Table III. Ions Observed in the Mass Spectrum of Vapors Generated by NH_4FeCl_4

mass no. range	species	% ion current scan 162	% ion current scan 258
14-18	N^+, NH^+, O^+, NH_2^+, NH_3^+, H_2O^+	3.3	2.8
28	N_2^+	1.2	0.6
35-38	Cl^+, HCl^+	25.9	20.7
51-57	$NHCl^+$, NH_2Cl^+, Fe^+	5.8	13.0
91-93	$FeCl^+$	10.7	22.0
106-110	$NHFeCl^+$, NH_2FeCl^+, NH_3FeCl^+	12.7	7.5
126-130	$FeCl_2^+$	4.4	7.2
141-147	$NHFeCl_2^+$, $NH_2FeCl_2^+$, $NH_3FeCl_2^+$	8.5	3.7
161-167	$FeCl_3^+$	1.3	1.9
176-184	$NHFeCl_3^+$, $NH_2FeCl_3^+$, $NH_3FeCl_3^+$	4.2	1.1
217-221	$Fe_2Cl_3^+$	0.11	0.3
252-254	$Fe_2Cl_4^+$	0.13	0.9
287-293	$Fe_2Cl_5^+$	0.08	0.6
324-326	$Fe_2Cl_6^+$	0.01	0.02

between 440 and 455 °C. Hence it is assumed that these values of K_3 characterize the decomposition of $NH_4FeCl_3(s)$.

Sample D-6. As this mixture of ammonia and $FeCl_2(s)$ warmed to room temperature, the ammonia pressure fell to ca. 5 torr. Variation of P with T at higher temperatures is shown in Figure 4. Equilibration was slow below 100 °C. Between 100 and 160 °C the number of moles of gas remained constant at ca. 40% of the amount of NH_3 initially added. Above 370 °C the number of moles of gas corresponded to $n°_{NH_3}$. The curvature of the ln P vs. $1/T$ line (Figure 4) between 200 and 370 °C suggests that the condensed phase is a solid solution of changing composition. Partial pressures of ammonia in mixtures described above are appreciably less than values observed with this sample, and it has been assumed that condensed ammoniates of $FeCl_2$ need not be included in the treatment of those mixtures.

Mass Spectra

Mass spectrometric analysis of the vapors generated by heating a solidified melt of NH_4FeCl_4 was carried out to obtain direct evidence for the dominant molecular species generated in the vaporization process. Facilities available only permitted study of the free vaporization of the solid directly into the vacuum of the ion-source chamber.

The direct-insertion probe of a Hewlett-Packard 5985 GC mass spectrometer was used.[23] An equimolar mixture of NH_4Cl and $FeCl_3$ in an evacuated Pyrex tube was melted by gentle flaming, and the dark yellowish green liquid was driven along the walls into an attached thin-walled capillary (1.6-mm o.d.). The sample would not sublime readily, presumably inhibited by N_2 and HCl formed by the reduction reaction as the system stabilized. The solidified product (a block ca. 0.5 cm long) was isolated by flame seal-off and the 1-in. length of capillary was wedged into the mass spectrometer sample probe. At the moment of insertion the tip (away from the solid block) was snipped off. The brief exposure is assumed to have led to some hydrolysis at the surface; however, the bulk of the sample appeared unaffected.

With the probe in the ionization chamber, the temperature was increased at 30 °C/min to a maximum of 250 °C, and mass spectra were scanned repeatedly over a 20-min period (iv 70; mass range 0–400). At 60 °C $HCl^+ + Cl^+$ accounted for 25% of the total ion current (the rest was background; there were no peaks attributable to species expected from NH_3FeCl_3). This surge of HCl is assumed to have come from decomposition of surface hydrolysis products. Between 100 and 200 °C, the $HCl^+ + Cl^+$ current fraction fell to ca. 2% but increased again as the sample temperature approached 250 °C. The major ion peaks observed after several minutes at 250 °C (scan 162 as representative) are listed in Table III. Mass distributions in the various ranges were consistent with isotopic abundances for the species indicated. The overall result offers strong support for the conclusion that NH_4FeCl_4 vaporizes by reaction 4. Ion currents in mass range 196–224 (for species such as $FeCl_4^+$, $NH_4FeCl_4^+$, etc.) were at background level. On the last scan (258) the amount of material vaporizing appeared to be falling off (total ion current was one-fourth that of scan 162) and contributions, albeit very small, from species expected from ionization of Fe_2Cl_6 were relatively larger. Ion currents for these peaks in scan 162 were only slightly above background level. The presence of trace amounts of Fe_2Cl_6 may indicate a slight dissociation of the ammine, some solubility of ferric chloride in the NH_4FeCl_4 phase, or possibly disproportionation of oxychloride, formed by hydrolysis, into ferric chloride and ferric oxide.

