

Molecular Orbital Calculations on Transition Metal Complexes. Part VIII.† Potential Energy Curves for Some $3d^6$ Complexes and their Relation to Tanabe–Sugano Diagrams

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Potential energy curves for the ground and some low energy excited states of a number of complexes with a $3d^6$ electronic configuration have been computed from INDO type MO calculations. The results agree extremely well with the known ground states of the complexes FeF_6^{4-} , CoF_6^{3-} , $\text{Co}(\text{H}_2\text{O})_6^{3+}$, and NiF_6^{2-} , in particular the crossover from high to low spin being predicted for the fluoro- and aqua-complexes of cobalt(III). In addition a successive decrease in metal–fluorine distance accompanied by a gradual increase in covalency for the series $\text{Fe}^{\text{II}} \longrightarrow \text{Co}^{\text{III}} \longrightarrow \text{Ni}^{\text{IV}}$ is indicated in harmony with crystallographic and spectroscopic data. The calculated contraction in metal–ligand distance on passing from the high spin to the low spin configuration is ca. 0.06 Å for all complexes studied, in very good agreement with the value indicated by pressure dependent magnetic measurements. Differences in these potential energy curves give diagrams which essentially reproduce the main features of the crystal field Tanabe–Sugano diagrams.

THE many different properties exhibited by complexes of the transition elements have been interpreted over the past twenty years by means of two separate theories, the crystal field theory¹ and the molecular orbital method. The former method has been widely used in a semi-quantitative manner in the form of the Tanabe–Sugano² diagrams to interpret the d – d electronic excitations within these complexes. For those octahedral complexes which possess the electronic configurations d^4 – d^7 the ground state is not uniquely defined since there is the possibility of a high spin or a low spin arrangement depending on the strength of the ligand field. This crossover from high to low spin appears as a marked change in the Tanabe–Sugano diagram and is accompanied by a change in the magnetic and spectroscopic properties of the complexes. Comparison of the crystal field and molecular orbital methods has not been attempted previously although Martin and White³ have discussed the general phenomenon of high spin–low spin crossover and potential energy curves in relation to magnetic properties of complexes which lie close to the crossover point.

In the present paper we have used total molecular ion energies, calculated using a modified INDO method,⁴ to generate the potential energy curves for the ground and low energy excited states of some complexes with the $3d^6$ electronic configuration. In particular the two curves which represent the high and low spin states of the complexes are obtained. These curves are then used to derive a Tanabe–Sugano type diagram which is quantitative within the level of the approximations of the method employed.

In view of the computer time required we have chosen to confine extensive investigations to the hexafluoro-complexes of the ions Ni^{IV} , Co^{III} , and Fe^{II} . The hexa-

fluoronickelate(IV) ion is known⁵ to possess a low spin (t_{2g}^6) $1A_{1g}$ ground state, and an analysis of its electronic spectrum using the Tanabe–Sugano matrices has yielded a Dq/B ratio of 3.9, considerably removed from the crossover value of 2. On the other hand the hexafluorocobaltate(III) ion has a high spin ($t_{2g}^4e_g^2$), $5T_{2g}$ ground state with a Dq/B ratio very close to the crossover position.⁶ In fact for octahedral complexes of Co^{III} only the hexahalogeno-complexes are high spin and for this reason we have also included the hexa-aquacobalt(III) ion in our studies. This will provide a crucial test of the method to see whether it can satisfactorily account for the crossover from high to low spin on passing from a fluoro-complex to an aqua-ion. In addition calculations have also been made for the isoelectronic hexafluoroferrate(II) ion, which is expected to be high spin. The complex fluoride KFeF_3 possesses the perovskite structure⁷ and can be considered to contain the above complex ion; in view of the fact that the absorption spectrum of this compound has not yet been fully characterised we have prepared and recorded the spectrum of KFeF_3 and fitted the observed bands to the Tanabe–Sugano matrices to obtain the crystal field Δ and B parameters.

METHOD

The INDO–SCF–MO method⁸ is a refinement of the CNDO^{9,10} scheme where the one-centre exchange integrals ($\mu\nu/\mu\nu$) are included. This enables the different electronic levels arising from a given orbital occupancy to be distinguished and in addition provides for a better description of spin delocalisation. Valence orbitals considered are $3d$, $4s$, and $4p$ for the transition element, $2s/2p$ for the first row elements, and $1s$ for hydrogen. The parametrisation of the method has already been given.⁴ Gouterman exponents¹¹

⁶ G. C. Allen, G. A. M. El Sharkawy, and K. D. Warren, *Inorg. Chem.*, 1971, **10**, 2538.

