the importance of the ion pairing on the reactivity of $Na_2Fe(CO)_4$,[27] and we have found that the solution reactivity of complex II can be interpreted in terms of the existence of the ion pair such as VII.[28] While the reaction of carbon monoxide with cobalt(I) complexes, that do not allow the ion pairing,[29] produces a stable monocarbonyl species, reaction of II with CO is a multistep process giving finally $[(Co(salen))_2NaCo(CO)_4THF]$.[9,30] Moreover, complex II reacts in solution with CO_2, giving isolable adducts.[10,11,28]

The X-ray structural determination carried out on one of these CO_2 complexes showed that both metal centers are involved in fixing the CO_2, which is C bonded to the cobalt and O bonded to the alkali cation. The fixation likely involves concerted attack of the nucleophilic cobalt(I) on the electrophilic carbon of the CO_2, while the acid M^+ partner of the bifunctional system interacts with the basic oxygens.[10,11]

The potential of such bifunctional complexes for activating other small molecules is being studied.

Supplementary Material Available: Bond lengths and angles within salen and THF ligands for complexes III and IV (Tables SI and SII), least-squares planes for complexes III and IV (Tables SIII and SIV), calculated positional parameters for hydrogen atoms for III and IV (Tables SV and SVI), and structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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Stereochemistry of Equatorial Photosubstitution Reactions. The Chromium(III)–Fluoropentaamine Case

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It is shown that the observed stereomobility of equatorial photosubstitution reactions can be accommodated within the framework of ligand field theory. By use of orbital and state energy correlation diagrams, electronic selection rules can be seen to be operative in governing the course of the photoreaction. Possible complications due to radiationless deactivation processes are discussed.

Introduction

The substitution photochemistry of Cr(III) complexes has been at the basis of a number of experimental rules, whose formulation has greatly stimulated inorganic photochemistry as a whole.[1-5] In a series of recent papers,[6-9] we have shown how the main facts could be rationalized within the framework of ligand field considerations. As for the stereochemistry of

the Cr(III) complexes, our treatment was limited to the so-called "axial labilization". An illustrative example of this type of labilization is provided by the photoreaction[11]

$$trans\text{-}Cr(en)_2(NH_3)F^{2+} + H_2O \xrightarrow{h\nu}$$
$$cis\text{-}Cr(en)_2(H_2O)F^{2+} + NH_3$$
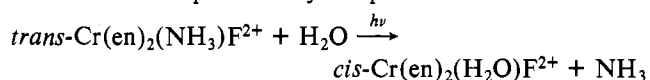
where the axial amine ligand is replaced by a solvent molecule
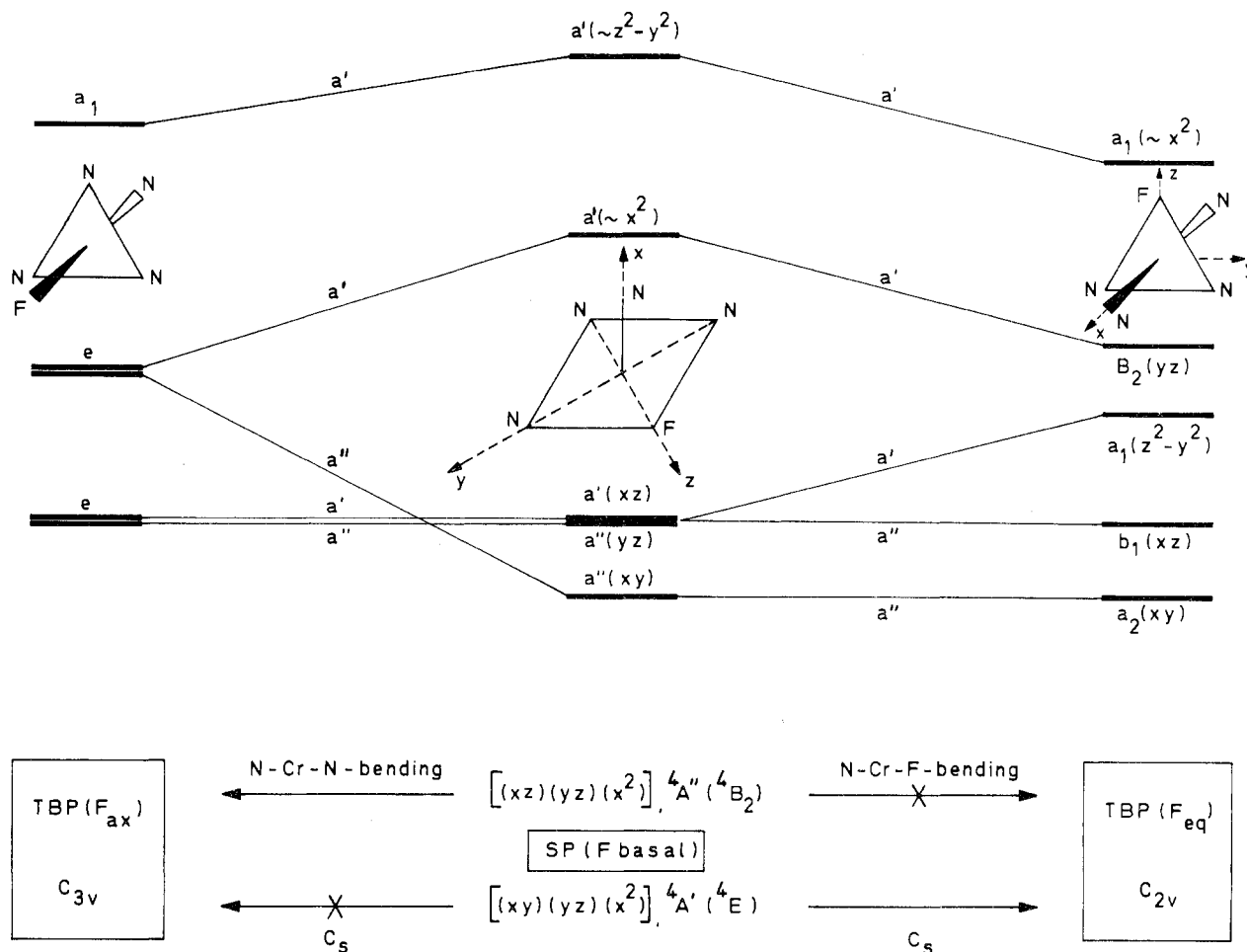
Figure 1. Correlation diagram between the square pyramid SP (F basal) and the two trigonal bipyramids TBP (F ax) and TBP (F eq).

