125. *Covalency and the Iron Group of Complexes.*

By T. M. Dunn.

The covalent character of the bonds in first-row transition-metal hydrates and other complexes is considered from a number of points of view. Pauling's electroneutrality principle appears to apply in the sense that in both di- and tri-positive metal-ion complexes the metal ion attains a local electrical condition close to neutrality at the expense of its ligands. This conclusion is reached by a consideration of ionisation potentials, ligand-field perturbations, and spin–orbit coupling-constant data.

UNTIL relatively recently many inorganic complexes were thought of as either predominantly " ionic " or predominantly " covalent " with respect to their magnetic moments and in their reactions. Which view was taken depended upon the property under consideration and, to a large extent, upon the interpretative theory used. The successes of ligand-field theory (crystal field approximation) emphasised the ionic point of view, although several writers (*e.g.*, Owen [1] and Stevens [2]) have recognised that this cannot be rigidly maintained and a molecular-orbital point of view allowing partial covalent character has sometimes been adopted.

It is interesting to consider the degree to which, in the light of such discussions, the overall charge on the central metal can be treated according to the electroneutrality principle. As early as 1948, Pauling [3] enunciated the postulate " of the essential electrical neutrality of the atoms in a complex " in which he assumed that the net charge is very evenly distributed so that there is always less than about one positive or negative charge on any one atom. This is equivalent to rejecting highly charged structures as unimportant in the final resonance hybrid, even though magnetically and, to some extent, spectroscopically the central atom sometimes behaves almost as a field-free ion.

Such a postulate requires charge transfer to or from the central ion (depending upon whether the formal charge on the central ion is positive or negative) through the formation of a co-ordinate bond. That this charge transfer does in fact occur, as well as its magnitude, can be inferred from several independent types of data.

(1) *Reductions in the Free Atom Term Separations.*—In 1951, Abragam and Pryce [4] in a study of the paramagnetic resonance of crystalline $Co(NH_4)_2(SO_4)_2,6H_2O$, *i.e.*, Co(II), observed that to obtain agreement with experiment it was necessary to postulate that the lowest excited quartet term [5] (^4P) lay only about 11,500 cm.$^{-1}$ higher than the ground term (^4F) instead of 14,560 cm.$^{-1}$ higher as in the free ion.

This reduction in free ion term separation for a complex has been observed by Tanabe and Sugano,[6] Owen,[1] Orgel,[7] and Stevens,[2] all of whom found that the free ion values were not consistent with the interpretation of the spectra of complexes containing the ion. The matter has since been taken up by Jørgensen in some detail, particularly for manganese [8] and nickel [9] complexes.

He considered that the reductions in the term separations (which are equivalent to a reduction in the magnitude of the interelectronic repulsion integrals variously described by their Slater–Condon parameters [10] F_k or by their Racah parameters [11] A, B, C) could

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[1] Owen, *Proc. Roy. Soc.*, 1955, *A*, **227**, 183; *Discuss. Faraday Soc.*, 1955, **19**, 127.
[2] Stevens, *Proc. Roy. Soc.*, 1953, *A*, **219**, 542.
[3] Pauling, *J.*, 1948, 1461.
[4] Abragam and Pryce, *Proc. Roy. Soc.*, 1951, *A*, **206**, 173.
[5] " Atomic Energy Levels," Vol. II, Nat. Bureau of Standards (U.S.A.) (1952).
[6] Tanabe and Sugano, *J. Phys. Soc.* (*Japan*), 1954, **9**, 766.
[7] Orgel, *J. Chem. Phys.*, 1955, **23**, 1824.
[8] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 53.
[9] Bostrup and Jørgensen, *ibid.*, p. 1223.
[10] Condon and Shortley, " Theory of Atomic Spectra," Cambridge Univ. Press, 1953.
[11] Racah, *Phys. Rev.*, 1943, **63**, 367.

arise from (*a*) the shielding of the central field by electrons donated from the ligands and/or (*b*) spreading of the partially filled *d* shell over the ligands, thereby increasing the available orbital space.

Jørgensen found (*b*) proved [8] but did not comment further upon (*a*).