⁷ K. Knox, *Acta Cryst.*, 1961, **14**, 583.

⁸ J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026.

⁹ J. A. Pople, G. A. Segal, and D. P. Santry, *J. Chem. Phys.*, 1965, **43**, S129.

¹⁰ D. W. Clack, N. S. Hush, and J. R. Yandle, *J. Chem. Phys.*, 1972, **57**, 3503.

¹¹ M. Zerner and M. Gouterman, *Theor. Chim. Acta*, 1966, **4**, 44,

† Part VII, D. W. Clack, *Theor. Chim. Acta*, in the press.

¹ H. Bethe, *Ann. Phys.*, 1929, **3**, 133.

² Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, 1954, **9**, 753, 766.

³ R. L. Martin and A. H. White, *Transition Metal. Chem.*, 1968, **4**, 113.

⁴ D. W. Clack, *Mol. Phys.*, 1974, **27**, 1513.

⁵ G. C. Allen and K. D. Warren, *Inorg. Chem.*, 1969, **8**, 753.

have been used for the transition-metal orbitals and Slater exponents for first-row atoms. The empirical Slater-Condon parameters from Oleari's paper¹² have been adopted for the transition elements. Hamiltonian matrix elements for the transition elements will be published elsewhere.⁴ Programs have been written in FORTRAN and a calculation for a hexafluorometallate ion involving 33 orbitals, making use of two-fold symmetry, required 1 min execution time. The hexafluoro-complexes were treated as being regularly octahedral in all the electronic configurations examined. An octahedral co-ordination of oxygens around the central metal, with a tetrahedral disposition about the oxygens was assumed for the aqua-complex.¹³

EXPERIMENTAL

KFeF₃ Was prepared according to the method of Nuka.¹⁴ An aqueous solution of ferrous chloride (1 mol equiv.) was added to a boiling aqueous solution of potassium fluoride (3 mol equiv.), slightly acidified with hydrofluoric acid. The resulting solution was boiled and the precipitated product filtered, washed with a dilute solution of HF, followed by alcohol, and then dried *in vacuo*. The reflectance spectrum was recorded on a Beckmann DK2A spectrometer.

RESULTS AND DISCUSSION

CoF₆³⁻.—Figure 1 shows the dependence of the total energy of the complex ion CoF₆³⁻ on the internuclear Co-F separation for a number of different orbital occupancies: Curves A and C thus represent the high and low spin configurations respectively, the high spin state being slightly more stable than the low spin one in agreement with spectroscopic⁶ and magnetic data.¹⁵ The difference in the calculated equilibrium energies of the high and low spin configurations is 0.27 eV. The calculated equilibrium internuclear Co-F separation is *ca.* 0.1 Å larger than the crystallographic value (1.89 Å).¹⁶ Curve B represents an excited state of the same spin as the ground state and is formed by promotion of an electron from the *t*_{2g} level to the *e*_g orbital. Curves C–E correspond to levels of different spin multiplicity to the ground state. The curves show that for all Co-F distances larger than the equilibrium value the ground state is high spin. Decrease of the metal-ligand distance below that of the equilibrium value results in a crossing of the high and low spin curves so that for Co-F distances <1.97 Å the ground state is given by curve C, the low spin state. The triplet state (*t*_{2g}⁵*e*_g¹) never constitutes the ground state as has been shown by Griffith¹⁷ using ligand field arguments. It is to be noted that the high spin *t*_{2g}⁴*e*_g² configuration (curve A) identifies the ⁵T_{2g} spectroscopic state, while the low spin, *t*_{2g}⁶, curve C represents the ¹A_{1g} state. The excited quintet *t*_{2g}³*e*_g³ (curve B) gives the ⁵E_g state and the triplet curve D is an average of the ³T_{1g} and ³T_{2g} levels. Curve E denotes an average of the terms ³A_{2g}, ³T_{1g}, ³T_{2g}, and ³E_g derived from the *t*_{2g}⁴*e*_g² configuration.

¹² E. Tondello, G. De Michelis, L. Oleari, and L. Di Sipio, *Co-ordination Chem. Rev.*, 1967, **2**, 65.

¹³ D. W. Clack and M. S. Farrimond, *J. Chem. Soc. (A)*, 1971, 299.

¹⁴ V. P. Nuka, *Z. anorg. Chem.*, 1929, **180**, 235.

