficient to destabilise d_{z^2} more than d_{xy}. As the ligands of type A are moved away from the central metal ion (*i.e.* $a = R_B/R_A$), then the energies
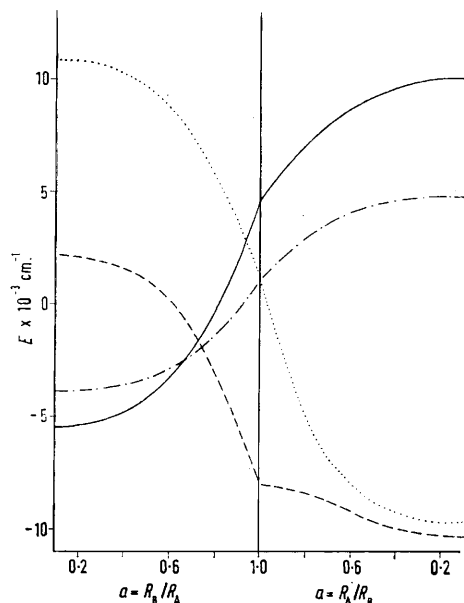

FIGURE 4   The variation of the d orbital energies with a when $\theta_A = 30°$ and $\theta_B = 75°$
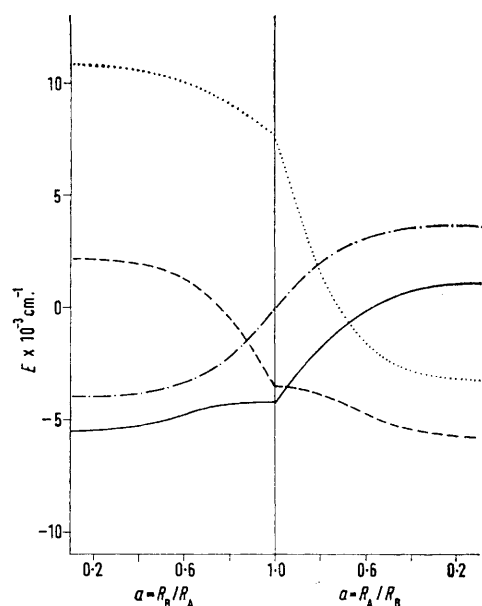

FIGURE 5   The variation of the d orbital energies with a when $\theta_A = 45°$ and $\theta_B = 75°$

of $d_{x^2-y^2}$ and d_{xy} increase, whilst those of d_{z^2} and the doubly degenerate pair decrease. At $R_B/R_A = 0.75$ the relative ordering of the d orbitals is $d_{xz},d_{yz} < d_{z^2} < d_{x^2-y^2} < d_{xy}$, and this order is maintained as the geometry tends to that of a square plane. On the other hand, as the ligands of type B are moved away from the central metal ion the energies of $d_{x^2-y^2}$ and d_{xy} decrease

whilst those of d_{z^2}, d_{xz} and d_{yz} increase. For $a < 0.92$ the ordering of the d orbitals is $d_{x^2-y^2} < d_{xy} < d_{xz},d_{yz} < d_{z^2}$ and this order is maintained as the elongated tetrahedral situation with $\theta = 30°$ is approached.

If the polar angle of the type A ligands is increased to 45°, then with $a = 1$, the relative ordering of the d orbitals is different from the case discussed (see Figure 3). The order is now $d_{z^2} < d_{x^2-y^2} < d_{xz},d_{yz} < d_{xy}$. As the ligands of type A are moved away from the central metal ion the qualitative behaviour of the d orbitals is the same as in the previous case. The same relative order is established when $a < 0.77$, but when a is greater than this value the ordering in the two cases is very different. If the type B ligands are moved away from the central metal ion then the qualitative changes in the energies of the various orbitals are similar to those observed for $\theta_A = 30°$ and $\theta_A = 45°$. However, there are two important differences, namely that in general the energy separations tend to be smaller when $\theta_A = 45°$ and that the final relative ordering of the d_{z^2} and d_{xz},d_{yz} orbitals is reversed as the elongated tetrahedral situation is approached.