Registry No. NH_4FeCl_4, 24411-12-9; NH_3FeCl_3, 78790-89-3.

---

[23] Purchased with financial assistance from the National Science Foundation, Department Grant 61-7206, which is gratefully acknowledged. Spectra were taken by Dr. James B. Callis, to whom thanks are expressed.

Contribution from the Department of Chemistry,
University of Leuven, 3030 Heverlee, Belgium

Role of Spin Change in the Stereomobile Reactions of Strong-Field d^6 Transition-Metal Complexes

L. G. VANQUICKENBORNE* and K. PIERLOOT

Received February 25, 1981

The isomerization, racemization, and stereomobile substitution reactions of low-spin d^6 complexes have been studied in the framework of a ligand field model. On the basis of orbital and state correlation diagrams for the different reaction mechanisms, it is concluded that stereomobility is only possible if a spin change takes place somewhere along the reaction coordinate. The lowest quintet state ($^5T_2$ octahedral parentage) plays an especially important role in this process. The ligand field expression for the activation energy is compatible with the experimentally observed negative correlation between $10Dq$ and the occurrence of stereomobility.

Introduction

Ever since the early fifties, ligand field theory has been applied to the kinetic and thermodynamic properties of transition-metal complexes.[1-3] Although the broad features of the relative stabilities and reactivities of the different d^n systems in solution can be rationalized in terms of ligand field theory,

---

(1) Orgel, L. E. *J. Chem. Soc.* **1952**, 4756.

0020-1669/81/1320-3673$01.25/0 © 1981 American Chemical Society

a detailed mechanistic description of the thermal reactions is not really available. It appears to be difficult to make even phenomenological generalizations, or to establish empirical rules that would allow the prediction of the leaving ligand, or to describe the stereochemistry of a substitution reaction. This situation is in marked contrast to what is found in transition-metal photochemistry, where both empirical rules and ligand field rationalizations have been formulated.[4-9] In part, this contrast is likely to be related to the fact that entropy effects play a more important role in thermal reactions.[10]

It is the purpose of the present paper to argue in favor of a specific mechanistic hypothesis, supposedly valid for *any* stereomobile thermal reaction of hexacoordinated strong-field d^6 complexes. By strong-field d^6 complexes we mean complexes, characterized by a well-defined spin quantum number $S = 0$; the geometry of the first coordination sphere will generally be described by an octahedron, or a slightly distorted octahedron. This is the case for a number of Fe(II) complexes, for nearly all Co(III), and for strictly all Rh(III) and Ir(III) compounds. Complexes of this type can give rise to stereomobile reactions in essentially two different ways.[11] In the first place, some of them can undergo an intramolecular twist, via a trigonal prism as transition state; examples are the racemization of $Fe(phen)_3^{2+}$, $Co(pyrdtc)_3$, $Co(ox)_3^{3-}$, $Co(Bz,Bz\text{-}dtc)_3$ and Co(α-(*R*)-tropolonato)$_3$.[12-18] In the second place, certain other complexes of the same type can undergo a dissociation (either of one ligand or of one end of a bidentate ligand), generating a square pyramid which can be rearranged to form a trigonal bipyramid. The last ligand or ligand end (or possibly another ligand in the case of a substitution reaction) then reattacks on the equatorial plane of the trigonal bipyramid. Examples of stereomobile reactions of this type are the racemization and cis–trans isomerization of cobalt(III) tris(β-diketonates),[19-21] the cis–trans isomerization of $Co(en)_2AX$ complexes,[22,23] and the aquation of *trans*-$Co(en)_2AX$ complexes, where X is the leaving ligand and A a π donor.[3,22]

For all the stereomobile reactions under consideration (isomerizations, racemizations, or substitutions), we intend to show that ligand field theory implies the necessity of a spin change along the reaction path.

Experimental Evidence

The appearance of a quintet state has been suggested by several authors in a number of specific and isolated reactions, where the experimental data seemed to point to a spin change.

On the basis of ^1H NMR spectral data, combined with magnetic susceptibilities at various temperatures, Purcell and Zapata[24] concluded that *cis*-$Fe(phen)_2(NCBPh_3)_2$ exhibits a synchronous enantiomerization and spin-state isomerization ($S = 0 \rightleftharpoons S = 2$) in CH_2Cl_2. Their findings raised the question as to whether the intersection between the singlet and the quintet surface is not in fact realized by a molecular distortion along a twisting coordinate. In a subsequent paper, Purcell[25] examined this possibility by calculating the rate constant for the racemization of $Fe(phen)_3^{2+}$, using the fact that intersystem crossing occurs during the reaction. His result is in good agreement with the experimental value.