Spectroscopists are especially interested in energy differences measured with respect to the ground state, and moreover those involved with electronic spectra are

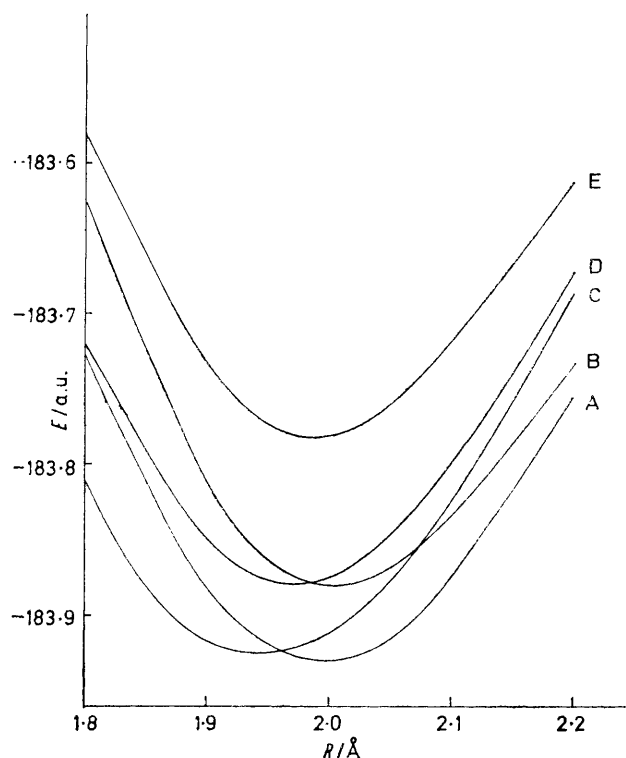


FIGURE 1 Variation in total molecular ion energy with internuclear metal-ligand separation for a number of strong field configurations of the hexafluorocobaltate(III) ion: A, quintet (*t*_{2g}⁴*e*_g²); B, quintet (*t*_{2g}³*e*_g³); C, singlet (*t*_{2g}⁶); D, triplet (*t*_{2g}⁵*e*_g¹); E, triplet (*t*_{2g}⁴*e*_g²).

primarily concerned with such differences occurring at a fixed internuclear configuration. With this in mind it is instructive to plot the energy curves of Figure 1 in an alternative way where the ground state is placed at zero energy with all other curves shown relative to this new zero. A diagram of this nature is shown in Figure 2. In view of the fact that the crystal field parameter, Δ, is inversely dependent on *R*, the metal-ligand distance, a decrease in *R* might be expected to produce an increase in Δ. For this reason the abscissa scale in Figure 2 is reversed to that in Figure 1 so that positive *x* in Figure 2 represents increasing Δ. Since curve A represents the ground state for *R*_{Co-F} distances >1.97 Å while the abscissa is given by curve C for distances <1.97 Å, a discontinuity which depicts the crossover from high to low spin occurs at the Co-F separation of 1.97 Å. This figure closely resembles the familiar Tanabe-Sugano diagram for the *d*⁶ configuration, although Figure 2 obtains from molecular orbital calculations whereas the Tanabe-Sugano diagram results from crystal field

¹⁵ W. Klemm, W. Brandt, and R. Hoppe, *Z. anorg. Chem.*, 1961, **308**, 179.

¹⁶ M. A. Hepworth, K. M. Jack, R. D. Peacock, and G. J. Westland, *Acta Cryst.*, 1957, **10**, 63.

¹⁷ J. S. Griffith, *J. Inorg. Nuclear Chem.*, 1956, **2**, 1, 229.

considerations. The discontinuity in Figure 2 clearly arises through a crossing of the high and low spin potential energy curves in Figure 1.

The difference between Figure 2 and the Tanabe-Sugano diagram is that the latter is only semi-quantitative but applicable to all d^6 complexes with the appropriate choice of parameters, whereas Figure 2 is specific for the CoF_6^{3-} ion and is quantitative to within the INDO approximations. The Tanabe-Sugano diagram, while admirably accounting for electronic energy levels at a fixed internuclear separation, gives no information about the equilibrium energies of the various states. The Tanabe-Sugano fit to the electronic spectrum of CoF_6^{3-} yields a Dq/B ratio of 1.84,⁶ which is very close to the crossover value of 2.00. The potential energy curves of Figure 1 are also a clear illustration of just how close the CoF_6^{3-} ion is to the crossover point. The vertical excitation energies through the minimum of the ground state curve to either pure states or to average of states are given in Table 1 and compare tolerably well with the observed values. It is clear that