with a quantum yield $\phi(NH_3)$ = 0.254 at 546 nm. On the basis of a dissociative reaction mechanism, the observed stereomobility can be understood in terms of a simple electronic selection rule.[7]

In addition to and competing with the loss of axial NH_3, the photosubstitution of *trans*-$Cr(en)_2(NH_3)F^{2+}$ gives rise to the loss of equatorial ethylenediamine. It is true that the latter reaction is quantitatively less important:[11] the corresponding quantum yield $\phi(en)$ = 0.07 at 546 nm. An earlier suggestion[12,13] that the equatorial labilizations of Cr(III) complexes are stereoretentive should probably be rejected.[14] On the contrary, from a comparative study of *trans*-$Cr(en)_2$-$(NH_3)F^{2+}$[11] and $Cr(NH_3)_5F^{2+}$,[10,11] Kirk[15] concluded that the reaction is predominantly *stereomobile*.

$$H_2O \; + \; \text{[structure]} \quad \xrightarrow{h\nu} \quad \text{[structure]}$$
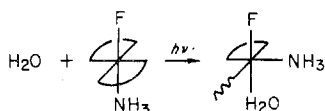
So far, a theoretical analysis of this phenomenon is lacking. It is the purpose of this paper to investigate whether or not the observed stereomobility can be accommodated within the ligand field methodology.

Ligand Field Correlation Diagrams

By adoption again of the dissociative reaction mechanism,[7,8] equatorial labilization leads to a five-coordinate square pyramid, with F in a basal position, SP (F basal). Figure 1 shows the orbital correlation diagram for the two bending modes of this SP: the N–Cr–N bending leads to a trigonal bipyramid with F in axial position, TBP (F ax), while the N–Cr–F

bending leads to a trigonal bipyramid with F in equatorial position, TBP (F eq). The potential stereoselectivity displayed in Figure 1 comes out quite clearly when considering the configurations corresponding to the relevant photoactive states.

(i) If the equatorial amine loss takes place from the $^4B_2$ state in the original six-coordinated C_{4v} complex, the excitation corresponds to a $d_{xy} \rightarrow d_{x^2-y^2}$ transition. As a consequence of the ligand removal and the resulting symmetry lowering, the excited state in the five-coordinated fragment corresponds more nearly to a $d_{xy} \rightarrow d_{z^2}$ transition ($^4A''$ in the C_s point group). Figure 1 shows how in the corresponding configuration $(xz)(yz)(x^2)$ the N–Cr–F bending is a forbidden process, while the N–Cr–N bending is an allowed process.[16,17]

(ii) If the equatorial amine loss takes place from the ^4E state (which is also the photoactive state for axial labilization), the excitation corresponds to $d_{xz}, d_{yz} \rightarrow (^3/_4d_{z^2}, ^1/_4d_{x^2-y^2})$. The symmetry lowering in the five-coordinated square pyramid gives rise to an energy splitting, $^4E \rightarrow {}^4A' + {}^4A''$, where the lowest state, $^4A'$, corresponds essentially to a $d_{xz} \rightarrow d_{z^2}$ transition. Now, in the $[(xy)(yz)(x^2)]$, $^4A'$ state, the selection rule operates in the opposite direction, allowing N–Cr–F bending and forbidding N–Cr–N bending.