Possibility (*b*) will, however, result from (*a*) if it is not merely due to a pure crystal field effect, *i.e.*, if the delocalisation is not caused simply by a reduction in the effective central field potential in which the *d* electrons move, owing to the ligands' screening off the outer parts of the orbits without actual charge transfer. In the event of charge transfer, however, it is by no means clear that (*a*) and (*b*) are, or even should be, essentially independent. Rather, (*b*) merely reflects the extent to which (*a*) has occurred since it has been amply shown [12] that the overlap between a 3*d* orbital on, say, a triply positive central ion and an orbital on a ligand such as water is negligible in the absence of some equalising perturbation, the 3*d* orbital being too tight or the ligand orbital too diffuse to overlap efficiently.

With this in mind, consider the term separations E of free atoms or ions and the changes which occur upon electron-transfer. In Table 1 the term separations known from atomic spectra [3] are compared with the experimental values,[1] E', found for the same ions in hexahydrate complexes from transitions which correlate with the atomic ${}^rF$–${}^rP$ transitions for zero perturbing fields. The latter values are compared with the separations found for isoelectronic ionic species differing only in their net charges.

TABLE 1. *Term separations (energies in cm.$^{-1}$).*

Metal	Interval	E	E' complex	B(i)	B'(iii)	B(ii)
V(III)	${}^3F$–${}^3P$	12,925	9,300	863	620	863
Ti(II)		10,420		695		755
Sc(I)		7,220		481		500
Cr(III)	${}^4F$–${}^4P$	13,770	10,200	918	680	918
V(II)		11,333	9,000	755	600	810
Ti(I) *		8,366		558		720
Co(II)	${}^4F$–${}^4P$	14,560	12,500	970	833	970
Fe(I)		11,196		746		843
Ni(II)	${}^3F$–${}^3P$	15,836	14,000	1030	933	1030
Co(I)		12,649		843		1000

* This value may be low, owing to the presence of a d^2s ${}^4F$ ground term only 860 cm.$^{-1}$ below the d^3 F term.

Table 1 shows that the values of the term separations in the complexes all lie between those for the singly and the doubly charged isoelectronic ionic species independently of whether the formal charge on the complex is three or two. The Racah B values are also included in Table 1 ($B = F_2 - 5F_4$ and the ${}^rF - {}^rP$ separation in free atoms is $15B$) and they are of three types: (i) The B values of isoelectronic ionic species of lower net charge; (ii) those calculated for less highly charged ions of the same atomic number but differing only in the number of *d* electrons present, *e.g.*, V(III), V(II), V(I); (iii) The experimental values.

It might be expected that the values of type (ii) would be better for comparison than those of type (i): nevertheless there should not be radical differences between them (as is clear from the values given), because the B values of a series of mono-, di-, or tri-positive ions increase with atomic number. For nickel(I) the configuration d^8s must be used to obtain a B value of type (ii).

Comparison of the experimental values of B with those of types (i) and (ii) suggests strongly in both cases that the central ion has approximately a single net positive charge, though for nickel(II) the result is uncertain, possibly owing to the large value of the spin–orbit coupling effects discussed by Bostrup and Jørgensen [9] (but even here on a straights interpretation the central atom would be closer to uncharged).

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[12] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332, 354.

By themselves these B values and term separations could be explained on either of the original bases with no distinction between the two subclassifications of (ii), but the closely coincident sets of B values suggest a simple interpretation of 1—2 electrons transferred to the central ion for dipositive and tripositive ions respectively. Further evidence is also available from results discussed in the next section.

(2) *Reduced Spin-Orbit Coupling Constants in Complexes.*—Owen [1] first drew attention to the fact that in many cases the spin-orbit coupling constants of ions involved in complexes, λ'' (these being found from paramagnetic resonance studies on the solid), are much lower than those for the free ion, λ, and he defined $\alpha^2 = \lambda''/\lambda$ as being a measure of the covalence tendencies. For $Ni(H_2O)_6^{2+}$ $\alpha^2 = 0{\cdot}83$ and Owen describes this as the $d_\gamma{}^*$ electrons spending 83% of the time in the central ion d_γ orbitals and about 3% in the σ^* orbitals essentially localised on the oxygen atoms.