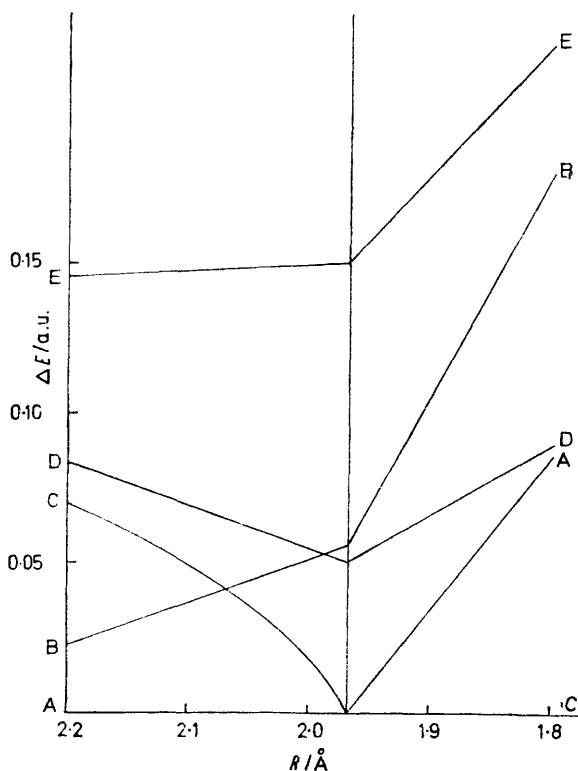


FIGURE 2 Energy differences between curves of Figure 1 plotted with respect to the ground state. The labelling is the same as in Figure 1

at the present level of MO calculations the Tanabe-Sugano curves afford a more complete if not more exact interpretation of the excited levels within the complex ion.

It is evident from the several curves of Figure 1 that

¹⁸ N. S. Hush and M. H. L. Pryce, *J. Chem. Phys.*, 1957, **26**, 143.

the equilibrium Co-F internuclear separation is governed by the specific electron occupancy within the d manifold. For example curve C (t_{2g}^6) has the smallest equilibrium

TABLE 1

Vertical transition energies (10^3 cm^{-1}) for CoF_6^{3-} without configurational interaction

	Calc.	Observed
$t_{2g}^4 e_g^2 ({}^3T_{2g}) \longrightarrow t_{2g}^6 ({}^1A_{1g})$	4.3	(2.7) ^b
$\longrightarrow t_{2g}^3 e_g^3 ({}^5E_g)$	11.4	11.8, 16.4 ^a (14.5) ^b
$\longrightarrow t_{2g}^5 e_g^1 (T_{1g}, {}^3T_{2g})$	12.3	5.5 (7.0, 11.0) ^b
$\longrightarrow t_{2g}^4 e_g^2 ({}^3A_{2g}, {}^3E_{2g}, {}^3T_{1g}, {}^3T_{2g})$	32.4	19.6–30.3

^a Jahn-Teller split. ^b Tanabe-Sugano fit.

separation while curve B ($t_{2g}^3 e_g^3$) shows the largest. The complete ordering is $C(t_{2g}^6) < D(t_{2g}^5 e_g^1) < A \sim E(t_{2g}^4 e_g^2) < B(t_{2g}^3 e_g^3)$ and the sequence from left to right corresponds to a decreasing occupancy within the t_{2g} level and increasing numbers of electrons in the e_g level. This contraction can be closely related to the double minimum phenomenon observed for the 'ionic radii' of high spin complexes across a transition series,¹⁸ which can be viewed in terms of either a shielding effect¹⁹ or a crystal field stabilisation energy contribution.²⁰ The former acknowledges that repulsions between metal e_g electrons and ligand electrons are greater than those between metal t_{2g} and ligand electrons; thus e_g electron density presents a greater shielding effect than does t_{2g} density. The latter considers the effect of the CFSE term in addition to the Madelung term on R_e , the equilibrium internuclear distance. The present calculations, as in most other approximate MO methods, use two-centre electron repulsion integrals which are averaged either over atoms or over a valence shell so that the coulomb repulsion integral $\langle d_{x^2-y^2} d_{x^2-y^2}^{\text{metal}} | p_x p_x^{\text{lig}} \rangle$ is put equal to the integral $\langle d_{xy} d_{xy}^{\text{metal}} | p_x p_x^{\text{lig}} \rangle$. On this basis the shielding effect is not explicitly taken into account. However, the two-centre core term $\mathcal{H}_{2p_z 3d_{z^2-y^2}}$ is considerably larger than the corresponding term between π -type functions $\mathcal{H}_{2p_y 3d_{xy}}$, the respective values for Co-F distance of 2.0 Å being 0.0555 and 0.0183 a.u. This will lead to a larger bonding-antibonding separation for the e_g levels than for the t_{2g} orbitals. It therefore follows that the transfer of an electron from e_g^* to t_{2g}^* reduces the amount of antibonding density within the complex and for this reason there is a gradual shortening of the Co-F distance for the sequence (1). The strongly

$$t_{2g}^6 < t_{2g}^5 e_g^1 < t_{2g}^4 e_g^2 < t_{2g}^3 e_g^3 \quad (1)$$

bonding e_g levels remain filled irrespective of the t_{2g}^* or e_g^* occupation.