The state energy level diagram for the two reaction paths is shown in Figure 2. If the reaction starts from the $^4B_2$ ($^4A''$) level, it is clear that the original heteroaxis remains unaffected throughout, and the photosubstitution has a pure "in-plane" character: the entering water ligand comes in cis of the F⁻ ion. Clearly, this mechanism does not allow for any trans-product formation and cannot explain the experimentally observed stereomobility. If the reaction starts from the $^4E(^4A')$ level, the square pyramid relaxes so as to generate the TBP
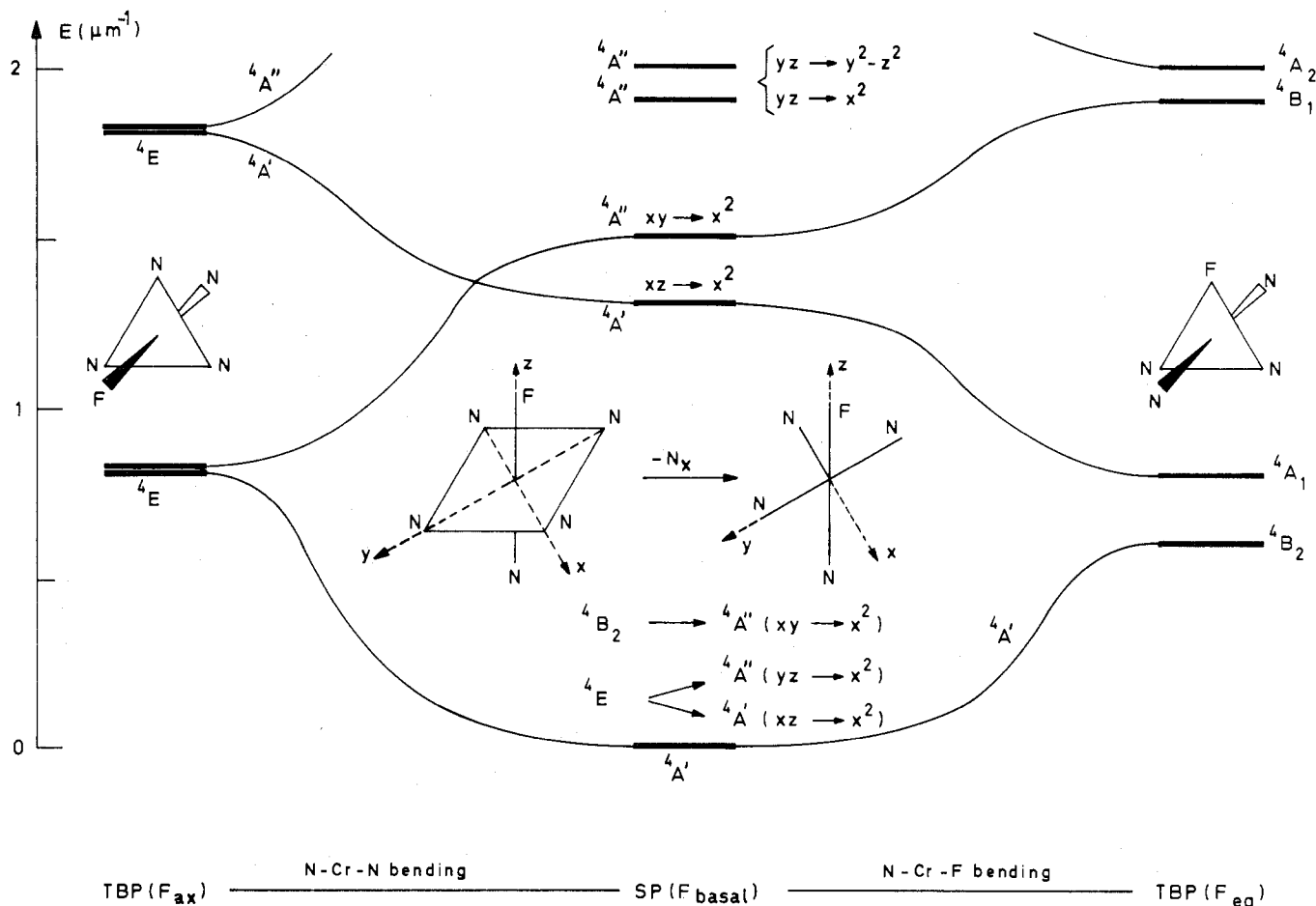
Figure 2. State correlation diagram for the reactions SP (F basal) → TBP (F ax) and TBP (F eq); the center of the figure shows the correlation between the states of the hexacoordinated C_{4v} initial product and those of the five-coordinated C_{2v} fragment resulting from equatorial amine loss (along the x axis).

