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Molecular Orbital Calculations on Transition Metal Complexes. Part IX

High Spin-Low Spin Crossover in d^5 Systems

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Potential energy curves for the ground and some low energy excited states of a number of complexes with a $3d^5$ electronic configuration have been computed from INDO type SCF MO calculations. The results agree extremely well with the known ground states of the complex ions MnF_6^{4-}, FeF_6^{3-}, CoF_6^{2-}, and $Fe(CN)_6^{3-}$, in particular the crossover from high to low spin being obtained for changes in both central metal ion oxidation state and ligand. The calculated contraction in metal ligand distance on passing from the high spin to the low spin state is ~ 0.05 Å for each complex in very good agreement with the value indicated by pressure dependent magnetic measurements. Computed electronic transition energies involving both d–d type and charge-transfer excitations compare favourably with observed spectroscopic values.

Key words: Transition metal complexes – High spin-low spin crossover

1. Introduction

The Crystal Field Theory and the Molecular Orbital Theory have been used in a complementary manner over the past two decades to describe the diverse properties and bonding modes within transition metal complexes. The former theory has been concerned in the main with providing information about the electronic energy levels within the d-electron configuration whereas the MO method lends itself to a description of covalency and related properties by explicitly evaluating the eigen functions of the complex molecular ion.

For those octahedral complexes which possess electronic configurations d^4–d^7 there is the possibility of either a high-spin or a low-spin arrangement depending on the strength of the ligand field. Martin and White [1] have discussed the consequences of a high-spin/low-spin equilibrium on the magnetic properties of complexes which lie close to the crossover point in terms of qualitative potential energy curves applicable to the complexes considered. In addition a series of papers by König [2, 3] has examined in detail the crossover situation in crystal field terms. We have recently reported potential energy curves obtained from MO calculations for a series of complex ions with the $3d^6$ configuration [4] which satisfactorily account for the crossover from high to low spin as both ligand and central metal ion oxidation state are varied. We report below the potential energy curves for the ground and low energy excited states of some $3d^5$ complex ions. In particular the two curves which represent the high and low spin states of the complexes are obtained. Calculations have been made for the hexafluoro complexes of the $3d^5$ ions manganese (II), iron (III), and Co(IV) in order to investigate the effect of central metal oxidation number. Limited calculations to examine the role of the ligand on the ground state have been carried out for the hexa cyano ferrate (III) ion.

2. Method

The INDO MO SCF method and its parametrisation for transitional elements is described elsewhere [5]. All complexes were treated as having regular octahedral geometry in each of the different electronic states examined. Wave functions and total molecular ion energies were computed for each strong-field configuration along the symmetric stretching distortion and in this way potential energy curves have been obtained for the α_{1g} mode.

3. Results

The potential energy curves showing the α_{1g} symmetric distortion for a number of strong field electronic configurations of the $\mathrm{Co^{IV}F_6^{2-}}$ and $\mathrm{Fe^{III}F_6^{3-}}$ ions are given in Figs. 1 and 2. In each diagram Curves A and B correspond to the high and low spin states, $t_{2g}^3e_g^2$ and t_{2g}^5. Curves C and D are quartet states with the respective configurations $t_{2g}^4e_g^1$ and $t_{2g}^3e_g^2$. A higher excited doublet level corresponding to the configuration $t_{2g}^4e_g^1$ is denoted by Curve E. It is to be noted that the high spin configuration $t_{2g}^3e_g^2$, Curve A, identifies the ${}^6A_{1g}$ spectroscopic state, while the low spin state (Curve B) represents the ${}^2T_{2g}$ state. Curve C corresponds to an average of the ${}^4T_{1g}$ and ${}^4T_{2g}$ states. Curves D and E are averages of states derived from their respective strong-field configurations. The principal difference between Figs. 1 and 2 lies in the relative positions of the high spin and the low spin curves. In Fig. 1 ($\mathrm{CoF_6^{2-}}$) the low spin curve clearly has a lower equilibrium energy than the high spin state, the equilibrium energy difference being 0.03 a.u. On the other hand the reverse is true in Fig. 2, where the high spin configuration is more stable at equilibrium than the low spin curve by 0.08 a.u. These results are in complete agreement with magnetic [6, 7] and spectroscopic [8, 9] data for both complex ions. It can be seen from the figures that several of the curves cross one another; however, although Curve C crosses both Curves A and B at different distances at no point does Curve C lie lower in energy than both Curve A and Curve B. This means that Curve C, the intermediate quartet state, never constitutes the ground state of the complexes. Griffith has shown this property to be of general validity using ligand field arguments [10].