Another set of experimental data, suggesting the occurrence of a spin flip during the chemical reaction, is provided by the activation volumes and activation entropies of certain reactions. Indeed, a normal intramolecular twist process can be expected to be characterized by an activation volume in the neighborhood of zero: the bond lengths remain unaffected, and the reaction path is adequately described by angular variations only.[26] Such a twist process is also expected to have a low Arrhenius frequency factor, and thus a negative activation entropy due to the time interval needed to get the activation energy in the appropriate vibrational modes, and a correspondingly large deactivation probability.[27]

These expectations are borne out for the Cr(III) complexes: for $Cr(bpy)_3^{3+}$, $Cr(bpy)_2(ox)^+$, $Cr(phen)_2(ox)^+$, and $Cr(phen)_3^{3+}$, ΔV^* is found to be 3.4 ± 0.3, -1.0 ± 0.1, -1.5 ± 0.2, and 3.3 ± 0.2 $cm^3\ mol^{-1}$, respectively, while ΔS^* values are all large and negative[28] (of the order of -60 or -70 $J\ K^{-1}\ mol^{-1}$).

The racemization of the corresponding d^6 systems, on the other hand, is characterized by much larger activation volumes: for $Co(pyrdtc)_3$, ΔV^* equals 5.4–7.8 $cm^3\ mol^{-1}$ (depending on the solvent),[13] and for the $Fe(phen)_3^{2+}$ racemization, ΔV^* is even higher,[12] namely, 14.2–15.6 $cm^3\ mol^{-1}$. The large positive value of ΔV^* is taken to be an (indirect) indication for the quintet nature of the transition state. Indeed, it seems reasonable to assume that the occupation of the σ-antibonding e_g orbitals, which is characteristic of the high-spin state, will contribute to a metal–ligand bond lengthening and therefore to a volume increase.

The positive ΔV^* values for these reactions are paralleled by positive ΔS^* values. This is again an indication for the occurrence of a low-spin/high-spin crossover along the reaction path. Indeed, a high-spin state is characterized by the larger value of both the magnetic and the vibrational contributions to the entropy. The former term is simply given by $R \ln (2S + 1)$; the latter term is related to the vibrational frequencies of the molecules under consideration. It has been shown[29] that the stretching frequencies for certain Fe(II) complexes are roughly twice as large in low-spin states as in high-spin states.[30]

A spin flip has also been suggested to occur in the course of the aquations[12,32] of $Fe(phen)_3^{2+}$ and of $Fe(bpy)_3^{2+}$; as a matter of fact, the diaquo product of these reactions is a high-spin complex in both cases. Two other instances where a spin flip has been invoked are the optical inversion, involved in the reaction[33,34] of cyanide ion with

---

(2) McClure, D. S. *J. Chem. Phys.* **1957**, *26*, 988.

(3) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions"; Wiley: New York, 1958.

(4) Adamson, A. W. *J. Phys. Chem.* **1967**, *71*, 798.

(5) Kirk, A. D. *Mol. Photochem.* **1973**, *5*, 127.

(6) Zink, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 8039.

(7) Wrighton, M.; Gray, H. B.; Hammond, G. S. *Mol. Photochem.* **1973**, *5*, 164.

(8) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977**, *99*, 2208.

(9) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1978**, *100*, 475. Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1978**, *17*, 2730.

(10) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.

(11) Serpone, N.; Bickley, D. G. *Prog. Inorg. Chem.* **1972**, *17*, 391.

(12) Lawrance, G. A.; Stranks, D. R. *Inorg. Chem.* **1978**, *17*, 1804.

(13) Lawrance, G. A.; Suvachittanont, S.; Stranks, D. R.; Tregloan, P. *J. Chem. Soc., Chem. Commun.* **1979**, 757.

(14) Broomhead, J. A.; Lauder, I.; Nimmo, J. *J. Chem. Soc. A* **1971**, 645.

(15) Palazzotto, M. C.; Duffy, D. J.; Edgar, B. L.; Que, L., Jr.; Pignolet, L. M. *J. Am. Chem. Soc.* **1973**, *95*, 4537.

(16) Eaton, S. S.; Holm, R. H. *J. Am. Chem. Soc.* **1971**, *93*, 4913.

(17) Eaton, S. S.; Hutchison, J. R.; Holm, R. H.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 6411.

(18) In what follows, phen stands for 1,10-phenantroline, bpy for 2,2′-bipyridyl, ox for oxalate, pyrdtc for pyrrolidinecarbodithioate, Bz for benzoyl, Ph for phenyl, and en for ethylenediamine.

(19) Fay, R. C.; Girgis, A. Y.; Klabunde, U. *J. Am. Chem. Soc.* **1970**, *92*, 7056.

(20) Girgis, A. Y.; Fay, R. C. *J. Am. Chem. Soc.* **1970**, *92*, 7061.

(21) Gordon, J. G.; Holm, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 5319.

(22) Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* **1974**, *11*, 47.