(F eq). The crucial point is, however, that this trigonal bipyramid is not produced in its $^4B_2$ ground state but in its $^4A_1$ first excited state

$$[(xy)(yz)(x^2)]^4A' \rightarrow [(xy)(xz)(yz)]^4A_1$$
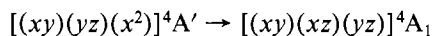
Now it has been shown in a previous paper[3] that the two states $^4A_1$ and $^4B_2$ have diametrically different behaviors as far as association reactions are concerned. Indeed, the $^4B_2$ state which is produced in the earlier considered axial labilization aquates preferentially in cis to F. For the $^4A_1$ state on the other hand, the cis aquation is a forbidden reaction and the aquation proceeds by a trans attack.

Figure 3 schematizes the situation. First of all, the axial labilization proceeding from the ^4E photoactive state gives rise to a TBP (F eq) via an allowed N–Cr–N bending. This TBP (F eq) is produced in its ground state, $^4B_2[(xy)(xz)(x^2-y^2)]$, which exhibits a clear-cut preference for cis attack, thereby accounting for the observed stereomobility of the axial labilization mode.[7]

When an equatorial amine ligand is removed, the excited five-coordinated fragment can relax in either of two ways, depending on whether it arises from the $^4B_2$ or ^4E photoactive state. The N–Cr–N bending reaction leads to the production of TBP (F ax) in its ground state and, therefrom, by addition of H_2O along either one of three sides of the equatorial triangle, to cis-$CrN_4(H_2O)F^{2+}$. The alternative pathway provided by N–Cr–F bending leads to the TBP (F eq) in its excited $^4A_1$ state, characterized by the configuration $(xy)(xz)(yz)$. The population of d_{yz} and the vacancy of $d_{z^2-y^2}$ are responsible for the reversal of the stereoselectivity with respect to the $^4B_2$

ground state. Therefore, trans attack is favored and the reaction is stereomobile.

The general picture of Figure 3 suggests *one* important complication, due to the possible deactivation of the $^4A_1$ state into the $^4B_2$ ground state—either in the TBP itself or else somewhere in the course of the bending process. Population of $^4B_2$ eventually leads to a cis product.