It is evident from all the curves of Figs. 1 and 2 that the equilibrium metal-ligand distance is determined by the specific electron occupancy within the d-manifold. For example curve B (t_{2g}^5) has the smallest internuclear separation while Curve A ($t_{2g}^3e_g^2$) shows the largest. The complete ordering for the five curves is $B(t_{2g}^5) < C \sim E(t_{2g}^4e_g^1) < A \sim D(t_{2g}^3e_g^2)$ 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.

Although it is not possible to measure experimentally the equilibrium metal-ligand separations for both the high and the low spin configurations estimates

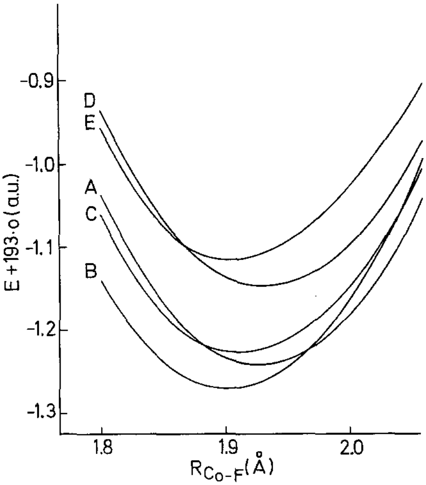


Fig. 1

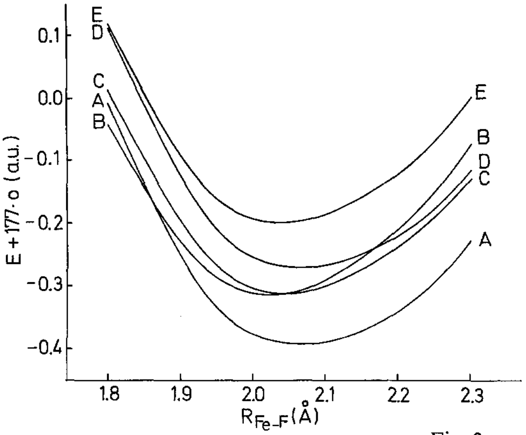


Fig. 2

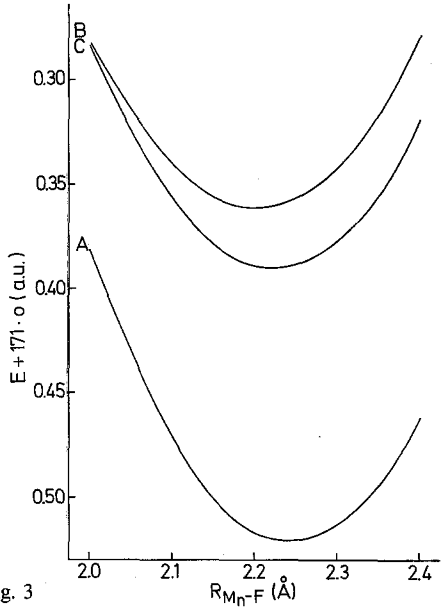


Fig. 3

Fig. 1. Potential energy curves for a number of strong-field configurations of the hexafluoro cobalt (IV) ion. *A* – sextet $(t_{2g}^3e_g^2)$, *B* – doublet (t_{2g}^5), *C* – quartet $(t_{2g}^4e_g^1)$, *D* – quartet $(t_{2g}^3e_g^2)$, *E* – doublet $(t_{2g}^4e_g^1)$

