

Comparative Ligand Field Studies

III. The Decrease of the Integrals F^k for Manganese(II) Complexes as Evidence for Partly Covalent Bonding

CHR. KLIXBÜLL JØRGENSEN

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

The relative energy differences between the terms of an electron configuration with a partly filled d -shell can be expressed as multiples of the integrals F^2, F^4, \dots, F^{2k} . Tanabe and Sugano, Owen, and Orgel pointed out that the ligand field theory agrees much better with absorption spectra of octahedral d^n -complexes, if the values of F^k are assumed to be only 40–90 % of the values found for gaseous ions. This decrease of F^k can have two causes: the central field is decreased by electrons, donated from the ligands, and the partly filled shell is partly present in the ligands. The latter effect is proven by the extrapolation from F^k to values of the average radius $r_0 \sim 0.8-2 \text{ \AA}$ of the partly filled shell, which are larger than the ionic radii 0.5–0.8 Å. Manganese(II) complexes are especially discussed with respect to Schläfer's investigation.^{34,41} The present author assumes (1) that chloro complexes are formed, (2) that the aquo ion is octahedral and not tetrahedral, (3) that Schläfer's matrix for 4T_1 is wrong, and (4) that the red shifts of the bands of strong MnCl_2 -solutions only can be interpreted by partly covalent bonding. Generally, anion complexes are shown to have smaller values of F^k than complexes with neutral ligands. The principle of electroneutrality and the Pauling theory of covalent bonding are discussed. The explanation by Orgel of band widths is further discussed. The highly fluorescent tetraethylammonium manganese(II) bromide with tetrahedral environment of Mn(II) is described.

[THE INTEGRALS F^k FOR PARTLY FILLED SHELLS

The ligand field theory for a regular octahedral complex describes the energy levels as function of one ligand field * parameter Δ and of linear combinations of the energy levels of the gaseous ion. The latter energy levels cor-

* Orgel, Nyholm, J. Bjerrum and the present author proposed at the Xth Solvay Conference, Bruxelles, May 1956, to use the word "ligand field theory" to denote the crystal field theory extended with the molecular orbital theory for partly intermixing with the orbitals of the ligands, when applied especially to the action of the first co-ordination sphere on the partly filled d -shell in a transition group complex.

† Further, it was proposed to denote the energy difference between the partly filled γ_3 - and γ_5 -orbitals in a regular octahedral complex by Δ (as proposed by Owen⁴) rather than $10 Dq$ (cf. Schlapp and Penney³) or $(E_1 - E_2)$ (cf. Hartmann and Ilse³).

respond to more or less favourable average positions of the electrons, relative to each other, within the same shell. Slater, Condon, and Shortley ⁴ calculated the relative l^n -term energies as multipla

$$f_2 F^2 + f_4 F^4 + \dots + f_{2l} F^{2l} \quad (1)$$

of the integrals

$$F^k = e^2 \int_0^\infty \left[\int_0^{r_2} \frac{r_1^k}{r_2^{k+1}} R^2 dr_1 + \int_{r_2}^\infty \frac{r_2^k}{r_1^{k+1}} R^2 dr_1 \right] R^2 dr_2 \quad (2)$$

e is the electronic charge, R^2 the square of the radial function of the l -electron, and r_1 and r_2 are the variable distance of the electron from the nucleus.

For convenience, several linear combinations of the integrals F_k are used. For obtaining integral values of the coefficients f_k of eqn. 1, Condon and Shortley ⁴ defined for d -electrons:

$$F^2 = 49 F_2 \text{ and } F^4 = 441 F_4 \quad (3)$$

while Racah ⁵ later defined the linear combinations:

$$B = F_2 - 5 F_4 \text{ and } C = 35 F_4 \quad (4)$$

The energy differences between the terms with the maximum value of the total spin S (among which the term with the highest L is the lowest in the free ion, according to Hund's rule) are multipla of B alone.

When applying the matrices ⁶ for d^n -systems in ligand fields with the symmetry O_h , Tanabe and Sugano ⁶, Owen ¹, and Orgel ^{7,8} reported the possibility of smaller values of the term distances (and thus of F^k) for complexes than for the gaseous ions. Fig. 1 is a plot of the ligand field parameter Δ as function of B for the complex divided by B for the gaseous ion. It is seen that a rough linear correlation exist for all the considered elements. However, for a given central ion, the complexes with anions, such as chloride, oxalate or cyanide, have much smaller values of B than complexes with neutral molecules, such as water or ammonia.

Thus, the Orgel diagram, *i. e.* the energy levels as function of Δ , will be partly distorted by the new variables F^k . For nickel(II) complexes, it has been demonstrated in the two earlier papers of this series ^{9,10} that the slopes of the lines in the Orgel diagram deviate rather much from the values, predicted from the simple ligand field theory ¹¹. This was originally ^{9,12} ascribed to the interaction with other electron configurations, *viz.* $3d^{n-1}4s$. The perturbation of the d^n -states of the gaseous ion, when imbedded in the complex, can formally be described as a complicated interaction with many other states with the same $2S+1\Gamma_n$ of other electron configurations.* On the other

* The ligand field ⁴⁴ can be expanded in a series of contributions: G_0, G_2, G_4 . Two orbitals with defined values of l equal to l_1 and l_2 can only be intermixed by quantities F^k or G_k , where $|l_1 - l_2| \leq k \leq l_1 + l_2$ and k has the same parity as $l_1 + l_2$. Thus, the spherically symmetrical contribution G_0 can only intermix orbitals with the same l , but different n . As discussed elsewhere ⁵⁷, this corresponds to a variation of the central field ⁴ and hence a decrease of F^k for the partly filled shell. It is not believed that the characteristic cubic contribution G_4 is so large that the physical significance of the treatment in terms of F^k -values is invalidated.

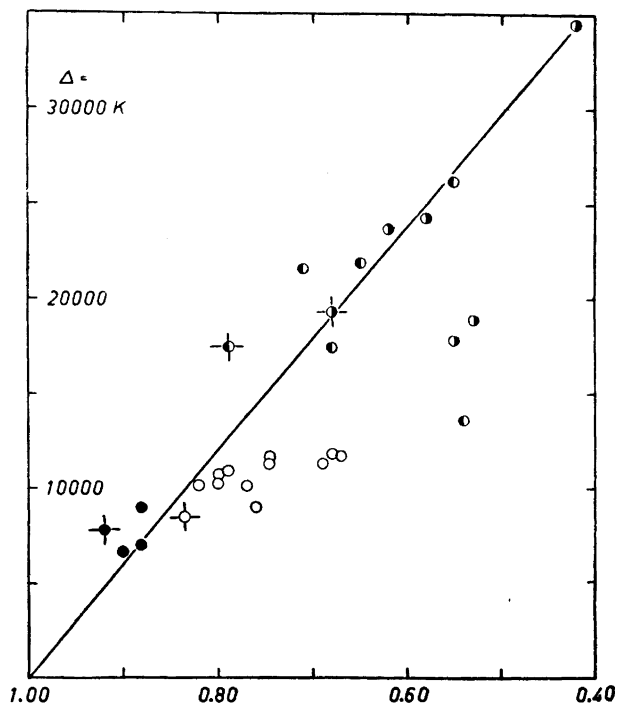


Fig. 1. The correlation between the ligand field parameter Δ and the ratio B in the complex: B in the gaseous ion. Filled circles correspond to manganese(II) complexes, empty circles to nickel(II), \odot to chromium(III) and \bullet to cobalt(III). The hexaquo ions, which have *inter alia* the highest values of B , i.e. the smallest decrease relative to the gaseous ion, are marked by a cross outside the circle.

hand, it can also to a first-order approximation be described as an interaction between the d -orbitals and the other molecular orbitals with the same γ_n and parity, i.e. the even γ_3 - and even γ_5 -orbitals in octahedral complexes^{1,13,14}. In the latter approximation, the effects of partly covalent bonding will only appear as a contribution to Δ and as decreased values of F^k , as discussed below.