This shortening of the Co-F distance on passing from the high spin arrangement, through the intermediate triplet state, to the low spin case may be viewed in terms of the covalency which changes through the series (1). An estimate of the extent of covalency may be

¹⁹ F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, New York, 1966.

²⁰ N. S. Hush, *Discuss. Faraday Soc.*, 1959, **26**, 145.

obtained by examining the amount of d electron density on the metal, values of which for the various states of the complexes studied are shown in Table 2. The d

TABLE 2

d Electron densities for different strong-field configurations of NiF_6^{2-} , CoF_6^{3-} , and FeF_6^{4-}

	FeF_6^{4-}		CoF_6^{3-}		NiF_6^{2-}	
	t_{2g}	e_g	t_{2g}	e_g	t_{2g}	e_g
Singlet (t_{2g}^6)	6.000	0.132	6.000	0.555	6.000	1.338
Triplet ($t_{2g}^5 e_g^1$)	5.002	1.103	5.014	1.480	5.050	2.211
Triplet ($t_{2g}^4 e_g^2$)	4.007	2.061	4.024	2.465	4.221	2.988
Quintet ($t_{2g}^3 e_g^3$)	4.005	2.057	4.028	2.325	4.121	3.020
Quintet ($t_{2g}^2 e_g^4$)	3.007	3.031	3.049	3.226	3.345	3.634

electron density over and above that of integral occupation arises through metal participation in the bonding 'mainly ligand' orbitals, and the greater the involvement of the metal d orbitals in these orbitals the larger is the d electron density on the metal. The d electron density, and therefore the covalency, is seen to decrease in the order (1) above. The overall bonding density therefore increases as successive electrons are removed from the e_g^* orbital and placed in the t_{2g}^* level and because of this the fluorines are drawn in closer to the metal ion.

Although it is not possible to measure experimentally the equilibrium metal-ligand separations for both the high and the low spin configurations, estimates may be made for some systems which lie close to the high spin-low spin crossover point. For these systems the magnetic susceptibility is pressure dependent and measurements of this kind for some iron(III) dithiocarbamates²¹ have indicated that there is a decrease in molar volume on passing from the high spin to the low spin arrangements, and that the change in the metal-ligand separation is *ca.* 0.07 Å. The calculated difference in the equilibrium internuclear distances for the high and low spin curves of CoF_6^{3-} is 0.06 Å, which compares extremely well in magnitude to the experimentally derived value for the iron complexes.

$\text{Co}(\text{H}_2\text{O})_6^{3+}$.—The three potential energy curves corresponding to the low spin A, the high spin B, and the intermediate triplet state C of $\text{Co}(\text{H}_2\text{O})_6^{3+}$ are shown in Figure 3. A more extensive study of other states was not possible due to time limitations. The singlet state is calculated to lie lowest in energy in agreement with spectroscopic²² data for this complex ion, which can be interpreted in terms of a low spin t_{2g}^6 configuration. The minimum position of the low spin curve is more stable than that of the high spin curve by 2.31 eV, thus this complex is considerably removed from the crossover point. This accords with the much higher value of Dq/B (2.7) compared with that of CoF_6^{3-} , the crossover value being 2.0. As was previously noted for CoF_6^{3-} , at no point does the intermediate triplet state C lie lower than both the singlet and quintet levels. The calculations therefore satisfactorily account for the crossover

²¹ A. M. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc.*, 1964, **A280**, 235.

from high to low spin for the hexafluoro- and hexa-aqua-complexes of cobalt(III).