Further illustrations of the sensitivity of the d orbital energies to a and geometry are shown in Figures 4 and 5, where the previous calculations have been repeated with $\theta_B = 75°$. When $a = R_A/R_B$, the change from a square-planar arrangement of ligands B to this particular flattened tetrahedron does not have any very marked effects on the energy diagrams. However, when $a = R_B/R_A$ there can be some changes in the ordering of the lowest energy orbitals, *e.g.* when $\theta_A = 45°$ and $\theta_B = 75°$ d_{z^2} is always the lowest energy orbital, whereas when $\theta_A = 45°$ and $\theta_B = 90°$ this is only true in the range $0.77 < a < 1.0$, otherwise the degenerate pair d_{xz},d_{yz} are lowest in energy.

(b) *The effect of varying* θ_A *and* θ_B. The variations in the d orbital energies with some changes in co-ordination geometry are presented in Figures 6 and 7 for fixed values of Dq, Cp, a, and the ligand angle θ_B. When ligands of type B are placed in a square-planar arrangement and those of type A are varied in position with $a = 1$, we find that starting with $\theta_A = 0$ (an artificial situation where the four A ligands are concentrated along the z axis) the splitting pattern is as expected *i.e.* $d_{x^2-y^2} < d_{xz},d_{yz} < d_{xy} < d_{z^2}$ [see Figure 6(b)]. However, as θ_A is increased, the energy of the d_{z^2} orbital rapidly decreases and it becomes the most stable orbital when θ_A has increased to *ca.* 42°. Corresponding to this decrease in energy of the d_{z^2} orbital, the energies of d_{xy} and $d_{x^2-y^2}$ increase whilst the pair d_{xz},d_{yz} go through a maximum in energy at $\theta_A = 30°$. The d orbital splitting pattern for $\theta_B = 90°$ and $R_A/R_B = 0.8$ is shown in Figure 6(c). Qualitatively the variation of the energies of the d orbitals with θ_A is the same as when $a = 1$. However, there are some differences in the relative ordering of the orbitals particularly at low values of θ_A where d_{xy} is now lower in energy than the d_{xz},d_{yz} pair. On the other hand when R_B/R_A is 0.8 the d_{xy} orbital is the most energetic at all values of θ_A, because

of the larger effect of the planar ligands on this orbital compared with the other ligands on d_{z^2}. Also the degenerate pair d_{xz},d_{yz} become the most stable orbitals when $22° < \theta_A < 44°$, a situation which is very different for the cases discussed.
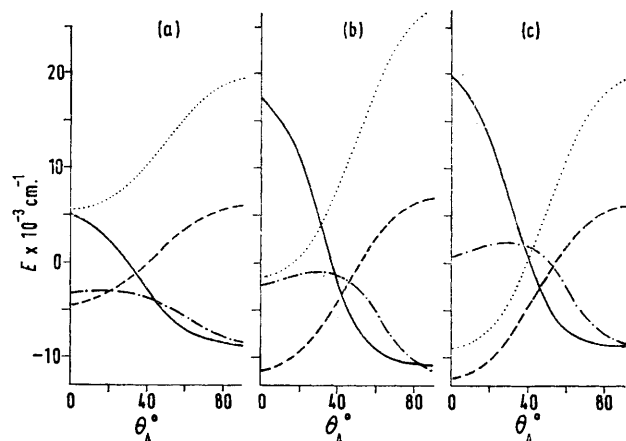

FIGURE 6 The variation of the d orbital energies with θ_A when $\theta_B = 90°$, $Dq = 1000$ cm.$^{-1}$, $Cp = 4000$ cm.$^{-1}$, and (a) $a = R_A/R_B = 0.8$, (b) $a = 1.0$, and (c) $a = R_A/R_B = 0.8$