The analogous description of configuration interaction⁴ by statistical methods in atomic spectroscopy was given by Trees¹⁵, who added a correction term to the energies of d^n -terms:

$$f_2 F^2 + f_4 F^4 + a L(L + 1) \quad (5)$$

and improved the agreement much by assuming values of $a \sim 100 \text{ K}^*$. Racah¹⁶ pointed out that this empirical correction corresponds to a mutual polarization of the d -orbitals by the electrons, which occupy them. It can be seen from eqn. 2 that isomorphous wavefunctions R^2 , which are only differing by

* The unit cm^{-1} for wavenumber σ will now be called $\text{K} = \text{Kayser}$, as proposed by the Joint Committee for spectroscopy.

a multiplication factor in the distance r , correspond to values of F^k which are inversely proportional to r_{\max} or another characteristic distance. Thus, the average distance of d -electrons from the nucleus must be larger in complexes than in the corresponding gaseous ions.

The perturbation theory states that the energy of two wavefunctions, totally imbedded in a sphere of negative charge, is increased by the same constant amount, thus not changing the energy difference¹⁷. If the excited wavefunction is partly present outside the sphere, the energy difference will be decreased. Thus, it must be assumed that a more negative charge is present in average between the central nucleus and the d -electron in the complexes than in the gaseous ion. This effect can be realized in two different ways:

I. Electrons from orbitals of arbitrary symmetry (*e. g.* the σ -bonding even γ_1 or odd γ_4) are donated from the ligands to the central ion, thus decreasing the effective charge by decreasing the central field in the theory of Condon and Shortley⁴.

II. Linear combinations of atomic orbitals are formed with the symmetries γ_3 and γ_5 from d -electrons and respectively σ - and π -orbitals from the ligands. Orgel^{7,8} discussed possibility I on the analogy of the influence of $4s$ -electrons on the term distances of $3d^n$ -configurations, while most authors have suggested II from Van Vleck's old discovery¹⁸ that the molecular orbital theory and Bethe's electrostatic theory both lead to a considerable value of Δ , implying magnetically anomalous complexes when Δ in octahedral d^4 - and d^7 - or 2Δ in d^5 - and d^6 -systems is larger than the necessary spin-pairing energy. The latter multipla of F^k , which are reported by Tanabe and Sugano⁶, were discussed by Griffith¹⁹. The present author has found that the average spin-pairing energy (when the terms are weighted by factors $2L + 1$) to go from q to $q - 2$ spins is:

$$\begin{aligned} q \cdot 15/4 F_2 & \quad \text{for } p^n\text{-systems} \\ q \left(\frac{35}{12} F_2 + \frac{105}{4} F_4 \right) & \quad \text{for } d^n\text{-systems} \\ q \left(\frac{35}{4} F_2 + \frac{231}{8} F_4 + \frac{1001}{4} F_6 \right) & \quad \text{for } f^n\text{-systems} \end{aligned} \quad (6)$$

if no restriction is made on the seniority number⁵. These energies are multiplied by the factor $\frac{2l + 2}{2l + 3}$, if only the maximum values of the seniority numbers are considered. Thus, the average spin pairing energy is $q \cdot 0.15 F^2$, $\sim q \cdot 0.10 F^2$, and $\sim q \cdot 0.08 F^2$ in the three cases.

Owen¹ has given experimental evidence for the possibility II from paramagnetic resonance, partly from hyperfine-structure*, due to the halogen nuclei and iridium nucleus in IrCl_6^{--} and IrBr_6^{--} , and partly from the g -values in complexes, which can be written¹

$$g = 2.00229 + \frac{k\zeta_{nd}}{\Delta} \quad (7)$$

* Recently, Tinkham⁵⁴ reported similar evidence for partly covalent bonding to fluoride ligands of Mn(II), Fe(II), Co(II), and Cr(III) imbedded in ZnF_2 . Tinkham proposes that both $2s$, $2p$, $3s$ and $3p$ orbitals of the fluoride ions are involved.

k is a constant, characteristic for the number of d -electrons, and ζ_{nd} is the Landé multiplet splitting factor. The measured g -values of complexes can be made compatible with eqn. 7 by assuming ζ_{nd} being between 10 and 40 % less in the aquo ions than in the gaseous ions of the first transition group. Owen¹ assumes that this can be directly translated to the partly filled shell containing 10–40 % of the ligands' orbitals in the squares of the wavefunction.

However, another evidence for partly covalent bonding can be obtained from the actual values of F^k of complexes. It is possible¹⁷ to extrapolate from the values of F^k to the integral:

$$W = e^2 \int_0^\infty \frac{R^2}{r^4} dr \quad (8)$$

and to define an average radius of the partly filled shell:

$$r_0 = \frac{e^2}{W} \left(\text{in } \text{Å } r_0 = \frac{116\,000 \text{ K}}{W} \right) \quad (9)$$

If the partly filled shell was concentrated on a spherical surface, all the integrals W and F^k would be equal. For a broader radial function R^2 the inequalities

$$W > F^2 > F^4 > F^6 > \dots \quad (10)$$

will be valid. For most actual ions¹⁷, F^2 will be $\cong \frac{1}{2} W$. The present author¹⁷ calculated the values of W and F^k for a rectangular function

$$R^2 = \frac{1}{n-1} \text{ for } 1 \leq r \leq n \text{ and elsewhere } R^2 = 0 \quad (11)$$

Thus, if n is written $1 + \delta$, the series can be expanded:

$$\begin{aligned} \frac{F^k}{e^2} &= \frac{1}{(n-1)^2} \left[\frac{2n}{k+1} - \frac{2}{k} + \frac{2}{n^k k(k+1)} \right] = \\ &= 1 - \frac{k+2}{3} \delta + \frac{(k+2)(k+3)}{3 \cdot 4} \delta^2 - \dots \end{aligned} \quad (12)$$

while $W = \frac{\ln n}{n-1} e^2$

If R^2 is distributed on several peaks with the areas A_n , arranged according to increasing values of r_n , it is approximately valid¹⁷:

$$\frac{F^k}{e^2} \cong \sum_n \frac{A_n^2}{r_n} \left\{ 1 - \frac{k+2}{3} \delta_n + \dots \right\} + \sum_{m>n} \frac{2 A_n A_m^k}{r_m^{k+1}} \quad (14)$$

Eqn. 14 is useful for anti-bonding combinations of atomic orbitals, which have at least two maxima of R^2 , one in the central ion and one in the ligands.