(23) In $Co(en)_2(NH_3)OH^{2+}$ and $Co(en)_2(OH)_2^+$ however a twist mechanism cannot be excluded: Farago, M. E.; Page, B. A.; Mason, C. F. V. *Inorg. Chem.* **1969**, *8*, 2270.

(24) Purcell, K. F.; Zapata, J. P. *J. Chem. Soc., Chem. Commun.* **1978**, 497.

(25) Purcell, K. F. *J. Am. Chem. Soc.* **1979**, *101*, 5147.

(26) Lawrance, G. A.; Suvachittanont, S. *Inorg. Chim. Acta* **1979**, *32*, L13.

(27) Fay, R. C.; Piper, T. S. *Inorg. Chem.* **1964**, *3*, 348.

(28) Lawrance, G. A.; Stranks, D. R. *Inorg. Chem.* **1977**, *16*, 929.

(29) Takemoto, J. H.; Hutchinson, B. *Inorg. Chem.* **1973**, *12*, 705; *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 769.

(30) In fact, it has been suggested in ref 31 that the driving force of the magnetic crossover, observed in certain stable (nonreacting) first-row transition-metal complexes, is the difference in entropy between the two states involved in the transition.

(31) Gütlich, P., paper presented at the 179th National Meeting of the American Chemical Society, Houston, Texas, 1980.

(32) Twigg, M. V. *Inorg. Chim. Acta* **1974**, *10*, 17.

(33) Archer, R. D., Suydam, L. J.; Dollberg, D. D. *J. Am. Chem. Soc.* **1971**, *93*, 6837.

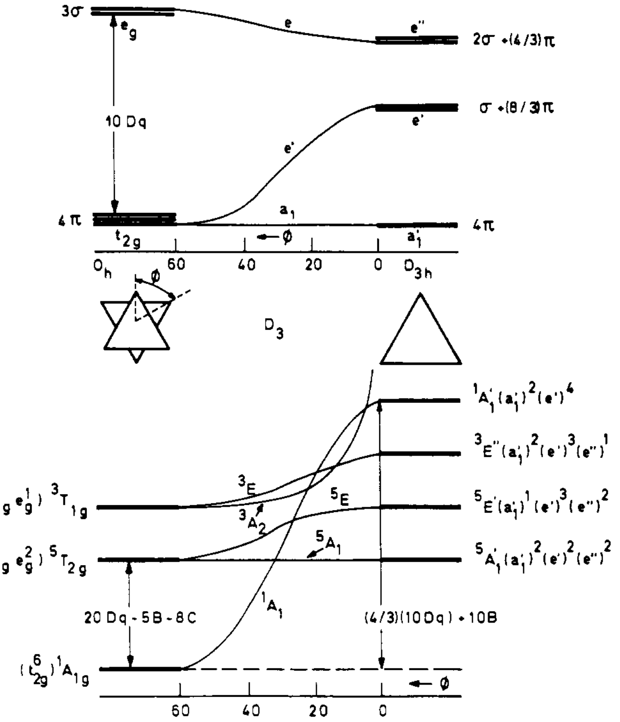

Figure 1. Schematic orbital and state correlation diagrams for the Bailar twist; the abscissa is the twist angle ϕ ($\phi = 0°$ for the trigonal prism and $\phi = 60°$ for the octahedron). The relative order of the states corresponds to a situation, characteristic of complexes of the first-row transition-metal ions. Dominant configurations are given in parentheses. For simplicity, the spin–orbit coupling effects are not shown, although they are of course essential in determining the details of spin flip.

aqueous $Fe(phen)_3^{2+}$, and the concerted base hydrolysis–Bailar inversion[35] of $Co(en)_2Cl_2^+$.

In summary, it would be hard to deny that a certain amount of experimental evidence is available in favor of a spin change in the course of the reactions under consideration. This evidence is admittedly limited, sporadic, and sometimes indirect; more often than not, the hypothesis of a spin flip has been advanced on a very tentative basis, or it has been suggested as one possibility among others.[36,37] Perhaps this is the reason that so far the idea seems to have gained only very slow acceptance. Yet, as we will show on the basis of very simple ligand field considerations, one has to conclude that spin flip is predicted to be a necessary condition for stereomobility in d^6 complexes.

Twist Mechanism

Figure 1 shows the well-known orbital and state correlation diagrams connecting the octahedron and the trigonal prism as a function of the twist angle ϕ. For the sake of simplicity, the six ligands were taken to be equal, and the two triangles were kept at a constant distance.[38,39] The orbital energies are expressed in terms of the ligand field parameters σ and π; as usual $3\sigma - 4\pi = 10Dq$.

Along the reaction coordinate, the t_{2g} level is split, and while the a_1 orbital remains virtually unaffected, the energy of the e′ orbital increases considerably from 4π to $\sigma + {}^8/_3\pi$. At the same time the e_g orbital in O_h is stabilized to some extent, so that the energy difference between the two highest orbitals decreases very significantly.