NiF_6^{2-} .—The sets of curves for the two cobalt complexes above indicate that the method is able to account for the relative positions of the fluoro- and aqua-coordinators in the spectrochemical ligand series and in view of this it is useful to examine the effect of the central metal ion oxidation state on the computed ground state. Analysis of the electronic spectrum of the isoelectronic NiF_6^{2-} ion, which contains nickel in the oxidation state of four, yields a low spin t_{2g}^6 ground state⁵ and the computed potential energy curves for this ion (Figure 4) substantiate this finding. The low spin state is calculated to lie 3.10 eV lower than the minimum energy of the high spin state. It can be seen from the table of d electron densities that the Ni^{IV} complex is

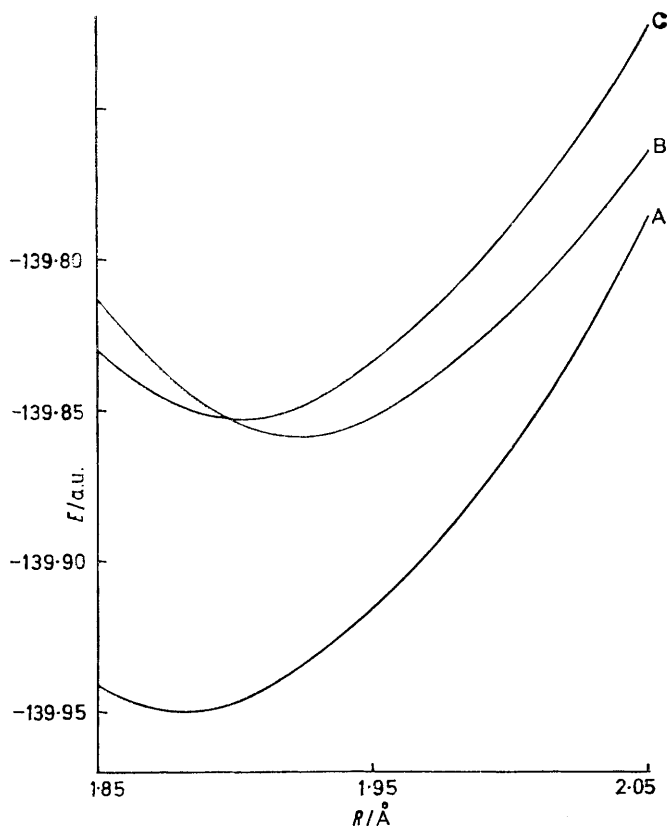


FIGURE 3 Potential energy curves for the hexa-aquacobalt(III) ion: A, singlet (t_{2g}^6); B, quintet ($t_{2g}^4 e_g^2$); C, triplet ($t_{2g}^5 e_g^1$)

considerably more covalent than the isoelectronic CoF_6^{3-} ion. In addition the calculated equilibrium metal-ligand distance of the low spin curve of NiF_6^{2-} is 1.8 Å (experimental distance 1.7 Å)²³ so that the calculations predict extremely accurately the contraction of 0.2 Å in the M-F distance on going from Co^{III} to Ni^{IV} .

Convergence problems were encountered for some of the states of $\text{Ni}^{\text{IV}}\text{F}_6^{2-}$ using a Ni-F distance of 2.0 Å and

²² C. K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon, Oxford, 1962.

²³ H. Bode and E. Vose, *Z. anorg. Chem.*, 1956, **286**, 136.

for this reason the full curves of these states are not shown. It is believed that this difficulty arose through the choice of a neutral nickel atom ($3d^84s^2$) configuration

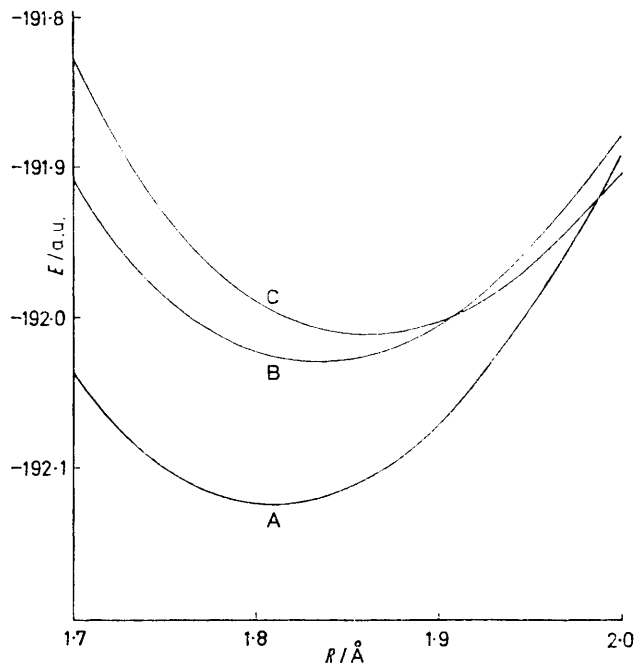


FIGURE 4 Potential energy curves for the hexafluoronickelate(IV) ion: A, singlet (t_{2g}^6); B, triplet ($t_{2g}^5e_g^1$); C, quintet ($t_{2g}^4e_g^2$)

for selecting the core terms, and for large distances this assumption is not valid because the covalency within the complex is insufficient to reduce the positive charge on the metal to anywhere near a neutral species.