Table 1 gives the values of r_0 for gaseous ions and complexes under the assumption $W = 2 F^2$. While the analogous values¹⁷ of r_0 for 4f-shells in trivalent lanthanide complexes vary between 0.80 Å for Pr^{+++} and 0.58

Å for Tm^{+++} , somewhat smaller than the ionic radii (and are increased slightly in anion complexes, at most to 0.84 Å in the *A*-form of Pr_2O_3), it is seen from Table 1 that the values of r_0 are distinctly larger than the ionic radii given by Goldschmidt²⁰.

Table 1.

Electron configuration	F^2 for the gaseous ion	Decrease of F^2 in complexes	r_0 of gaseous ion	r_0 of complexes	Ionic radius
3 d^3 Chromium(III)	74 000 K	21–47 %	0.78 Å	0.99–1.43 Å	0.55 Å
3 d^5 Manganese(II)	66 000	8–12	0.87	0.94–0.99	0.80
3 d^6 Cobalt(III)	~82 000	32–58	0.71	1.04–1.68	0.47
3 d^8 Nickel(II)	88 000	17–35	0.66	0.79–0.99	0.68
4 d^8 Rhodium(III)	~62 000	38–62	0.93	1.3–2.5	0.69

Thus, the gaseous ion will be strongly perturbed, if it is surrounded by other ligands in the distance ~ 2 Å known from crystallography. The maximum of the $3d$ -radial function will approximately be situated* on the boundary between the central ion and the ligand in the crystals. If the approximation of distinct molecular orbitals is assumed, the anti-bonding orbitals γ_3 and γ_5 (corresponding to the partly filled d -shell) will achieve a minimum of the square of the radial function between the ligand and the central ion, because the anti-bonding wavefunction will have one node more than the corresponding bonding wavefunction.

OVERLAP INTEGRALS BETWEEN ATOMIC ORBITALS OF THE LIGANDS AND THE CENTRAL ION

If the overlap integral is $S = \int \psi_1 \psi_2 d\tau$ between the two wavefunctions ψ_1 and ψ_2 , their linear combinations can be written

$$\begin{aligned} \psi_b &= a \psi_1 + b \psi_2 & a^2 + b^2 + 2abS &= 1 \\ \psi_a &= c \psi_1 - d \psi_2 & c^2 + d^2 - 2cdS &= 1 \end{aligned} \quad (15)$$

It must be realized that the orthogonalization condition

$$ac - db + (bc - ad)S = 0 \quad (16)$$

can be satisfied in infinitely many different ways. Thus, both functions do not need to differ from the unperturbed functions, *e. g.* ψ_1 and $\frac{1}{1-S} \psi_2 - \frac{S}{1-S} \psi_1$ are orthogonal. Only when the energy is minimized, the bonding orbital ψ_b with lowest energy may contain large coefficients a and b of eqn. 15.

* Recently, Hartree⁵⁵ has calculated the self-consistent $3d$ -wavefunctions in several divalent transition group ions in the gaseous state. The deviation of the radial functions from the hydrogen-like corresponds to higher electron densities both for small and large values of the distance r from the nucleus, while they are lower for intermediate values of r . Thus, the maximum occurs at a smaller value than at r_0 given above, while on the other hand, the tail for large r is very long. The conclusions on partly covalent bonding are not essentially altered from those presented above.

The secular determinant for wavefunctions with overlap integrals S_{mn} has the diagonal elements $E_{nn} - E$ and the symmetrical non-diagonal elements $E_{mn} - S_{mn}E$. For two levels, the eigenvalues of the energy will be given by the roots E of the equation

$$(E_{11} - E)(E_{22} - E) - (E_{12} - S_{12}E)^2 = 0 \quad (17)$$

It is often assumed^{21,22} that

$$E_{12} = kS_{12} \cdot \frac{E_{11} + E_{22}}{2} \quad (18)$$

with k a constant between 1.6 and 2. The diagonal sum rule (which always is valid for $S_{mn} = 0$), *viz.*, that the sum of the roots of E is equal to the sum of E_{nn} is only valid, if $k = 1$.

The sum of the roots of eqn. 17 is:

$$E_a + E_b = (E_{11} + E_{22}) \cdot \frac{1 - kS_{12}^2}{1 - S_{12}^2} \quad (19)$$

Since $E_{11} + E_{22}$ generally is negative, $k > 1$ corresponds to relatively increased values of the average energy of the levels.

It is very difficult to derive quantitative information about the parameters S_{mn} and E_{nn} of eqns. 17—19. Many authors have discussed Slater's proposal²³

$$R^2 = r^{2n} \exp\left(-\frac{2Z_*r}{n}\right) \quad (20)$$

which has the maximum value at

$$r_{\max} = \frac{n^2}{Z_*} \quad (\text{in atomic units}) \quad (21)$$

If $r_0 \sim 1.5$ atomic unit ($= 1.5 \cdot 0.528 \text{ \AA}$) from Table 1 is identified with r_{\max} of eqn. 21 with $n = 3$, then Z_* equals 6. (*Cf.* the foot-note p. 58).

Fig. 2 gives the two radial functions R_1 and R_2 from the central ion and the ligand under the assumption that R_2 has the same dependence on distance as R_1 , but is distributed on two halves, one in the direction towards the central ion and one in the opposite direction. This is of course a rather rough approximation to the actual radial function. It is seen that the overlap between R_1 and the left-hand half part of R_2 is rather complete. While S_{12} in bi-nuclear complexes with a ligand between two metal ions might achieve large values near 1, S_{12} cannot exceed the upper limit $\sqrt{0.5}$ in mono-nuclear complexes as seen of Fig. 2, and will probably²⁴ be near 0.5. Fig. 2 gives further R_1^2 and the bonding orbital R_1^2 and anti-bonding orbital R_b^2 , normalized to the same area. Due to the normalization factors, R_a^2 will contain most of the right-hand part of R_2 , which does not overlap appreciably with R_1 . Thus, F^k of R_a^2 (which is the partly filled shell of the complex) would be 20 % of the value for R_1^2 , because only about a third of R_1^2 is refound as the first of the three maxima of R_a^2 (however, nearer to the central nucleus). This is not very different from the value 25—30 % implied by more simple reasoning on linear combination of atomic orbitals without consideration of overlap integrals.

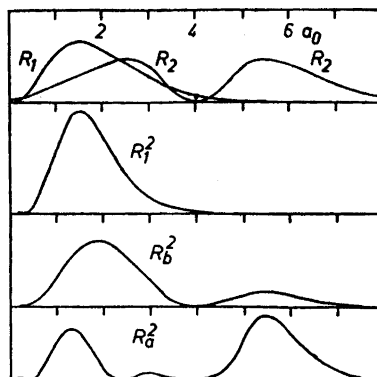


Fig. 2. The radial wavefunctions R_1 and R_2 in a complex with the centres of the central ion at 0 and of the ligand at $4 a_0$. The squares of the bonding, R_b^2 , and the anti-bonding radial function R_a^2 are given below after intermixing of R_1 and R_2 . The partly filled d-shell in a complex near the Pauling case corresponds to R_a^2 on the figure, while a complex near the electrostatic limiting case has the partly filled shell nearly as R_1^2 .