The ground state of the octahedral complex is always $^1A_{1g}$, but the relative position of $^5T_{2g}$ and $^3T_{1g}$ depends on the relative value[40] of the ligand field parameters and the Racah repulsion parameters (B, C). For the first-row ions, Fe(II) and Co(III), the quintet state will be the lower one (Figure 1) except for the strongest ligands; for the second- and the third-row ions, Rh(III) and Ir(III), the repulsion parameters are smaller, while the ligand field parameters are larger; as a consequence, the triplet drops below the quintet. At the D_{3h} side of the diagram, the ground state will be either $^5A_1'$, with configuration $(a_1')^2(e')^2(e'')^2$, or $^1A_1'$, with configuration $(a_1')^2(e')^4$. For Fe(II) and Co(III), the ground state will be $^5A_1'$, while $^1A_1'$ is at much higher energy (Figure 1); for Rh(III) and Ir(III), the $^1A_1'$ level will be closer to $^5A_1'$ and for very strong metal–ligand interactions, $^1A_1'$ will drop below $^5A_1'$.

The energy required to carry out a Bailar twist depends on whether or not the reaction takes place on the singlet potential surface. The energy difference between $^1A_{1g}(O_h)$ and $^1A_1'(D_{3h})$ equals ${}^4/_3(10Dq) + 10B$. For the first-row ions Fe(II) and Co(III), coordinated by oxygen or nitrogen ligands, this amounts to an energy barrier of the order of 400 kJ/mol.[41] For Rh(III) and Ir(III), the activation energy is predicted to be even much higher. Since no significant solvent assistance can be invoked for an intramolecular twist, the ligand-field value might be considered as a realistic approximation of the activation energy.

Therefore, one can only conclude that an isomerization on the singlet surface should be a highly forbidden process. Figure 1 shows however that, at least for Fe(II) and Co(III), a spin crossover takes place between ^1A and ^5A. If the transition probability for a spin change is sufficiently large—which is very likely[24,25]—the activation energy will be lowered to roughly $20Dq - 5B - 8C$. Indeed, this expression corresponds to the singlet–quintet energy difference in the octahedron; the quintet energy is nearly independent of the twist angle ϕ. When the quantity $20Dq - 5B - 8C$ is calculated for a number of d^6 ML_6 complexes, one obtains the following order:[41]

$$Co^{III}O_6 < Fe^{II}N_6 < Co^{III}N_6 < Rh^{III}A_6 < Ir^{III}A_6$$

where O and N indicate the coordinating atoms, while A may be any ligand. It is an experimental fact that the three rightmost classes of complexes (largest singlet–quintet gap) are stable with respect to isomerization or racemization. For instance, for $Co(en)_3^{3+}$ the numerical value of $20Dq - 5B - 8C$ is still quite large, namely, 170 kJ/mol, which explains the stability of individual enantiomers.[42] On the other hand, molecules belonging to the two leftmost classes of the series do racemize and can sometimes even be classified as nonrigid molecules.[16,17] This fact is in agreement with the smaller singlet–quintet energy differences for $Fe(phen)_3^{2+}$ (100 kJ/mol), Co(α-(R)-tropolonato)$_3$, and $Co(ox)_3^{3-}$ (60 kJ/mol). So the general trends are quite well understood by assimilating the activation energy with the singlet–quintet energy gap. Some problems do remain however: for instance, both Co(α-(R)-tropolonato)$_3$ and $Co(ox)_3^{3-}$ are $Co^{III}O_6$ systems and as such are taken to be characterized by the same activation energy. Experimentally, $\Delta H^{\ddagger} = 69$ kJ/mol for the former[16] and 106 kJ/mol for the latter complex.[43] The π-electronic structure of both ligands is of course rather different, and this might result in different $10Dq$ values.[44] The essential point

---

(34) Archer, R. D.; Dollberg, D. D. *Inorg. Chem.* **1974**, *13*, 1551.

(35) Kwak, W. S.; Archer, R. D. *Inorg. Chem.* **1976**, *15*, 986.

(36) Archer, R. D. *Adv. Chem. Ser.* **1967**, *No. 62*, 452.

(37) Archer, R. D. *Coord. Chem. Rev.* **1969**, *4*, 243.

(38) The implication is that certain ligand–metal–ligand angles vary from 90° in the octahedron to 70.52° in the trigonal prism. This may not be very realistic, but it will not affect our qualitative conclusions.

(39) Although the diagrams are constructed for a trigonal (Bailar) twist, the state correlations for a rhombic (Ray–Dutt) twist are essentially the same,[25] so our conclusions are valid for both cases.

(40) Tanabe, Y.; Sugano, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 753.