Therefore, the equatorial amine loss is characterized by the branching scheme:
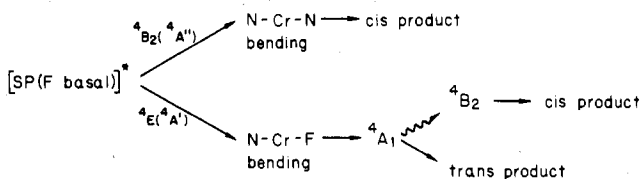
The relative probabilities of the two branching processes are difficult to evaluate, and therefore, it is equally difficult to predict a priori the ratio of cis/trans product. However, when the irradiation takes place in the lowest ligand field band, the $^4B_2$ state will not (or only slightly) be populated. More specifically, in the case of $trans$-$Cr(en)_2(NH_3)F^{2+}$, the N–Cr–N bending will be sterically hindered, so as to render this path even less probable. Kirk et al.[18] showed that photoreactions in quartet states can occur within a very short time (picoseconds), so that deactivation processes such as $^4A_1 \rightsquigarrow ^4B_2$ are probably rather unlikely. On consideration of these points, together with the stereochemical results,[15] it is strongly suggested that the photosubstitution in $trans$-$Cr(en)_2(NH_3)F^{2+}$ proceeds predominantly via ^4E population and that the ste-
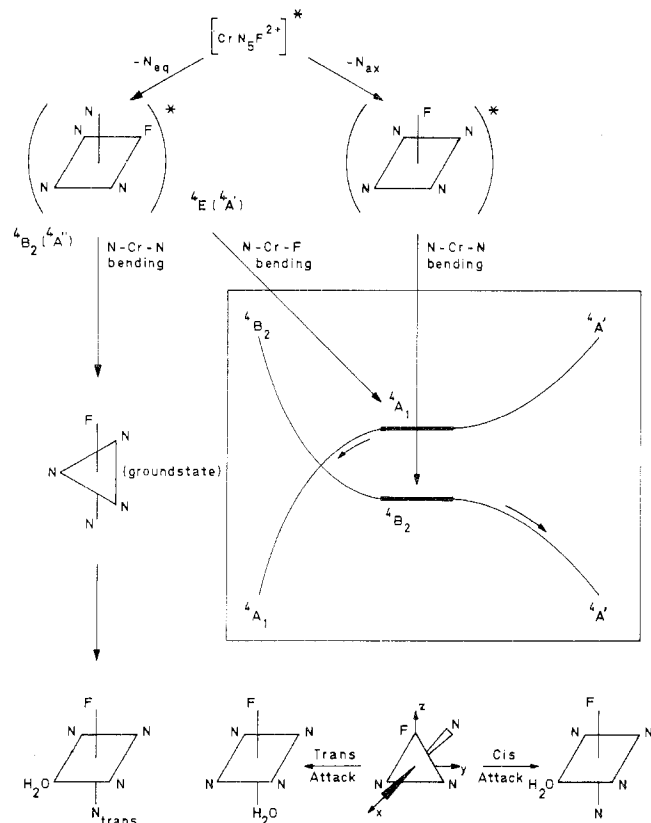
Figure 3. Schematic pattern of the photosubstitutions in fluoropentaaminechromium(III). "N_{trans}" in the final product of TBP (F ax) stands for the amine that was trans to F in the initial complex (for instance NH_3 in trans-$Cr(en)_2(NH_3)F^{2+}$). The insert in the figure shows the relevant part of the correlation diagram[7] for the association reactions of the TBP (F eq); the reaction paths can be inferred from the bottom part of the figure.

reochemical behavior of the TBP (F eq) is mainly determined by the properties of the $^4A_1$ state, in which it is produced.

In summary, equatorial labilization appears to be structurally different from the earlier considered axial labilization. In future experimental work along these lines, such as for instance the stereochemistry of difluorotetraamines, due attention should be paid to the appearance of branching schemes, similar to the one introduced in Figure 3.

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(16) It should be stressed that the electronically allowed N–Cr–N bending can be expected—at least in a dissociative mechanism—to be sterically hindered for a bidentate ligand such as trans-$Cr(en)_2(NH_3)F^{2+}$, where the five-coordinated fragment still contains one bidentate bridge in the (x,y) plane.
(17) The forbidden (a″,a″) crossover in Figure 1 (N–Cr–N bending) is quasi-allowed, due to a holohedron effect: in the C_{2v} holohedron, d_{xz} and d_{yz} belong to different irreducible representations.
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Synthesis and Crystal and Molecular Structure of *catena*-Bis[μ-(*N*-methylpiperidinium-4-thiolato)]-cadmium(II) Perchlorate Dihydrate

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The reaction of cadmium perchlorate hexahydrate with *N*-methyl-4-mercaptopiperidine in aqueous methanol gives *catena*-bis[μ-(*N*-methylpiperidinium-4-thiolato)]-cadmium(II) perchlorate dihydrate. Crystallization occurs in the tetragonal space group *I*4̄ in a unit cell of dimensions $a = 18.78$ (2) Å and $c = 6.66$ (1) Å. Solution of the structure by direct methods led to a final weighted R factor of 0.055 for 796 independent reflections. The crystal structure consists of infinite chains of cadmium atoms, each of them tetrahedrally coordinated to four sulfur atoms of four different *N*-methylpiperidinium-4-thiolato groups. Each sulfur atom acts as a bridge between two consecutive cadmium atoms. The four cadmium–sulfur bond distances average 2.548 (9) Å. The coordination geometry around the chlorine atom of each perchlorate anion is that of a distorted tetrahedron due to hydrogen bonding with a water molecule. The compound represents the first polymeric cadmium complex of γ-mercaptoamine ligands reported.

Introduction

The metal complexes of several β-mercaptoamine ligands have been widely studied in the solid state as well as in solution. Ligands such as 2-aminoethanethiol, 2-aminobenzenethiol, and 8-mercaptoquinoline form stable chelates with many metal

ions.[2] However metal complexes of γ-mercaptoamine ligands have had much less attention up to now. Complexes of 4-pyridinethiol with Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pt(II), Sn(IV), and Bi(III) have been reported. In all these cases bonding appears to be through sulfur rather than nitro-