FeF_6^{4-} .—The high spin state of $\text{Co}^{\text{III}}\text{F}_6^{3-}$ was calculated to be only slightly more stable than the low spin state. Replacement of the central Co^{III} by Fe^{II} should

TABLE 3
Reflectance spectrum of KFeF_3

Observed band position 10^{-3} cm^{-1}	Intensity F_R	Assignment	Calculated energy ^a
7.9	0.56	${}^5T_{2g} \rightarrow {}^5E_g$	9.1
10.3	0.51		
13.3	0.24	$\rightarrow {}^3T_{1g}$	13.1
16.9	0.17	$\rightarrow {}^3T_{2g}$	16.8
19.7	0.24	$\rightarrow {}^3T_{1g}$	19.5
21.3	0.21	$\rightarrow {}^3T_{2g}$	21.1
		$\rightarrow {}^3T_{2g}$	26.0
		$\rightarrow {}^3T_{2g}$	27.3
		$\rightarrow {}^3T_{1g}$	28.0
		$\rightarrow {}^3E_g$	28.2
35	0.88	?	
44	1.25	?	

^a After Tanabe and Sugano with $Dq = 910 \text{ cm}^{-1}$, $B = 965 \text{ cm}^{-1}$, and $C/B = 4.41$.

further increase the stability of the high spin configuration with respect to the low spin state. The only

²⁴ G. D. Jones, *Phys. Rev.*, 1967, **155**, 259.

²⁵ G. C. Allen and K. D. Warren, *Structure and Bonding*, 1971, **9**, 49.

previous spectroscopic study of KFeF_3 was carried out by Jones,²⁴ but the range covered extended between 7000 and 13,000 cm^{-1} where only the spin allowed transition could be observed and therefore no estimate of the covalency could be made. Table 3 gives the observed band energies and intensities together with the corresponding assignments of the bands. The spectrum consists of a rather broad asymmetric band which splits into two components at liquid nitrogen temperature representing transitions from the quintet ground state to the Jahn–Teller split 5E_g excited state (cf. CoF_6^{3-}).⁸ A number of spin forbidden bands are observed, in particular a sharp band at 19,700 cm^{-1} can be assigned to the intra-shell transition ${}^5T_{2g}(t_{2g}^4e_g^2) \rightarrow {}^3T_{1g}(t_{2g}^4e_g^2)$. Following Tanabe and Sugano with $C/B = 4.41$, $Dq = 910 \text{ cm}^{-1}$, and $B = 965 \text{ cm}^{-1}$ all the observed bands can be fitted reasonably well. The nature of the absorption bands at 35,000 and 44,000 cm^{-1} is uncertain. They are neither due to charge-transfer transitions since these lie much higher in energy,²⁵ nor to Fe^{III} impurities.⁶ It is possible that they arise through some metal-metal interaction similar to that observed for some binuclear copper(II) complexes.²⁶

The computed potential energy curves for this complex are given in Figure 5 and compared with the

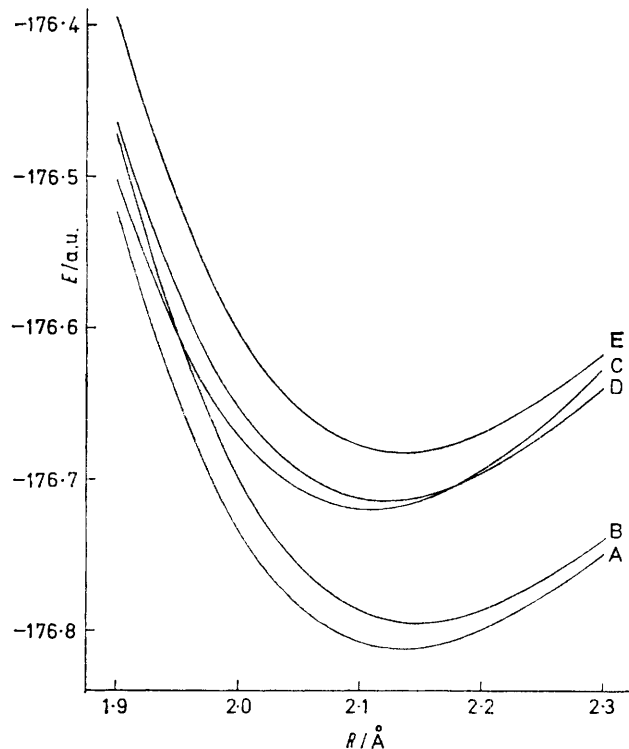


FIGURE 5 Potential energy curves for the hexafluoroferrate(II) ion: A, quintet ($t_{2g}^4e_g^2$); B, quintet ($t_{2g}^3e_g^3$); C, singlet (t_{2g}^6); D, triplet ($t_{2g}^5e_g^1$); E, triplet ($t_{2g}^4e_g^2$)