Fig. 2 represents the Pauling hybridization case with equal energies of the two orbitals and equal radial dependences. Since F^k in complexes actually is decreased 8—62 % (Table 1) and not 80 %, all the complexes exemplify intermediate cases between the electrostatic model with pure d -wavefunctions and the Pauling case. This is the situation, described by Pauling²⁵ in the somewhat cumbersome language of valence-bond orbitals applied to the groundstates. Thus, Pauling²⁵ does not recognize the magnetic criterion as distinguishing ionic and covalent complexes, but rather between complexes, where the resistance towards spin-pairing of the d -electrons is larger or smaller than the tendency towards more favourable use of the orbitals for covalent bonding. This is described by the ligand field theory as the competition between spin-pairing energy, *i. e.* multipla of F^k -integrals, and ligand field strength Δ in the cases, where the slopes of the levels with low total spin are more negative in the Orgel diagram than the slope of the lowest level with the maximum spin^{6,19,26}.

It may be questioned, if σ -bonding is much more important than π -bonding in the d^n -complexes. Since the bond lengths^{27,28} to the first approximation are an increasing linear function of the number of γ_3 -electrons, the σ -anti-bonding character of these electrons seem well established. However, the F^k -integrals seem to be decreased by the same amount for the levels 2I_3 (G) of γ_5^2 in chromium(III) complexes* and 1I_3 (D) of $\gamma_5^6 \gamma_3^2$ in nickel(II) complexes as for the levels 4I_4 and 3I_4 , respectively, which contains in average 1.5 γ_3 -electron more than the groundlevels. Thus, the delocalization of γ_5 -electrons (which are π -anti-bonding with respect to filled molecular orbitals with less energy and π -bonding with respect to empty molecular orbitals with higher energy) does not seem to be less than of γ_3 -electrons.

* as also Mo(III) and Re(IV). Cf. this journal 11 (1957) 82.

Probably, the large overlap integrals make π -bonding more important²⁴ than usually believed. Williams²⁹ assumes that the small values of Δ for iodo-, bromo-, and chloro-complexes and high values of Δ for cyanide complexes are due to the influence of donation of π -electrons respectively, in the direction from the ligands to the central ion and in the opposite direction. Wolfsberg and Helmholz²¹ assume so strong π -bonding in CrO_4^{--} and MnO_4^- that the negative sign of Δ for tetrahedral complexes, implied by both the electrostatic and the σ -bonding models, is reversed.

The experimental evidence from the absorption spectra that the degree of intermixing of d -electrons with γ_3 - and γ_5 -electrons of the ligands is 10–30 % rather than 50 % corresponds to higher energy of the unperturbed d -electrons than of the ligands' electrons. It can be estimated from Latimer's data²⁹ that the energy necessary for the reaction in aqueous solution



is between 4.5 and 5 eV ($\sim 40\,000$ K). Thus, it can be estimated from the oxidation potentials (when entropy effects are neglected) that the removal of a $3d$ -electron from $\text{Co}(\text{NH}_3)_6^{++}$ demands $\sim 4\text{eV}$ and from $\text{Co}(\text{H}_2\text{O})_6^{++} \sim 6$ eV. However, the optical transitions to states of a nearly free electron are not possible with so small an energy, because the ligands have not sufficient time for finding the new equilibrium positions, due to the Franck-Condon principle²⁸. Further, it is only approximatively valid that the ionization potentials are equal to the energies of the orbitals, since the other orbitals rearrange slightly during the ionization process. The ionization potentials of most ligands will be ~ 8 eV, but this value refers probably to π -electrons, while the σ -electrons have somewhat lower energies¹⁴. ($1 \text{ eV} = 8\,067$ K).

If complexes with ~ 50 % intermixing of γ_3 -electrons exist (*i. e.* the Pauling case), weak Laporte-forbidden electron transfer bands would be observed due to transition of bonding γ_3 -electrons to γ_5 at nearly the same wavenumbers as the ligand field bands, which are caused by $\gamma_5 \rightarrow \gamma_3$ transitions within the partly filled shell. This case has not been observed, and only in systems, which have a strong tendency towards internal redox processes, such as¹⁴ IrBr_6^{--} or Pt I_6^{--} , the electron transfer bands occur at lower wavenumber than the predicted ligand field bands.

The donation of electrons from the ligands, *e. g.* the σ -bonding γ_1 - and odd γ_4 -electrons, corresponding to the sp^3 -part of the Pauling $d^2 sp^3$ -hybridization in octahedral complexes, decrease the effective charge on the central ion. Since the integrals F^k are roughly proportional to Z_0 , where $Z_0 - 1$ is the external charge, this effect co-operates in decreasing F^k for complexes. The "principle of electroneutrality", as discussed by Pauling²⁵, seems to allow a residual charge between +1 and +2 in the domain of the central ion. Since the potential energy of a sphere with the electrical charge z and the radius r is proportional to z^2/r , one would expect small ions with high charges to be unstable. However, chemistry is remarkably unsymmetric with respect to the existence of cations and anions. While elementary anions are not easily provided with more negative charge than -2 (and even divalent anions seem to be highly polarized and only stable near cations), thorium(IV) aquo ions are definite entities. Since the ionic radius increases with negative charge and

decreases with positive charge, the effect can perhaps be described as the breakdown of highly negative anions with large radius, due to the presence of small cations with strong electrostatic fields. However, only the molecular orbital theory can explain the actual complicated behaviour of complexes, and recent investigations^{25,27,30} have emphasized the importance of mutual donation of *e. g.* σ -electrons from the ligands and π -electrons to the ligands. That these subtle effects have strong influence on the chemistry of ions without inert gas configurations is evident from the highly different *cyclopentadienide* complexes formed by thorium(IV) and uranium(IV)³¹.

The increased acidity of water or ammonia, when bound to cations, might be taken as evidence for partly covalent bonding. However, pK of the complexes is probably not a linear function of the induced charge of the ligands, assuming *e. g.* the charge $+\frac{1}{2}$ on each water molecule of an aquo ion with $pK = 7$. It is necessary to consider the possibility of stronger covalent bonding of the hydroxo- or amido-group than of ammonia and water. Thus, the acidity¹⁴ of $\text{Pt}(\text{NH}_3)_6^{+4}$, which is stronger than of NH_4^+ , does not imply with certainty a charge above $+1$ of each ligand. Of purely electrostatic reasons, complex-bound H_2O and NH_3 would have the same energy of proton dissociation as H_3O^+ and NH_4^+ , when the charge of the central ion is $\frac{3.3 \text{ \AA}}{1.3 \text{ \AA}} \sim 2.5$, since the distances from the proton to the hydroxyl group and the central ion are roughly 1.3 \AA and 3.3 \AA , respectively.

MANGANESE(II) COMPLEXES

The absorption spectra measured by Gielessen³² of manganese(II) salt hydrates and by the present author³³ of the aqueous solution of MnSO_4 were interpreted by Orgel⁸ on basis of the ligand field theory for an octahedral d^5 -system^{6,7} (*cf.* Fig. 3). Ten transitions from the groundstate ${}^6T_1(S)$ to quartet levels are predicted, and the present author¹² reported later the missing weak bands in the ultraviolet. Table 2 gives the bands with the identification of their excited levels of MnCl_2 and MnSO_4 in aqueous solution and the other complexes with ethylenediaminetetraacetate, ethylenediamine, and tartrate. The hexaquo ion has nearly the same spectrum (found in dilute MnCl_2) as the un-ionized complex $\text{MnSO}_4(\text{H}_2\text{O})_5$ probably occurring in strong sulfate solutions.