Fig. 2. Potential energy curves for a number of strong field configurations of the hexafluoroferrate (III) ion. *A* – sextet $(t_{2g}^3e_g^2)$, *B* – doublet (t_{2g}^5), *C* – quartet $(t_{2g}^4e_g^1)$, *D* – quartet $(t_{2g}^3e_g^2)$, *E* – doublet $(t_{2g}^4e_g^1)$

Fig. 3. Potential energy curves for the hexafluoromanganate (II) ion. *A* – sextet $(t_{2g}^3e_g^2)$, *B* – doublet (t_{2g}^5), *C* – $(t_{2g}^4e_g^1)$

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 for some Fe(III) dithiocarbamates [11] have indicated that there is a decrease in molar volume on passing from the high spin to the low spin arrangements; the change in the metal-ligand speparation has been estimated to be of the order of 0.07 Å. The calculated difference in the equilibrium internuclear distances for the high and low spin curves is 0.07 Å (FeF_6^{3-}) and 0.03 Å (CoF_6^{2-}) in good agreement with the experimental data for the iron dithiocarbamates.

Potential energy curves for the high spin (A), the low spin (B) and the intermediate quartet (C) of the iso-electronic fluoro complex MnF_6^{4-} are shown in Fig. 3. As expected the high spin state is now considerably more stable than the low spin curve compared with the iron fluoro complex in agreement with the spectral analysis of this ion [12]. Although the computed equilibrium metal-fluorine separations in the ground state of these complexes are slightly larger than the experimental values, the calculations satisfactorily produce a contraction in M–F separation on passing from a complex containing a divalent metal ion, through a trivalent ion to a tetravalent central metal ion.

It has been seen from the preceeding potential energy curves that the present calculations yield the correct ground states for complexes when the central metal ion is varied. A change of ligand to cyanide in the iron (III) complex is known to change the ground state from high spin to low spin [13]. Figure 4 shows the high and low spin curves for the hexacyanoferrate (III) ion. In agreement with spectroscopic work the calculations give rise to a low spin ground state, which is more stable than the high spin state at equilibrium by 0.12 a.u. The computed Fe–C bond length for the low spin state of 1.89 Å is very close to the experimental value of 1.90 Å [14].

The present MO calculations give an indication as to the difference in *equilibrium* energies of the high and low spin forms, a quantity which cannot be obtained from either the electronic spectrum or from the crystal field Tanabe-Sugano diagrams [15], 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 ${}^6A_{1g}$ ground state to the excited ${}^2T_{2g}$ (t_{2g}^5) configuration (or vice versa) becomes zero. The equilibrium energy separations should however be dependent on the crystal field energy Δ since the further apart the vertical excitation the larger the separation between the potential energy curves. A plot of the differences between the equilibrium energies of the high and low spin configurations against Dq/B derived from the electronic spectrum is given in Fig. 5, and a fairly good linear correlation is obtained for all four complexes. The graph also shows that at the crossover point (Dq/B 2.8) the high and low spin states have identical *equilibrium* energies. If a correlation of this sort can be expected to hold for all d^5 complexes Fig. 5 provides a means of obtaining the equilibrium energy difference from the absorption spectrum of a complex.