The results of repeating the calculations with $\theta_B = 75°$, *i.e.* flattened tetrahedral array of type B ligands, are shown in Figure 7. When $R_A/R_B = 0.8$, the orbital splitting pattern is very similar to that obtained when $\theta_B = 90°$. With $a = 1$ the major difference from the situation where $\theta_B = 90°$ occurs at $\theta_A < 30°$. Here the displacement of the ligands out of the plane tends to reduce the energy of d_{xy} relative to d_{xz},d_{yz} and for the particular value of θ_B chosen d_{xy} is the lowest in energy.
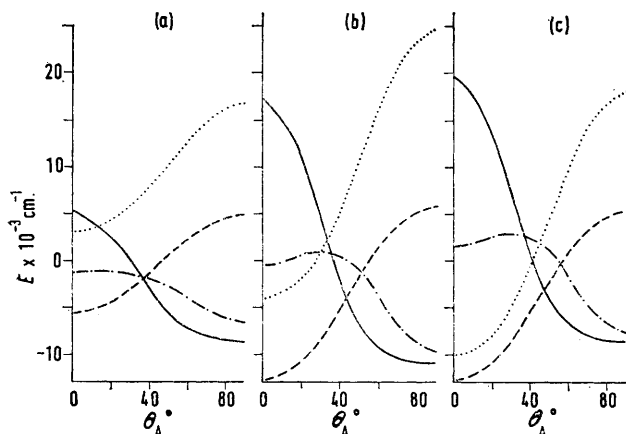

FIGURE 7 The variation of the d orbital energies with θ_A when $\theta_B = 75°$, $Dq = 1000$ cm.$^{-1}$, $Cp = 4000$ cm.$^{-1}$, and (a) $a = R_A/R_B = 0.8$, (b) $a = 1.0$, and (c) $a = R_B/R_A = 0.8$

When $R_B/R_A = 0.8$ the general trends in the variation of the orbital energies are again very similar to the situation obtained with $\theta_B = 90°$. The major differences

[14] D. A. Langs and C. Hare, *Chem. Comm.*, 1967, 890; C. D. Garner and S. C. Wallwork, *J. Chem. Soc. (A)*, 1966, 1496; J. G. Bergman, jun., and F. A. Cotton, *Inorg. Chem.*, 1966, **5**, 1420.

are that the doubly degenerate pair of orbitals now never become lowest in energy and that at values of $\theta_A < 13°$ d_{z^2} is now higher in energy than d_{xy}.

(*c*) *The effect of varying θ_A and θ_B for bidentate ligands.* The variations in the geometry of the ligands that we have made so far have assumed no particular relationship between the two interpenetrating tetrahedra. There are, however, a number of eight-co-ordinate complexes, belonging to the point-group D_{2d}, which involve co-ordination by four bidentate ligands.[7,14,15] The geometry of the ligands themselves thus places restriction on the value of θ_B relative to θ_A. The variations in the energies of the d orbitals with the angle subtended at the metal by the bidentate ligand are illustrated in Figure 8, using $Dq = 1000$ cm.$^{-1}$ $Cp = 4000$ cm.$^{-1}$, and $a = 1.0$. The ligand positions are specified in terms of θ_A, since θ_B is related to this by the angle subtended at the metal by the ligand.
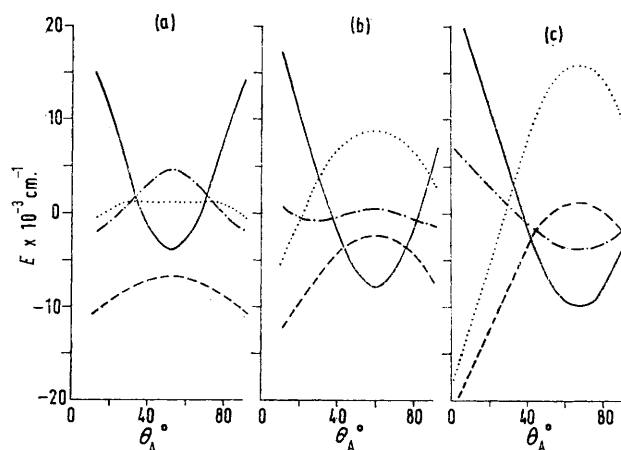