Schläfer³⁴ applied also the ligand field theory to the absorption spectra of $\text{MnCl}_2 \cdot 4 \text{ H}_2\text{O}$ and $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{ H}_2\text{O}$, which were assumed to contain the ions $\text{Mn}(\text{H}_2\text{O})_4^{++}$ and $\text{Fe}(\text{H}_2\text{O})_6^{+++}$. Schläfer's assignment of levels deviate rather much from that of Orgel⁸ and the present author²⁶. The three levels 4T_5 seem to be shifted erroneously $\sim 6000 \text{ K}$ towards lower wavenumbers. The problem, whether the manganese(II) aquo ion is tetrahedral or octahedral, cannot be decided from the quantum numbers T_n , since the matrices for d^5 -systems are symmetrical⁶ with respect to a change of sign of Δ . However, the value of $\Delta = 7800 \text{ K}$ for manganese(II) suggests an octahedral co-ordination, when compared to $\Delta = 10400 \text{ K}$ for iron(II), 9300 K for cobalt(II) and 8500 K for nickel(II) hexaquo ions. In a tetrahedral complex with purely electrostatic ligand fields, Δ would be³⁵ multiplied by

Table 2. The absorption bands of manganese(II) complexes, assigned to the excited levels (cf. Fig. 3). Wave-length λ in $m\mu$, wavenumber σ in K , one-sided halfwidth δ in K , and molar extinction coefficient ϵ of each band maximum. Shoulders in parenthesis.

	${}^4\Gamma_4(G)$	${}^4\Gamma_5(G)$	${}^4\Gamma_1(G)$ and ${}^4\Gamma_3(G)$	${}^4\Gamma_5(D)$	${}^4\Gamma_3(D)$	${}^4\Gamma_4(P)$	${}^4\Gamma_3(F)$	${}^4\Gamma_4(F)$	${}^4\Gamma_5(F)$
1. 8M $MnSO_4$ $\Delta = 7800 K$	λ 532	435	400, (396)	356	337	304	279	262	248
	σ 18 800	23 000	25 000, (25 250)	28 100	29 700	32 800	(35 800)	(38 400)	(40 400)
	δ 1 200	900	200, 200	600	400	1 500	400	—	—
	ϵ 0.017	0.014	0.036, 0.018	0.023	0.021	0.04	—	—	—
2. 3M $MnCl_2$	λ 528	435	(405), 400, (395)	359	340	313	283	272	(268)
	σ 18 900	23 000	(24 700), 25 000, (25 300)	27 800	29 400	32 000	(35 400)	36 800	(37 400)
	δ 1 150	1 000	—	600	—	1 300	—	—	—
	ϵ 0.018	0.014	0.029	0.039	0.024	0.022	0.01	0.04	0.08
1M $MnCl_2$, 6M HCl	λ 521	428	412, 408	360	345	319	285	274	253
	σ 19 200	(23 400)	24 300, 24 500	27 800	29 000	31 400	(35 100)	(36 500)	(39 600)
	δ 1 200	1 200	—	800	—	—	—	—	—
	ϵ 0.023	0.027	0.040	0.08	0.04	0.038	—	0.07	—
1M $MnCl_2$, 9M HCl	λ 517	442	425, 412	362	347	320	—	—	—
	σ 19 300	22 700	23 500, 24 300	27 700	28 900	31 300	—	—	—
	δ 1 200	—	—	—	—	—	—	—	—
	ϵ 0.023	0.035	0.048, 0.046	0.12	0.06	0.06	—	—	—
1M $MnCl_2$, 1.5M KSCN $\Delta = 7900 K$	λ 546	440	(410), 405, (401)	361	339	—	—	—	—
	σ 18 300	22 800	(24 400), 24 700, (24 900)	27 700	29 500	—	—	—	—
	δ 1 400	—	—	—	—	—	—	—	—
	ϵ 0.021	0.018	0.036, 0.050, 0.034	0.080	0.028	—	—	—	—
Mn <i>enta</i> ²⁺ $\Delta = 6800 K$	λ 532	471	411	367	343	—	—	—	—
	σ 18 800	(21 200)	24 300	27 200	29 200	—	—	—	—
	δ 1 500	—	(-) = 400, (+) = 100	—	—	—	—	—	—
	ϵ 0.044	0.04	0.25	0.03	0.03	—	—	—	—
Mn ²⁺ + in tartrate + NH_3 $\Delta = 7000 K$	λ 550	462	425, 415	—	—	—	—	—	—
	σ 18 200	21 700	23 500, 24 100	—	—	—	—	—	—
	δ 1 600	900	400, 400	—	—	—	—	—	—
	ϵ 0.09	0.12	0.32, 0.36	—	—	—	—	—	—
Mn <i>en</i> ₃ ²⁺ $\Delta = 9100 K$	λ 630	494	422	372	—	—	—	—	—
	σ 15 900	20 300	23 700	26 900	—	—	—	—	—
	δ 1 500	1 500	300	—	—	—	—	—	—
	ϵ 0.055	0.063	0.10	0.05	—	—	—	—	—

a factor $\frac{1}{3}$. The molecular orbital theory may cause strong deviations from this ratio, as discussed p. 61, but the evidence from CoCl_4^{--} suggests very low values of Δ in tetrahedral complexes. Hartmann and Fischer-Wasels³⁶ assume also tetrahedral co-ordination of paramagnetic nickel(II) complexes. However, the only certain case of this is found by Weyl³⁷ as a purple nickel glass in rubidium silicate. J. Bjerrum³⁸ demonstrated a regular development in the absorption spectra of Ni^{++} with from zero to six ammonia molecules. The latter type of argument can also be applied to manganese(II): as can be calculated from Table 2, $\Delta = 9\ 100$ K of the tris(ethylenediamine) complex³⁸ is only 18 % larger than for the aquo ion, agreeing well with the usual effects of exchanging water and amines in octahedral complexes.

The terms of the gaseous Mn^{++} are known from atomic spectroscopy³⁹:

6S	0 K
4G	26 800
4P	29 200
4D	32 300
4F	43 600

The levels ${}^4F_1(G)$, ${}^4F_3(G)$ and ${}^4F_3(D)$ should have the same wavenumbers as 4G and 4D , respectively, if the integrals F^k and thus the term distances were not decreased in complexes. It is seen from Table 2 that these energy differences are decreased 8 % in $\text{Mn}(\text{H}_2\text{O})_6^{++}$, 12 % in $\text{Mn} \text{enta}^{--}$ and 12 % in $\text{Mn} \text{en}_3^{++}$.

Orgel^{7,8} assumed that the presence of two $4s$ -electrons is sufficient to explain this effect, thus applying possibility I on p. 56. However, with the value of τ_0 from Table 1, it is probable that ~ 5 % intermixing with the ligands' orbitals occur. The highest term 4F seems more decreased, ~ 19 % in $\text{Mn}(\text{H}_2\text{O})_6^{++}$. It seems generally valid that high terms are systematically depressed, thus the ratio between the wavenumbers of the spinforbidden transitions to 2F_3 and 2F_5 in chromium(III) complexes⁴⁰ is only ~ 1.5 rather than 6 1.66 . . . This effect in Mn^{++} is perhaps caused by interaction with other electron configurations, which are situated above 50 000 K. It cannot be certainly decided, if an extra band does not occur of $\text{Mn}(\text{H}_2\text{O})_6^{++}$ at 37 400 K. It may be due to a doublet level*, which is highly intermixed with the quartet levels. 2F_5 is predicted at 28 000 K of $\text{Mn}(\text{H}_2\text{O})_6^{++}$ and at 23 000 K of $\text{Mn} \text{en}_3^{++}$, while the doublet levels of γ_5 ${}^4\gamma_3$ are distributed $\sim 8\ 000$ K above these wavenumbers.