The electronic excitation energies of the complexes should correspond to a first approximation to the vertical energy differences of the curves through the minimum of the ground state curve. Thus for the two high spin complexes MnF_6^{4-} and FeF_6^{3-}, transitions to the lowest quartet levels ($t_{2g}^4e_g^1$) are calculated to occur at 28.7 kK and 18.3 kK respectively, while observed bands to quartet states with this configuration lie at 19.2 kK and 23.1 kK for MnF_6^{4-}, and 16.6 and 21.7 kK for FeF_6^{3-}. Transitions from the ${}^2T_{2g}$ ground state of CoF_6^{2-} are calculated at

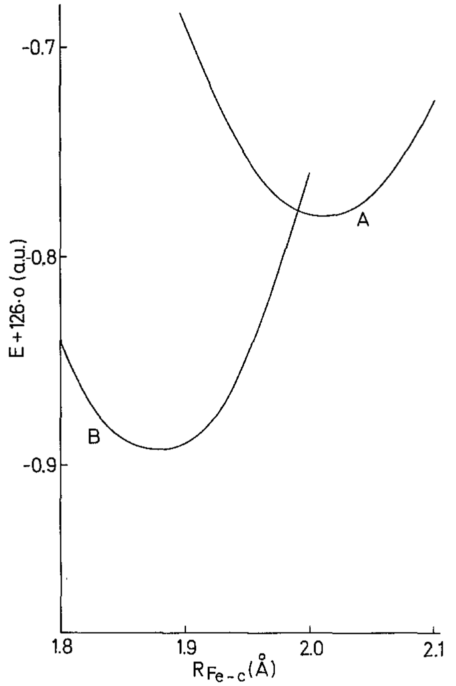
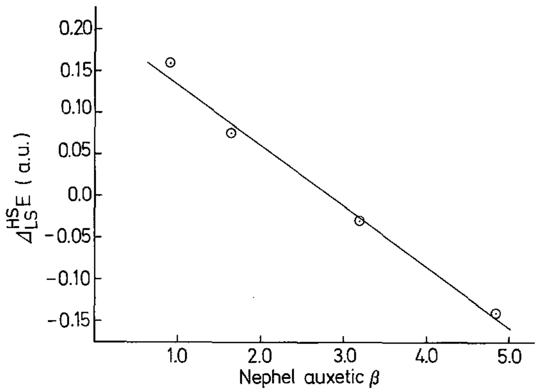


Fig. 4. High and low spin potential energy curves for the hexacyanoferrate (III) ion. *A* – low spin (t_{2g}^5), *B* – high spin ($t_{2g}^3 e_g^2$)

Fig. 5. Correlation between the Equilibrium Energy Differences of High and Low spin configurations and the optical Dq/B value for some $3d^5$ complexes



10.2 kK (quartet) and 29.3 kK (doublet). The spin-forbidden quartets are observed at 6.3 and 10.9 kK while the six spin-allowed bands span 17.3–32.1 kK.

In addition to these *d–d* excitations the charge-transfer type transitions may also be interpreted using molecular orbital basis. The energies of some charge-transfer states of the hexafluorocobaltate (IV) ion have been calculated and are given together with the *d–d* transitions and the observed values in Table 1. The calculated charge-transfer transitions from the almost non-bonding t_{1u} and t_{2u} π-type ligand orbitals to the t_{2g} metal orbitals are very close to the observed bands. The computed transition energies from t_{1u}, $t_{2u} \rightarrow e_g$ lie beyond the spectroscopic region examined. Thus the previous assignment of the bands for CoF_6^{2-} at 28.3 and 37.1 kK to charge-transfer $\pi \rightarrow t_{2g}$ is substantiated by these calculations.

Table 1. Excited state energies of CoF_6^{2-}

d–d	Calculated kK.	Observed kK.
$^2T_{2g}(t_{2g}^5) \rightarrow t_{2g}^4 e_g^1$(quartet)	10.2	6.4, 10.3
$\rightarrow t_{2g}^4 e_g^1$(doublet)	29.3	17.3, 18.9, 20.5 24.8, 32.1
Charge transfer transitions		
$t_{1u} \rightarrow t_{2g}$	24.8	28.3
$t_{2u} \rightarrow t_{2g}$	35.3	37.1
$t_{1u} \rightarrow e_g$	57.6	—
$t_{2u} \rightarrow e_g$	62.5	—

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