FIGURE 8 The variation of the d-orbital energies with bidentate ligands which subtend angles at the metal of (a) 75°, (b) 60°, and (c) 45°

The behaviour of the $d_{x^2-y^2}$ and d_{z^2} orbitals are qualitatively similar in each of the three cases illustrated, the variations in energy being more extreme as the angle subtended by the ligand becomes smaller. Also, as this angle becomes smaller, the value of θ_A at which d_{z^2} has a minimum and $d_{x^2-y^2}$ a maximum energy, shifts to a higher value. On the other hand the d_{xy},d_{xz}, and d_{yz} orbitals behave differently in the three situations. With a subtended angle of 75°, the energy of d_{xy} has a very flat maximum in energy at this same angle. The reason for the near constant energy of the d_{xy} orbital over the range of $\theta_A = 30$—75° is that the component of the potential in the direction of the d_{xy} orbital remains very nearly constant. This behaviour is due to the particular choice of 75° for the angle subtended at the metal. As the subtended angle is decreased to 60°, the d_{xy} orbital has a maximum energy at $\theta_A = 60°$, whilst the energies of d_{xz},d_{yz} go through minima at $\theta_A = 30$ and 90°, and a maximum at $\theta_A = 60°$. Reduc-

[15] J. G. Bergman, jun., and F. A. Cotton, *Inorg. Chem.*, 1966, **5**, 1208.

ing the subtended angle further to 45° causes a much greater variation in the energies of the orbitals and now d_{xy} has a maximum energy at $\theta_A = 67.5°$, whilst d_{xz}, d_{yz} have only a single minimum in energy which occurs at this same angle.
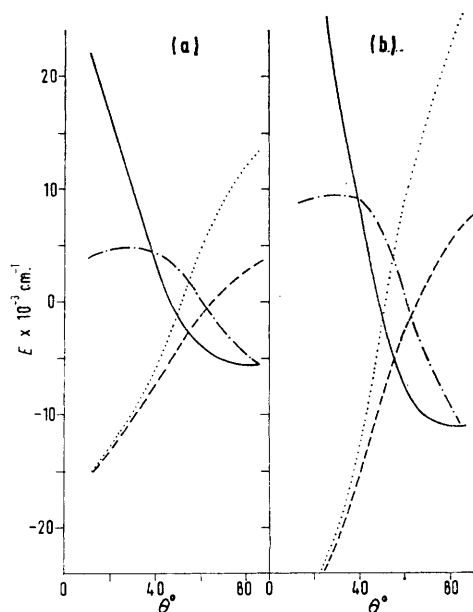

FIGURE 9 The variation of the d-orbital energies when the bidentate ligands, which subtend an angle of 45° at the metal, are replaced by single ligands at the mean position of the bidentate ligands with (a) $Dq = 1000$ cm.$^{-1}$ and (b) $Dq = 2000$ cm.$^{-1}$

It has been suggested [15-17] that the crystal-field energy diagram for complexes involving bidentate ligands of a short 'bite' may be approximated by the replacement of the donor atoms of each bidentate ligand by a single atom located at their 'centre of gravity'. Specifically this has been applied to calcium copper acetate hexahydrate [17] and to the $[Co(NO_3)_4]^{2-}$ [15] complex which contains eight-co-ordinate cobalt(II) and approximates closely to the point-group D_{2d}, but which exhibits spectral and magnetic properties characteristic of tetrahedral cobalt(II). We have performed calculations to test the validity of this concept in these systems. Figure 9 illustrates the variation of the d-orbital energies for four-co-ordinate complexes of the point-group D_{2d} with the angle, θ, that the metal–ligand vectors make with the four-fold inversion axis. The ratio $Cp/Dq = 4$ has been retained; however, results for two different values of Dq have been included. These diagrams should therefore be compared with those in Figures 8(a)—(c) remembering that for these latter diagrams θ_A corresponds to $\theta - 37.5°$, $\theta - 30°$, and $\theta - 22.5°$. It is seen that there is very little correlation between these diagrams, even if Dq is varied. In some cases the relative ordering of the d orbitals is