CoF_6^{3-} ion the high spin configuration is now considerably more stable than the spin paired low spin

²⁶ M. L. Tonnet, S. Tamada, and I. G. Ross, *Trans. Faraday Soc.*, 1964, **60**, 840.

arrangement in harmony with the low Dq/B value of 0.94 derived from the electronic spectrum. The changes in the vertical excitation energies from CoF_6^{3-} to FeF_6^{4-} are in the same direction as indicated by the spectra of these two complexes, with the triplet ($t_{2g}^3 e_g^1$) moving to higher energy and the quintet ($t_{2g}^3 e_g^3$) occurring at lower energy.

The preceding total energy curves illustrate quantitatively a number of features which have previously been assumed to be true from qualitative arguments. Thus the equilibrium metal-fluorine distances are seen to decrease in the order $\text{Ni}^{\text{IV}} < \text{Co}^{\text{III}} < \text{Fe}^{\text{II}}$ although each distance is calculated to be *ca.* 0.1 Å longer than the observed value. This contraction in the M-F separation is closely related to the covalency within each complex as given by the d orbital participation in the bonding molecular orbitals; the computed d electron densities parallel the nephelauxetic β parameters derived from the optical spectra. Moreover the anticipated shortening of the metal-ligand bond length as electrons are transferred from the metal e_g orbital to the t_{2g} level is quantitatively predicted. One of the most satisfying results of the calculations is the prediction of the correct ground states and the crossover from high to low spin for changes in both ligands and metal oxidation state. It is also gratifying that MO calculations can lead to a description of excited energy levels which vary with distance (or Δ) in essentially the same way as described by the Tanabe-Sugano diagrams. In view of the fact that all the curves have more or less the same shape the fundamental reason for curve crossing lies in the different equilibrium distances for the various states. In addition since the curves for states derived from the same orbital occupation (curves A and E for CoF_6^{3-}) have the same equilibrium separation, the excited state (E) does not cross curve A but lies parallel to it. Although the energies given by the present results refer in some cases to an average of states arising from a given strong field configuration the vertical excitation energies for all complexes examined are of similar magnitude to those observed spectroscopically.

Finally these MO calculations give an indication as to the difference in *equilibrium* energies of the high and low

spin forms, a quantity which cannot be provided by the Tanabe-Sugano diagrams because these give energy differences at a fixed metal-ligand distance. In fact it should be remembered that the crossover point on the Tanabe-Sugano diagram refers not only to a change in the spin state but also to a change in the metal-ligand distance, thus there is no situation when the vertical excitation energy from the minimum of the high spin ${}^5T_{2g}$ ground state to the excited spin paired ${}^1A_{1g}$ configuration (or *vice versa*) becomes zero. The equilibrium energy separations should however relate to the crystal

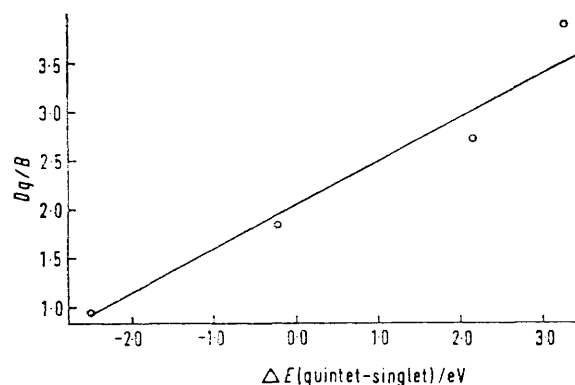


FIGURE 6 Correlation between equilibrium energy differences of high and low spin configurations and the optical Dq/B value for some $3d^6$ complexes

field energy Δ since the larger the separation between the potential energy curves the further apart are the vertical excitation energies. A plot of the differences between the equilibrium energies of the high and low spin configurations against Δ/B derived from the electronic spectrum is given in Figure 6, and a fairly good linear correlation is obtained for the four complexes including the hexa-aqua-ion. The graph also shows that at the crossover point ($Dq/B = 2$) the high and low spin states have identical *equilibrium* energies. If a correlation of this sort can be expected to hold for all d^6 complexes Figure 6 provides a means of obtaining the equilibrium energy difference from the absorption spectrum of a complex.

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