(41) Typical values for the ligand field parameters can be extrapolated from ref 8; for $Fe(II)N_6$, one can use $B = 0.07\ \mu m^{-1}$, $C = 0.29\ \mu m^{-1}$, and $10Dq = 1.755\ \mu m^{-1}$ as in ref 25; for $Co^{III}O_6$, we used $\sigma = 0.832$, $\pi = 0.154$, $B = 0.06$, and $C = 0.37\ \mu m^{-1}$, on the basis of an analysis of amino acid complexes.

(42) Douglas, B. E. *J. Am. Chem. Soc.* **1954**, *76*, 1020. Busch, D. H. *Ibid.* **1955** *77*, 2747.

(43) Bushra, E.; Johnson, C. H. *J. Chem. Soc.* **1939**, 1937.

remains that both complexes belong to the low-lying quintet species and that they are both characterized by stereomobility.

It is interesting to note here that the activation energy of the Bailar twist has been calculated before by both Wentworth[45] and Larsen et al.,[46] equally on the basis of ligand field theory. The energies were calculated as a function of the number of d electrons on the central metal ion. For the low-spin d^6 systems, the reaction was assumed to take place on the singlet potential surface; consequently the activation energy of d^6 systems was found to be very large—larger than for any other d^n system (low spin or high spin). Still, both references[45,46] claim good agreement between theory and experiment. The reason is that they did not compare the calculated activation energies to rate constants but rather to the geometrical structure of the complexes: it was assumed that there exists a correlation between their calculated activation energy of the twist mechanism and the distortion of the octahedral ground state toward a trigonal prism. And, indeed, low-spin Fe(II) and Co(III) complexes are characterized by a structure, which is closer to the octahedron than most other d^n systems. The important point is that, for low-spin Fe(II) and Co(III) complexes, there is no correlation whatsoever between the ground-state distortion and the ease of rearrangement: despite the fact that these complexes have a structure which is close to the octahedron, they rearrange easily. Although this point had been noted before,[17,44] so far it has not been connected with the role of the quintet state.

Yet, it is obvious that the breakdown of the correlation can be understood quite readily from Figure 1. At the onset of the distortion, the system is still on the ^1A surface, and, therefore, a small angular variation corresponds to a large energy increase. But the abrupt change of potential surface at the singlet–quintet crossover renders the comparison to other d^n systems inappropriate.

Dissociative Mechanism

The dissociation of one ligand from the octahedron leaves a square-pyramidal (SP) C_{4v} structure. An isomerization or a stereomobile substitution is only possible if this five-coordinated fragment gets reorganized into another geometry, which must be close to trigonal bipyramidal (TBP, D_{3h}). This reorganization has to take place before the square pyramid reassociates with a ligand molecule; therefore, the energy barrier from the C_{4v} to the D_{3h} structure should not be very different from zero. Figure 2 shows the orbital and state correlation diagrams for the angular displacement of the two ligands over 30°, connecting SP and TBP. The d_{yz} orbital is the most strongly destabilized orbital, developing from purely π antibonding into predominantly σ bonding. As a consequence, the $^1A_1$ ground state increases in energy to the extent of $^3/_4(10Dq) + C$. Even for Fe(II) complexes, this amounts to ~200 kJ/mol, and for Co(III) or Rh(III) complexes, one can obtain values of 250 kJ/mol or more.[41] Clearly, a reaction characterized by an activation energy of this magnitude is not competitive with a direct stereoretentive reassociation of a ligand to the square pyramid.

Since the reaction will not take place on the singlet potential surface, the experimentally observed stereomobility must again be traced back to a level crossing. Actually, the idea of a level crossing has been put forward at several occasions by Archer;[36,37] the most detailed treatment however was given by Spees, Perumareddi, and Adamson.[47] They argued that the octahedron has a singlet ground state, while the TBP cannot possibly have a singlet ground state. Indeed, the $(e'')^4(e')^2$ configuration gives rise to three states: $^1A_1'$, ^1E, and $^3A_2'$ to first order separated by energy intervals of $2C$ (see also Figure 2). Therefore, in accord with Hund's rule, the triplet $^3A_2'$ is $4C$ lower than $^1A_1'$, which correlates directly to the octahedral ground state. Consequently, Spees et al. proceeded on the hypothesis that the activation energy of a stereomobile substitution equals the energy difference between $^3A_2'(D_{3h})$ and $^1A_{1g}(O_h)$. This is undoubtedly a valid idea for the very strong-field Rh(III) and Ir(III) complexes; the activation energy for the angular displacement is then given by $^3/_4(10Dq) - 3C$. For any reasonable numerical value of the ligand field parameters, this leads to an energy barrier which is very large—in agreement with the observed thermal stereoretention of the Rh(III) and Ir(III) complexes.[48,49]