[16] F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, 1963, **2**, 1162.
[17] B. N. Figgis, M. Gerloch, J. Lewis, and R. C. Slade, *J. Chem. Soc. (A)*, 1968, 2028.

not even the same, whilst even when the relative order is correct the relative energy separations are hardly ever similar. We therefore conclude that the approximation is in general not valid for these systems. $[Co(NO_3)_4]^{2-}$ would appear to be a fortuitous case where the d orbital energies in the dodecahedral ligand field of the eight oxygens happen to resemble those for a tetrahedral one.[18]

(d) The effects of varying the crystal-field parameters Dq *and* Cp. The effects, on the d orbital energies, of changing the crystal-field parameters Dq and Cp for a fixed geometry are illustrated in Figures 10 and 11. These diagrams show that under certain circumstances the relative ordering of the d orbitals can be dependent on the ratio Cp/Dq. This is certainly the case when $R_B/R_A = 0.8$, where for $Cp/Dq = 8$ the relative order of the d orbitals is $d_{xy}, d_{yz} < d_{z^2} < d_{x^2-y^2} < d_{yx}$ whilst when this ratio is reduced to two the relative order is $d_{x^2-y^2} < d_{xz}, d_{yz} < d_{z^2} < d_{xy}$. The reason for the sensitivity of the relative energies of the d orbitals to the ratio Cp/Dq may be seen from the differing contributions these two parameters make to the energies of the individual orbitals (see Appendix).
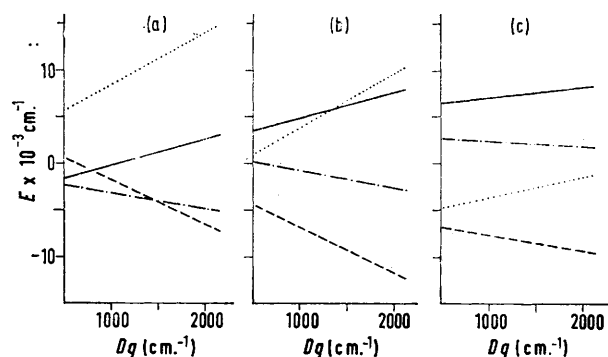

FIGURE 10 The variation of the d orbital energies with Dq when $\theta_A = 30°$, $\theta_B = 90°$ $Cp = 4000$ cm.$^{-1}$, and (a) $a = R_B/R_A = 0.8$, (b) $a = 1.0$, and (c) $a = R_A/R_B = 0.8$
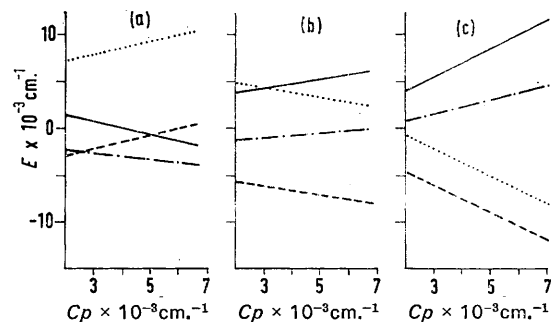

FIGURE 11 The variation of the d orbital energies with Cp when $\theta_A = 30°$, $\theta_B = 90°$, $Dq = 1000$ cm.$^{-1}$, and (a) $a = R_B/R_A = 0.8$, (b) $a = 1.0$, and (c) $a = R_A/R_B = 0.8$

More Highly Charged d-*Transition-metal Ions.*—The effect of increasing the formal charge on the central metal ion would be expected to lead to an increase in the magnitude of Dq. This will be particularly so

[18] J. Drummond and J. S. Wood, Abstract A34, Chem. Soc. Meeting, Keele, 1968.