Schläfer⁴¹ studied the absorption spectra of crystalline MnCl_2 , 4 H_2O and aqueous solutions between 1 M and 4.8 M MnCl_2 . The bands separated in

* It will be a rather difficult task to observe the doublet levels of manganese(II) complexes, corresponding to bands with $\epsilon \sim 10^{-4}$. Especially, the high overtones of vibration frequencies in the infra-red may produce similar bands. The intensity of quartet bands, even though only 1 % of spin-allowed bands of divalent $3d^n$ -complexes, is rather high³⁶. Since ζ_{3d} can be interpolated to 300 K, and the distances to the nearest sextet are $\sim 20\ 000$ K (either ${}^6F_1(S)$ or from other electron configurations), the spin intermixing would be expected to be only $\sim \left(\frac{300}{20\ 000}\right)^2 \sim 2 \times 10^{-4}$. Probably, the intensity is borrowed from some other configuration, where the total spin is less strictly defined than in $[A] 3d^5$.

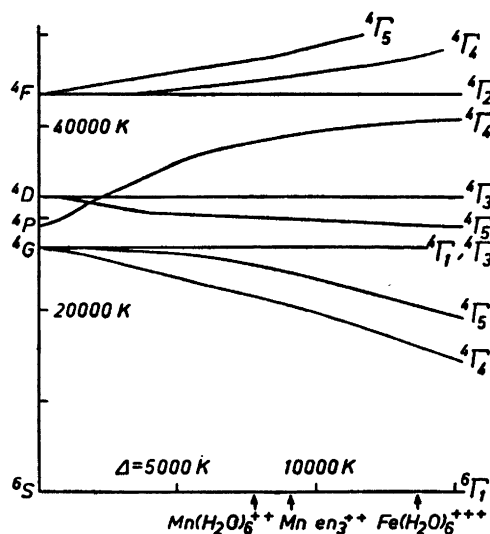


Fig. 3. The Orgel diagram of d^5 -systems, assuming no variation of the term distances i.e. the values of B and C from those of gaseous Mn^{2+} . Since the term distances are decreased to the latter values in $Fe(H_2O)_6^{3+}$, this ion can also find a place in this diagram with $\Delta = 13\,700\text{ K}$. The slopes of the levels can be compared with the observed band widths and with the variation of the wavenumbers of the individual bands as function of Δ in Table 2.

several components, whose intensities change as function of the chloride concentration. The general result is a shift $\sim 2\%$ towards lower wavenumbers, relative to the aquo ion. This was explained as a physical salt effect, caused by increasing concentration of the anion atmosphere around the manganese(II) ion. The present author believes that the spectral changes rather can be described to the consecutive formation of chloro complexes, and it is demonstrated¹⁷ that Schläfer's electrostatic model for the red shift of the bands of strong salt solutions actually is a translation of partly covalent bonding (cf. p. 57). If the values of the molar extinction coefficient ϵ , reported by Schläfer⁴¹ for the solid, which has a scattering back-ground, are decreased 0.04, the mani-fold of spectra can mainly be explained by the presence of two new complexes besides the hexaaquo ion:

Excited level	$MnCl(H_2O)_5^+$		$MnCl_2(H_2O)_4$	
	λ	ϵ	λ	ϵ
${}^4\Gamma_1(G)$ and ${}^4\Gamma_3(G)$	405 $m\mu$	0.038	405 and 408 $m\mu$	0.04
${}^4\Gamma_5(D)$	359	0.05	362 and 366	0.07
${}^4\Gamma_3(D)$	339	0.023	343	0.06
${}^4\Gamma_4(P)$	313	0.017	317	0.04

The two last bands have a minimum of ϵ in 2.5 M $MnCl_2$, where the monochloro complex probably is dominating. The absence of isosbestic points is not a strong argument against exchange of water with chloride in the first co-

ordination sphere, because the existence of three complexes and the small second-sphere effects probably will disturb the linear combinations of the absorption spectra.

While manganese(II) chloride solutions always will have \bar{n} well below 2, due to the presence of free chloride, which determines the formation curve of mono-nuclear chloride complexes³⁸, strong hydrochloric acid can produce higher values of \bar{n} . Table 2 gives the spectra of MnCl_2 in 6 M HCl and in 9 M HCl. In these solutions the red shifts are stronger than in $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$ except when the decreasing value of Δ shifts the band, e.g. to ${}^4\Gamma_4(G)$ in the opposite direction. The present author assumes that these complexes are all octahedral. However, in anhydrous solutions, the tetrahedral MnCl_4^{--} may perhaps occur. If MnCl_2 in 30 % ethanol + 60 % *t*-butanol is treated with PCl_3 , yellow solutions are obtained with higher bands at 440, 428, 424, 376 and 356 $m\mu$, while the bands at 406 and 400 $m\mu$ reversibly re-appear by addition of a few per cent of water. The yellow solutions exhibit much smaller Δ than the aquo ion and the F^k -integrals are decreased ~ 13 %, resembling the conditions in CoCl_4^{--} . Mr. Palle Andersen⁴⁸ has kindly informed me that yellow-green Cs_3MnCl_5 probably has tetrahedral co-ordination of manganese, while the octahedrally co-ordinated double chlorides are pink.

Cs_3MnCl_5 fluoresces yellowish green in ultraviolet radiation, as also the yellow-green salt $[\text{N}(\text{C}_2\text{H}_5)_4]_2 \text{MnBr}_4$ described in the experimental section. The latter salt does not deliquesce in air and can be prepared from aqueous solution of the components. The intensity of the fluorescence light by 366 $m\mu$ excitation is higher than that of uranyl salts. The reflection spectrum corresponds closely to that predicted of Mn(II) in tetrahedral environment*. A narrow peak at 448 $m\mu$, surrounded by a peak at 434 $m\mu$ and a shoulder at 476 $m\mu$ implies 17 % decrease of F^k , relative to gaseous Mn^{++} . The small value of Δ cannot be evaluated exactly, since the ligand field splitting is less conspicuous than the F^k -decrease. However, Δ seems to be between — 2 000 and — 3 000 K, when the hypothesis of negative sign is assumed. The fluorescent level is ${}^4\Gamma_4(G)$, as discussed by Orgel²⁸. A band at 382 $m\mu$ and a shoulder at 365 $m\mu$ correspond probably to ${}^4\Gamma_4(P)$ and ${}^4\Gamma_4(D)$, while the measured reflectance increases above 100 % below 350 $m\mu$ (perhaps caused by the fluorescence). As discussed in the experimental section, a broad, low band ~ 560 $m\mu$ may be due to octahedrally co-ordinated impurities, and a narrow band at 905 $m\mu$ to the vibrational over-tone $4 \sigma(\text{CH})$.