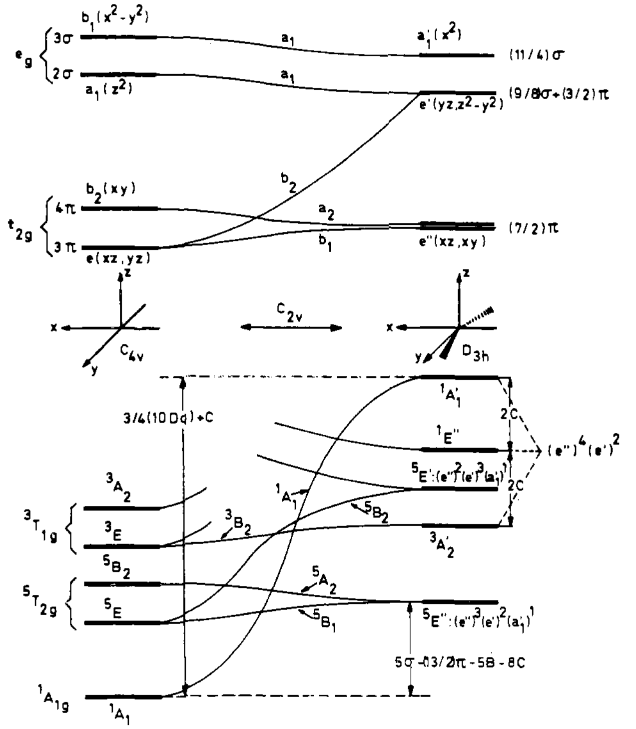

Figure 2. Schematic orbital and state correlation diagrams for the transition between a square pyramid (left) and a trigonal bipyramid (right). The state diagram is qualitatively appropriate to describe $3d^6$ systems (the relative order of certain states would be different for $4d^6$ or $5d^6$ systems). The dominant configurations are given for each D_{3h} state; in the C_{4v} structure, the octahedral parentage is indicated (compare Figure 1). The symmetry conserved along the reaction path is C_{2v}.

We believe, however, that the same line of reasoning should not be applied to Fe(II) or Co(III) complexes. Indeed, except for the strongest ligands such as CN^-, the $^5E''[(e'')^3(e')^2(a_1')^1]$ of these complexes drops below the $^3A_2'$ and becomes the ground state of the trigonal bipyramid. Therefore, in analogy to the twist mechanism, it appears quite reasonable to postulate a singlet–quintet spin flip, leading to an activation energy of only $5\sigma - {}^{13}/_2\pi - 5B - 8C$ (see also Figure 2). The weaker the ligands, the more the quintet gets stabilized with respect to the triplet, and the more the reaction will be determined by the quintet properties only. For intermediate ligands however, the triplet and quintet states of Co(III) complexes may be of comparable energy, and they may be both thermally accessible.

---

(44) Hoffmann, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 2484.

(45) Wentworth, R. A. D. *Coord. Chem. Rev.* **1972–1973**, *9*, 171.

(46) Larsen, E. N.; La Mar, G. N.; Wagner, B. E.; Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1972**, *11*, 2652.

(47) Spees, S. T.; Perumareddi, J. R.; Adamson, A. W. *J. Am. Chem. Soc.* **1968**, *90*, 6626.

(48) Johnson, S. A.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 1741.

(49) Bauer, R. A.; Basolo, F. *Inorg. Chem.* **1969**, *8*, 2231.

The expression $5\sigma - {}^{13}/_{2}\pi - 5B - 8C$ depends on the ligands in roughly the same way as $10Dq = 3\sigma - 4\pi$. The activation energy for stereomobility increases for larger σ and smaller π parameters, that is approximately for increasing $10Dq$. This is indeed the tendency which seems to summarize the experimental data.[33,37] For instance, for the Co(III) β-diketonates $5\sigma - {}^{13}/_{2}\pi - 5B - 8C$ is found to be negative, so that the dissociation and the $C_{4v} \rightarrow D_{3h}$ process may proceed in a concerted manner. In the aquation of *trans*-$Co(en)_2AX$ complexes, where X is the leaving ligand, the reactions are stereomobile when A is a π donor (Cl^-, OH^-, etc.); otherwise the reactions are stereoretentive.[3] This is consistent with the appearance of the negative π coefficient in the above expression. There is no need to invoke the role of metal 4p orbitals, as in the π-bonding theory of Basolo and Pearson.[3,50] A more detailed treatment of the $Co(en)_2AX$ complexes, accounting for the differences between the coordinated ligands, as well as for the different stereochemical aspects, will be published subsequently.[51]

Another confirmation of the spin flip hypothesis can be derived from the fact that even those $Co(en)_2AX$ complexes that do exhibit stereomobility upon aquation become stereoretentive when the amine ligands are replaced by the stronger diimine ligands.[52]

Conclusion

In racemizations, isomerizations, and stereomobile substitution reactions of strong-field d^6 complexes, a quintet state (exceptionally perhaps a triplet state) has to be formed somewhere along the reaction coordinate. Within the framework of ligand field theory, this conclusion appears to be inescapable.