when second- and third-transition series ions are considered. If the ratio of Cp/Dq remains constant then the only effect of increasing Dq will be to increase the energy separations between the orbitals, the relative ordering remaining unchanged. Thus when $Cp/Dq = 4$, the d-orbital splitting patterns will be qualitatively the same as those discussed previously. In a particular complex the approximate ratio of Cp/Dq may be estimated from the data of Ballhausen [13] or of Freeman and Watson [19] for $\bar{r}^n$. Using this ratio the appropriate energy-level diagrams may be constructed, for any particular value of Dq, using the equations in the Appendix. However, because the increased formal charge on the central metal ion will increase the covalency in the metal–ligand bonding we should not be surprised if the crystal-field model does not give a good description of the electronic structures of such complexes.

Summary.—The results we report for the crystal-field calculations under the point-group D_{2d} extend those of previous workers in that the effects of the detailed geometry and crystal-field parameters are considered. The information summarised in Figures 2—11 demonstrates that the d orbital energies for eight-co-ordinate complexes with this particular symmetry are sensitive to the detailed geometry and also to the crystal-field parameters. It also shows that within this model the effect of point charges at distances of up to two to three times that of the primary co-ordinating atoms may not be negligible. Thus when interpreting the electronic properties of such complexes care must be taken to choose an energy-level diagram appropriate to their detailed geometry.

APPENDIX

Algebraic Expressions for the d-*orbital energies when* $R_A < R_B$.

$$E_{d_{x^2-y^2}} = Dq/7 \left[(35 \cos^4 \theta_A - 30 \cos^2 \theta_A + 3) \right.$$
$$+ (R_A/R_B)^5 (35 \cos^4 \theta_B - 30 \cos^2 \theta_B + 3) \left] - 5Dq \left[\sin^4 \theta_A \right.\right.$$
$$+ (R_A/R_B)^5 \sin^4 \theta_B \right] - 2Cp \left[(3 \cos^2 \theta_A - 1) \right.$$
$$+ (R_A/R_B)^3 (3 \cos^2 \theta_B - 1) \right]$$

$$E_{d_{xy}} = Dq/7 \left[(35 \cos^4 \theta_A - 30 \cos^2 \theta_A + 3) \right.$$
$$+ (R_A/R_B)^5 (35 \cos^4 \theta_B - 30 \cos^2 \theta_B + 3) \left] + 5Dq \left[\sin^4 \theta_A \right.\right.$$
$$+ (R_A/R_B)^5 \sin^4 \theta_B \right] - 2Cp \left[(3 \cos^2 \theta_A - 1) \right.$$
$$+ (R_A/R_B)^3 (3 \cos^2 \theta_B - 1) \right]$$

$$E_{d_{z^2}} = 6Dq/7 \left[(35 \cos^4 \theta_A - 30 \cos^2 \theta_A + 3) \right.$$
$$+ (R_A/R_B)^5 (35 \cos^4 \theta_B = 30 \cos^2 \theta_B + 3) \right]$$
$$+ 2Cp \left[(3 \cos^2 \theta_A - 1) + (R_A/R_B)^3 (3 \cos^2 \theta_B - 1) \right]$$

$$E_{d_{xz},d_{yz}} = -4Dq/7 \left[(35 \cos^4 \theta_A - 30 \cos^2 \theta_A + 3) \right.$$
$$+ (R_A/R_B)^5 (35 \cos^4 \theta_B - 30 \cos^2 \theta_B + 3) \right]$$
$$+ Cp \left[(3 \cos^2 \theta_A - 1) + (R_A/R_B)^2 (3 \cos^2 \theta_B - 1) \right]$$

When $R_B < R_A$ the required energy expressions may be obtained by interchanging the subscripts A and B throughout.

[19] A. J. Freeman and R. E. Watson, ' Magnetism,' vol. IIA, d. G. T. Rado and H. Suhl, Academic Press, New York, 1965.