The decrease of F^k -integrals in anion complexes compared to aquo ions, was demonstrated for other manganese(II) complexes as seen from Table 2. Thus, 1.5 M KSCN produces 1.5 % smaller term distances, but the same Δ as the aquo ion, $\text{Mn} \text{ata}_2^{-4}$ (these strong manganese solutions are only clear with a large excess of sodium nitrogentriacetate) resembles much $\text{Mn} \text{enta}^{--}$; tartrate in aqueous ammonia gives a rather strong red shift; etc. These effects resemble much the red shifts of lanthanide complexes¹⁷ with citrate, tartrate,

* Similar arguments apply to FeCl_4^- of which Schläfer⁵⁶ reports the reflection spectrum. The narrow band ~ 525 $m\mu$ implies ~ 40 % decrease of F^k , while the broader ${}^4\Gamma_5(G)$ at ~ 610 $m\mu$ and ${}^4\Gamma_4(G)$ at ~ 680 $m\mu$ implies Δ about — 5 000 K. Cobalt-free FeCl_3 in 12 M HCl exhibit these bands at 600 and 684 $m\mu$, while a broad shoulder ~ 740 $m\mu$ probably is caused by another iron(III) complex.

and ethylenediaminetetraacetate, which are $\sim 1\%$ in Pr^{+++} , $\sim 0.7\%$ in Nd^{+++} and Sm^{+++} , and $\sim 0.3\%$ in Gd^{+++} , while they vanish in the heavy lanthanides.

Kleiner⁴² abandoned the electrostatic ligand field theory, because the Hartree self-consistent field $3d$ -wavefunction for chromium⁴³ produces a very small and even negative value of Δ for Cr^{+++} in the alums. This is a translation of the large overlap between $3d$ -electrons and the ligands, as seen from Fig. 2. Thus, the electrostatic model of Ilse and Hartmann⁴⁴ can be shown to lead to a contradiction, caused by the spatial extensions of the hydrogen-like wavefunctions¹². However, it is interesting to see that practically all information available on the energy levels of transition group complexes has been found by the electrostatic theory without taking partly covalent bonding into account (for a review, see Ref. 26). This is due to several reasons of quantum-mechanical nature: (1) The number of levels with a given value of $^{2S+1}L_n$ is independent of the intermixing and can be found, *e.g.*, from the strong field sub-shell configurations¹¹; (2) in complexes with high symmetry, such as O_h , the group-theoretical classification of levels and orbitals is very important; and (3) the molecular orbital theory without interaction of configurations is, contrary to the case of many simple molecules⁴⁵, able to predict the excited levels of transition group complexes with $\sim 2\%$ uncertainty with Δ and the decreased F^k -integrals as the only parameters (*cf.* Fig. 3 and Table 2). The success of the electrostatic theory with Δ as empirical parameter cannot be found only in the general feature of the perturbation theory that the energy levels usually are predicted much better than the wavefunctions; even the squares of the wavefunctions must be highly intermixed in highly covalent complexes such as $\text{Co}(\text{CN})_6^{-3}$ or RhCl_6^{-3} with small F^k -integrals. The problem is rather connected with the nearly equal energies of the purely ionic and purely covalent (*i.e.* 50% intermixing) limiting cases. It is very fortunate that complexes exist with partly filled shells, which can be in more than one state. It is possible in these cases to obtain much information from the excited levels, which is not available in general for closed shells. Especially, the absorption spectra can inform about the geometrical extension of partly filled shells. The only other type of experiment, which so far has presented such evidence, is the d -wavefunction, reported by Shull, Wollan, and Strausser⁴⁶ from neutron diffraction of manganese(II) salts. The maximum at 0.6 Å and the narrow half-width might suggest that the wavefunction is actually an anti-bonding combination of the type given in Fig. 2, but with a smaller density in the ligands, corresponding to much less than 50% intermixing.

The molecular orbital theory gives a much more unified theory for all the energy levels of all the transition group complexes than might earlier have been predicted. The valence bond-theory, which is cumbersome⁴⁷ even for simple molecules such as CO or O_2 , evolves extreme resonance possibilities for the groundstates of transition group complexes²⁵, and it is practically without value for the description of the excited levels. On the other hand, the electrostatic theory gives surprisingly good agreement with the observed energy levels, and the intermixing of the d -electrons with the ligands' orbitals can be said to be initiated by the perturbing effects of the ligands on the partly filled d -shell.

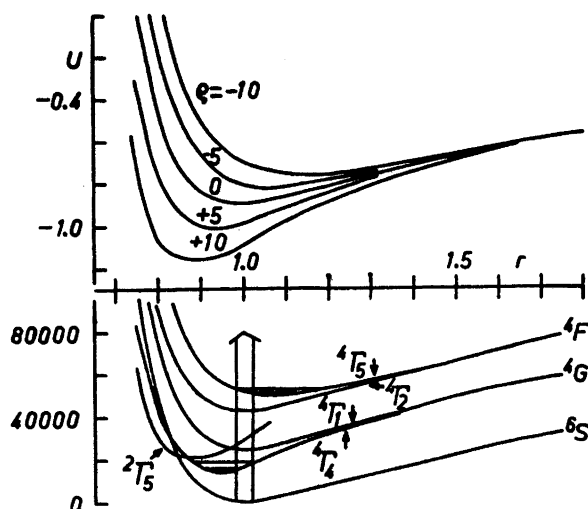


Fig. 4. The potential curve of eqn. (23) with different values of the ligand field stabilization parameter ρ . The lowest part of the figure exhibits several levels of manganese (II) complexes under the assumption of the same form of potential curves as given above and with the terms of gaseous Mn^{++} at the dissociation limit. The mechanism of band-widths is indicated by the vertical projection of the vibration of the ground-level on the potential curves of the excited levels.

THE WIDTH OF MANGANESE(II) ABSORPTION BANDS AND VIBRATIONAL EXCITATION DUE TO THE FRANCK-CONDON PRINCIPLE

Orgel⁸ pointed out that the width of absorption bands is roughly proportional to $\frac{d\sigma}{d\Delta}$, the difference in slope of the excited and the groundlevel in the Orgel diagram, using manganese(II) complexes³³ as examples. This effect is connected with the fact that the equilibrium distance between the central ion and the ligand increases regularly with the number of γ_3 -electrons. Thus, a transition between two levels with a different number of γ_3 -electrons corresponds to a broad absorption band, because the excited level will be vibrationally excited, since the Franck-Condon principle does not allow the complex to adjust itself to the new equilibrium distances during the very rapid optical excitation. Fig. 4 gives the potential curves $U(r)$ with the polynomial approximation in r^{-1} :

$$U = \frac{1}{9r^9} - \frac{0.02\rho}{r^5} - \frac{1}{r} \quad (23)$$

where the unit of r is chosen such that for $\rho = 0$, the minimum of U occurs at $r = 1$. The first of the three parts of the expression represents the mutual repulsion between the closed shells, the second the ligand field effects (with the ligand field stabilization parameter $\rho = 2n_5 - 3n_3, n_3$ and n_5 being the num-

ber of γ_3 - and γ_5 -electrons) and the third the electrostatic attraction of the ligand. The equilibrium distances r_L occur for:

$$\begin{array}{rccccc} \rho & = & +10 & +5 & 0 & -5 & -10 \\ r_L & = & 0.887 & 0.940 & 1.000 & 1.064 & 1.128 \end{array} \quad (24)$$

Thus, the present author is no longer inclined to assume, as earlier⁵⁰, that the equilibrium distances cannot increase $\sim 6\%$ for each new γ_3 -electron, even though the crystallographic distances suggest slightly smaller differences. The vibrational wavenumber 150 K found⁵⁰ of ReCl_6^{3-} cannot with certainty be identified with a definite one of the six fundamental frequencies of a regular octahedron. However, the order of magnitude of the frequencies is probably not very different from 200 K (*cf.* the recent results^{51,52} for UF_6 and PuF_6), and the amplitude of the zero-point vibration thus $\sim 0.08 \text{ \AA}$, corresponding to 0.04 units on Fig. 4. Since the differential quotient of U (eqn. 23) at $r = 1$ is 0.1ρ (while at $r = 0.9$, it is $-1.63 + 0.188\rho$), the manganese(II) complexes are expected to exhibit bandwidths $\delta \sim 1500 \text{ K}$ for a difference in $\rho = 5$.