Following the previous discussion, it seems meaningful to consider the reduction in λ as being due to simple charge-transfer from the ligands to the central metal ion. That this is so, as well as the magnitude of the transfer, is suggested by a comparison of the one-electron spin-orbit coupling parameters ζ_{3d}, obtained from atomic spectra,[5] with those given by Owen [1] (his λ and λ'' values need to be multiplied by the factor $2S$, S being the total spin, to convert them to ζ and ζ'' values respectively).

TABLE 2. (*Energies in cm.$^{-1}$.*)

Metal	Term	λ (free ion)	ζ_{3d}	ζ_{3d}M(II)	ζ_{3d}M(I)	ζ''_{3d}
V(III)	^3F	104	208	165	135	128
Cr(III)	^4F	91	273	225	185	171
V(II)	^4F	55·5	166·5		135	132
Ni(II)	^3F	−324	648		600	540

Table 2 compares the experimental values obtained [1] for the complexes ζ''_{3d} with the values known [5] from the d^n configurations of the same ion with lower net charge. This Table again shows close agreement between columns 6 and 7 and in fact $\zeta''_{3d} < \zeta_{3d}$ M(I). Nickel is again an exception, but the experimental value is at least lower than the ζ_{3d} M(I) value. It is possible to obtain an estimate of ζ_{3d} M(0) for nickel since, even though the configuration d^{10} obviously cannot yield a value, for all the transition-metal ions the spin-orbit constants for the neutral atom with configuration d^ns^2 is almost identical with that of the unipositive ion with configuration d^ns and this is, in turn, almost identical with the dipositive ion with configuration d^n. This allows a value of ζ_{3d} for Ni(IV) in the configuration d^7 to be placed equal to the value known for Ni(III) having the configuration d^7s, and the smooth curve so obtained for configurations d^7, d^8, and d^9 is then extrapolated to d^{10}. The value so obtained is in the range 500—550 cm.$^{-1}$ and probably near the latter figure so that again the nickel atom might somewhat naïvely be assumed to be effectively uncharged.

Since for a hydrogen-like atom or ion with nuclear charge Z

$$\zeta_{nl} = \text{const. } Z\int_0^\infty r^{-3}R^2(nl)\,\mathrm{d}r$$

the main contribution to ζ comes from regions of small r. This implies that the screening of the magnetic electrons by the electronic contribution from the ligand lone pairs is rather efficient *overall*, and it is at least consistent to regard this screening as resulting from charge transfer from σ bonding electrons in orbitals of the conventional d^2sp^3 type. Orgel [13] has commented on the fact that 4s- and 4p-electrons do not shield 3d-electrons in a complex, on the grounds that in a free ion the intervals between terms arising from the d^n, d^ns, and s^ns^2 configurations show only slight changes as the charge decreases, but

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[13] Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.

it must be that the twelve σ electrons contribute by force of numbers what they cannot do by virtue of their supposedly poor penetration.

Owen's procedure[1] amounts to a simple charge renormalisation of the *d* orbital to some fraction of unity (α^2) to account for the amount of the electrons lost to the ligand orbitals [the fraction being 0·87 for Ni(II), 0·79 for V(II), 0·62 for V(III), and 0·63 for Cr(III)]. The assumption is made that the d_ϵ shell is essentially unaffected by the $d_\gamma{}^*$ electron delocalisation,[14] and this seems to be true if considered only in the light that the d_ϵ functions have nodes along the line of the metal–ligand directions. However, another important factor affecting the d_ϵ shell would be any change in the central force field in which they move, and this will certainly be modified by such charge transfer as may occur even in the Owen model.

It thus seems difficult to assume that the spin–orbit coupling of a bound ion should be even nearly the same as that for the free ion; so this does not permit α^2 to be interpreted in such a simple manner. The equivalence of λ for free and bound ions requires, on a crystal-field picture, that the stabilisation of the d_ϵ shell relatively to the d_γ shell is exactly offset by the destabilisation of the whole $d_\epsilon d_\gamma$ set by the spherical term in the expansion of the perturbation potential in spherical harmonics. This is unlikely except in very special circumstances.