In all cases, the reason for the necessity of a spin flip is basically the same: both in the six-coordinated complex of Figure 1 and in the five-coordinated complex of Figure 2, the stereomobility forces one low-lying π orbital to become essentially a high-lying σ orbital. In the thermal reactions of low-spin d^6 systems, this orbital is doubly occupied, and the resulting destabilization is responsible for a very high energy barrier: in the Woodward–Hoffmann sense, the reactions are strongly forbidden. Apparently, when a reacting transition-metal complex is given the choice between a Woodward–Hoffmann type selection rule and a spin selection rule ($S = 0 \nrightarrow S = 2$), it overcomes the latter one more easily than the former one.

Acknowledgment. The authors are indebted to the Belgian Government (Programmatie van het Wetenschapsbeleid). K.P. thanks the Belgian Science Foundation (NFWO) for a predoctoral fellowship.

---

(50) Pearson, R. G.; Basolo, F. *J. Am. Chem. Soc.* **1956**, *78*, 4878.

(51) Vanquickenborne, L. G.; Pierloot, K., to be submitted for publication.

(52) Aprile, F.; Basolo, F.; Illuminati, G.; Maspero, F. *Inorg. Chem.* **1968**, *7*, 519.

Contribution from the Institut für Physikalische und Theoretische Chemie and the Physikalisches Institut,
Abteilung II, University of Erlangen-Nürnberg, D-8520 Erlangen, West Germany,
and the School of Chemistry, University of New South Wales, Kensington, NSW 2033, Australia

The Nature of Proposed Six-Coordinate "Spin-Triplet Iron(II)": Low-Spin Iron(II) Cation/High-Spin Iron(III) Anion Complexes. A Chemical Application of Magnetic Hyperfine Interaction

E. KÖNIG,* G. RITTER, and H. A. GOODWIN

Received March 4, 1981

The preparation of a number of low-spin iron(II) cation/high-spin iron(III) anion complexes of the type $[Fe^{II}(diimine)_3]_m[Fe^{III}(dianion)_3]_n$ (diimine = 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, or 2,2′-bipyridyl; dianion = oxalate, malonate; $m{:}n$ = 1:1, 3:2, 2:1) is reported. The ^{57}Fe Mössbauer effect shows, as the result of superposition of the two individual spectra, a single doublet characterized by $\Delta E_Q \sim 0.28$ mm s^{-1} and $\delta^{IS} \sim +0.30$ mm s^{-1}. An external magnetic field resolves the doublet into a central Collins-type iron(II) spectrum and a six-line hyperfine spectrum with $564 \leq H_{int} \leq 581$ kG typical for iron(III). The spectra are practically identical with those of a series of red iron compounds reported earlier, such as $Fe(phen)_2ox{\cdot}5H_2O$ and $Fe(phen)_2mal{\cdot}7H_2O$. A new formulation for the latter type compounds is proposed in terms of low-spin iron(II) and high-spin iron(III) species. The new formulation is consistent with the known physical properties of the red iron compounds, previously considered to have a spin-triplet ground state. The implications of the present results concerning the proposals for a triplet ground state in six-coordinate iron(II) complexes are considered.

Introduction

Several years ago, one of the present authors reported on the synthesis of a series of red heterocyclic (diimine)iron complexes that were believed to be representatives for the rare case of a spin-triplet ground state in iron(II).[1] Two characteristic species of this series may serve as an example, viz., the phenanthroline complexes described as (oxalato)bis(1,10-phenanthroline)iron(II) pentahydrate, $[Fe(phen)_2ox]{\cdot}5H_2O$, and (malonato)bis(1,10-phenanthroline)iron(II) heptahydrate, $[Fe(phen)_2mal]{\cdot}7H_2O$. Analogous products had been obtained with 4,7-dimethyl-1,10-phenanthroline and 2,2′-bipyridyl as ligands. The proposed $S = 1$ electronic ground state was supported by physical measurements such as the magnetism of the solid compounds, subsequently extended to below 1 K;[2] the magnetism in solution; the ^{57}Fe Mössbauer effect including magnetic hyperfine studies, albeit only for small Doppler velocities; the IR vibrational spectra; and the electronic spectra in the UV, vis, and near-IR regions. More recently, the preparation of the two characteristic 1,10-phenanthroline iron complexes was repeated under the rigorous exclusion of oxygen.[3] The resulting compounds are

---

* To whom correspondence should be addressed at the Institut für Physikalische und Theoretische Chemie, University of Erlangen-Nürnberg.

(1) König, E.; Madeja, K. *Inorg. Chem.* **1968**, *7*, 1848.

(2) König, E.; Ritter, G.; Kanellakopulos, B. *J. Chem. Phys.* **1973**, *58*, 3001.