Generally, the projection⁵³ of the lowest vibrational state of the ground-level on the potential curve U of the excited level is likely to produce an almost Gaussian-shaped absorption band

$$\varepsilon = \frac{\sigma}{\sigma_0} \cdot \varepsilon_0 \cdot 2^{-\frac{(\sigma_c - \sigma)^2}{\delta^2}} \quad (25)$$

with the half-width δ of the Gaussian part

$$\delta = 0.834 x_c \cdot \frac{dU}{dr} \quad (26)$$

since the square of the wavefunction of the lowest level of a harmonic oscillator is a Gauss-curve with the half-width $x_c \sqrt{\ln 2}$, where x_c is the classical amplitude. If the difference between the potential curves of two levels with ρ differing 5, *i.e.* Δ , is assumed to be proportional to r^{-5} , it will be valid for small values of x_c

$$\delta = 4.17 \frac{x_c}{r_L} \Delta \quad (27)$$

Since x_c is proportional to $(k\mu)^{-1/2}$, k being the force constant $\frac{d^2U}{dr^2}$ of the ground-level, and μ the reduced mass (the existence of more vibrational quanta in molecules with more than two atoms necessitates a more detailed treatment), x_c is not expected to vary more than between $0.03\text{--}0.08 \text{ \AA}$. Actually, manganese(II) and nickel(II) complexes have $\delta \sim 0.15 \Delta$, while¹⁴ rhodium(III) has $\delta \sim 0.09 \Delta$ and iridium(III) $\delta \sim 0.08 \Delta$, corresponding to higher values of $k\mu$ in the platinum group complexes.

However, if the vibrational wavenumber

$$\sigma_c = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (28)$$

is not much larger than 210 K (the mean Boltzmann energy at room temperature), transitions will occur from the n 'th vibrational state of the groundlevel, which has two strong maxima near $r_L \pm x_c \sqrt{2n+1}$ for $n = 1, 2, \dots$. The feet of the absorption bands will thus be too high and show a strong increase with the temperature T , while δ will be approximately proportional to \sqrt{T} for small σ_c . On the other hand, all bands will vanish too quickly towards low wavenumbers, because $\frac{dU}{dr}$ of eqn. 26 is no constant, but approaches 0 in the bottom of the potential hole. Since no vibrational structure generally can be observed, all the excited states discussed here must be rather diffuse, at least $\sim 0.2 \sigma_c$. It has earlier been discussed⁵⁰, if this broadening may be caused by collisions.

The lower part of Fig. 4 illustrates the potential curves of some manganese(II) levels with the assumption of eqn. 23. For decreasing values of r , corresponding to steeply increasing values of Δ , the levels with different values of ρ cross each other in a rather complicated way, actually depicting an Orgel diagram such as Fig. 3. Especially, the groundstates of magnetically anomalous complexes (*viz.* 2T_5 in Fig. 4) have intrinsically small values of r_L and high values of Δ , as pointed out by Orgel²⁷. The broad vertical arrow represents the possible transitions to excited levels, producing vibrational excitation of levels with r_L differing from that of the groundstate. Especially, excitations to ${}^4T_4(G)$, which may be fluorescent in manganese(II) complexes²⁸, correspond to a decreased value of r_L . The relatively long life of the excited state is made possible by this weak interaction with the environment, while excited states with increased values of r_L rapidly decay by transfer of energy to the thermal motion of other molecules.

EXPERIMENTAL

The stock solution of 2.3 M $MnCl_2$ was prepared from Merck's p.e., which was found to be free of iron. It was added to hydrochloric acid and to 3 M KSCN. $Mn\text{enta}^{--}$ was prepared from $MnSO_4 \cdot 4 H_2O$ (Merck's p.a.), 1.1 mole $H_4\text{enta}$ (Complexon II) and 2 moles Na_2CO_3 . The chamois solution is not oxidized by air or H_2O_2 , but turns brown (with a maximum at 450 and a narrow hump at 470 $m\mu$) of $Mn\text{enta}\text{OH}^{--}$ by addition of $KMnO_4$. This solution turns purple⁴⁹ (a maximum at 500 $m\mu$) by addition of $HClO_4$ under formation of $Mn\text{enta}\text{H}_2O^-$. However, this colour disappears after some minutes.

On the other hand, it is difficult to prevent the oxidation of most other manganese(II) complexes in alkaline solution, thereby forming brown precipitates. The greyish green solution of $Mn\text{en}_3^{++}$ (1 M $Mn\text{en}_3^{++}$, 1 M enH^+ and 3 M free en) can be protected against oxidation by a minute amount of ascorbic acid; however, especially in alkaline solution, this compound produces slowly a yellow decomposition product with a high maximum at 384 $m\mu$. Also manganese(II) and ammonium tartrate dissolved in aqueous NH_3 is oxidized by air to a brown solution, which can be reduced by ascorbic acid.

Tetraethylammonium manganese(II) bromide can be prepared by evaporation of a solution of manganese(II) bromide with slightly more than two moles of tetraethylammonium bromide in aqueous hydrobromic acid. After cooling, yellowish green crystals separate, which are washed with ethanol on a glass-sintered funnel and dried, *e. g.* by heating with an ultraviolet "black" mercury lamp, causing a bright green illumination. The yield is $\sim 60\%$. The analysis indicates the formula $[N(C_2H_5)_4]_2 Mn Br_4$: exp. 8.8 % Mn, 49.2 Br; theor. 8.7 % Mn, 50.4 % Br. In some cases, the content of Mn is higher, $\sim 10\%$, and the reflection spectrum then exhibits a very broad band 560 $m\mu$. It is

presumably caused by a complex with octahedral environment of Mn(II), either $[\text{N}(\text{C}_2\text{H}_5)_4] \text{MnBr}_2$ or a solvate. In one sample containing 0.08 mole % cobalt, bands were observed at 645, 670, 705 and 720 $\text{m}\mu$ of CoBr_4^{2-} . A narrow band at 900–910 $\text{m}\mu$ was found in all samples. It cannot be a Mn(II) ligand field band, but is rather four times the CH-stretching frequency, since it also appears in $\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$.

The spectra of the solutions were measured in 10 cm silica cells on a Cary Recording Spectrophotometer, model 11 MS–50.

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