Support for the change in the spin–orbit coupling constant for the bound ion comes from Brown's work;[15] he pointed out that in the spectrum of ruby [*i.e.*, Cr(III) with O^{2-} as anion] the two transitions ${}^2E_{2g} \longleftarrow {}^4A_{2g}$ and ${}^2T_{2g} \longleftarrow {}^4A_{2g}$ are separated by the interval $6B + 10F_4$ which has the value about 12,000 cm.$^{-1}$ in the free ion, whereas the value found in the ruby spectrum is about 7000 cm.$^{-1}$. These transitions are configurationally wholly t_{2g}, so that it appears that the potential, in so far as it affects the t_{2g}-electrons, has suffered a drastic reduction.

On the other hand, allowing charge transfer to occur so that the net charge on the central ion is never greater than unity allows d_ϵ and d_γ orbital expansion, so that overlap and subsequent delocalisation of both $d\sigma$ and $d\pi$ type may more readily occur.

The following further evidence also supports the foregoing conclusion.

(3) *Energetic Considerations.*—From a simple consideration of the ionisation potential of metal ions[3] and ligands it is possible to strengthen the above conclusions. The Figure shows a simple energy (not free-energy) diagram for the system H_2O–Fe. It emphasises the small difference in energy between Fe^{2+}–H_2O^+ and Fe^+–$2(H_2O^+)$ compared with the other possible canonical structures. The first-row transition elements all have similar features since their ionisation potentials are of the same order. In fact the central ion has only to take one-sixth of its total electronic requirements from each ligand molecule and this will further favour the Fe^+–$2(H_2O^+)$ and Fe–$3(H_2O^+)$ structures over the other possible ones if the ligands are supposed to be within the distance where hyperpolarisability may set in.[16] The existence of such a marked energy minimum for the Fe^+–$2(H_2O^+)$ system can thus be taken as further justification for regarding charge transfer as real in such molecules.

Conclusion.—The three independent sources of data agree not only with the concept of charge transfer but also approximately with its extent. The decrease in the one-electron spin–orbit parameters may be ascribed to a mixture of a decreased central field potential due to increased screening by the donated σ electrons and the *resulting* decreased effective potential field due to the antibonding nature of the $d_\gamma{}^*$ orbital so formed. Certainly it is physically impossible, once the final " equilibrium " between ligands and central ion is established, to separate the effects into components, but on the evidence presented it seems helpful to regard the charge transfer as the dominant feature.

The energetics alone suggests that charge transfer is unavoidable, at least to the extent

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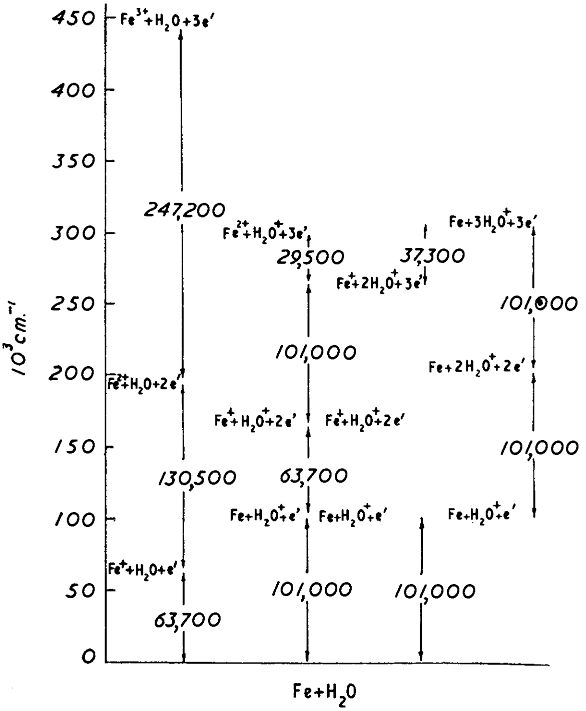
[14] Bleaney, Bowers, and Pryce, *Proc. Roy. Soc.*, 1955, *A*, **228**, 166.

[15] Brown, *J. Chem. Phys.*, 1958, **28**, 67.

[16] Coulson, Maccoll, and Sutton, *Trans. Faraday Soc.*, 1952, **48**, 106.

of one electron for a tripositive hydrate complex, and that the situation is at least favourable towards a further one-electron transfer for complexes of both di- and tri-positive ions.



It is concluded, therefore, that the Pauling electroneutrality principle appears to be strongly supported upon both experimental and theoretical grounds.

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