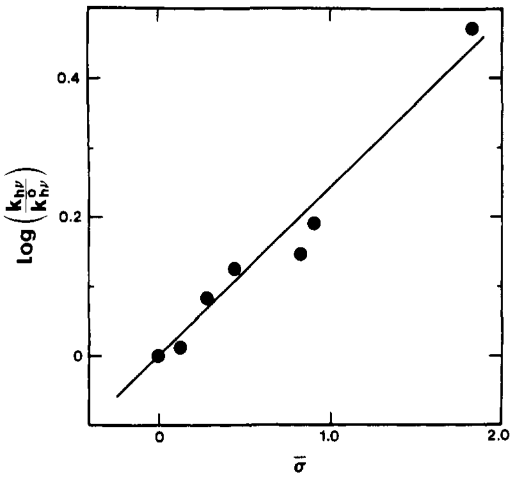

Figure 6. Derived, two-dimensional plot of the dual substituent parameter analysis of the rate constants for alkylcobalamin photolysis, $k_{h\nu}$, according to eq 12–15 ($\bar{\rho}$ = 0.242, λ = −0.239, f = 0.136).

CH_3, $CH_3CH_2CH_2$, CH_3OOCCH_2, and $CH_3OOCCH_2CH_2$) are included in our series, a fit of the logarithm of the ratio of the photolysis rate constant relative to that for CH_3Cbl gave an excellent fit (f = 0.05) with ρ^* = 0.31 and δ = −0.16, showing that both electron withdrawal *and* steric size increase the rate of photolytic C–Co cleavage.

This result was sufficiently encouraging to prompt us to measure photolysis rate constants for all eight of the organocobalamins in the present series. In agreement with Hogenkamp et al.,[5] we found the photolysis of the base-on R-(Cbl)'s to be first order and obtained satisfactorily linear semilogarithmic plots for at least 3 half-times leading to the rate constants ($k_{h\nu}$) listed in Table IV. Inspection of these data shows that the rate constants for CF_3Cbl photolysis are anomalously low. Clearly any correlation in which both electron withdrawal and increased steric bulk will promote photolytic C–Co cleavage will demand that CF_3Cbl photolysis be faster than that of CH_3Cbl. The reasons for the anomalous photostability of CF_3Cbl are not at all clear. However, the other seven rate constants correlate well with eq 11, where $k_{h\nu}^{\circ}$

$$\log (k_{h\nu}/k_{h\nu}^{\circ}) = \rho^*\sigma^* + \delta E_s^{\mathrm{R(Cbl)}} \tag{11}$$

is the photolysis rate constant for CH_3Cbl, giving ρ^* = 0.195, δ = −0.047, and f = 0.14, most of the deviation occurring in one data point (CF_3CH_2Cbl). This correlation is readily visualized with use of the graphical procedure of Wells et al.,[63] in which eq 11 is recast as eq 12

$$\log (k_{h\nu}/k_{h\nu}^{\circ}) = \bar{\sigma}\bar{\rho} \tag{12}$$

where

$$\bar{\rho} = \rho^* + |\delta| \tag{13}$$

$$\bar{\sigma} = (\sigma^* + \lambda E_s^{\mathrm{R(Cbl)}})/(1 + |\lambda|) \tag{14}$$

and

$$\lambda = \delta/\rho^* \tag{15}$$

A plot of these data (excepting CF_3Cbl) according to eq 12–15 is shown in Figure 6 and gives some degree of confidence in the utility of the new $E_s^{\mathrm{R(Cbl)}}$ values. However, further experimentation will be required to determine the general utility of this approach particularly in light of the failure of the $E_s^{\mathrm{R(Cbl)}}$ value for CF_3Cbl.

Acknowledgment. This work was supported by the Robert A. Welch Foundation, Grant Y-749 (K.L.B.), the Organized Research Fund of the University of Texas at Arlington (K.L.B.), and the National Institutes of Health, Grant AM 25406 (D.W.J.)

Registry No. α-Ribazole, 132-13-8; propyl bromide, 106-94-5; 2,2,2-trifluoroethyl iodide, 353-83-3; trifluorobromomethane, 75-63-8; methyl bromoacetate, 96-32-2; 4-bromobutyronitrile, 5332-06-9; methyl 3-bromopropionate, 3395-91-3; difluorochloromethane, 75-45-6; CNCbl, 68-19-9; H_2OCbl, 13422-52-1; $CH_3CH_2CH_2Cbl$, 13985-72-3; CF_3CH_2Cbl, 21180-98-3; $NCCH_2CH_2CH_2Cbl$, 89414-81-3; CH_3OOCCH_2Cbl, 15025-59-9; $CH_3OOCCH_2CH_2Cbl$, 14783-26-7; CF_3Cbl, 31532-05-5; CF_2HCbl, 28390-44-5.

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Contribution from the Department of Chemistry,
University of Leuven, Celestijnenlaan 200F, 3030 Heverlee, Belgium

Stereochemical Aspects of the Thermal Substitution Reactions of Cobalt(III) Complexes

L. G. VANQUICKENBORNE* and K. PIERLOOT

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On the basis of a simple ligand field model, the orbital and state correlation diagrams are calculated for the different five-coordinated structures intervening in the thermal substitution reactions of *cis-* and *trans-*$Co(en)_2AX^{n+}$ complexes (where X^- is the leaving ligand). Assuming a spin change along the reaction path of any stereomobile reaction, it is possible to derive general expressions showing the role of the inert ligand A in the activation energy. A comparison between theory and experiment reveals excellent agreement for the spontaneous and the induced aquations of *cis-* and *trans-*$Co(en)_2AX^{n+}$, the cis–trans isomerization of $Co(en)_2A(HO)^{m+}$, and the racemization of *cis-*$Co(en)_2A(H_2O)^{m+}$.

Introduction

In a previous paper,[1] it has been argued that any stereomobile reaction of a strong-field d^6 complex should be accompanied by a spin change somewhere along the reaction path. Here, we discuss a number of specific substitution reactions of $Co^{III}(en)_2AX^{n+}$ compounds in aqueous[2] solutions. By confining our attention to aqueous solutions—where the entering ligand E and the solvent molecule S are identical—we

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(2) We will restrict our attention exclusively to substitution reactions in acid solution. The corresponding base hydrolysis of the same complexes at higher pH apparently takes place by a D_{cb} mechanism, where one amine ligand loses a proton, giving rise to a strong π-donor amide. The presence of this second π ligand (in addition to A) modifies the picture to such an extent that significant changes can be expected, both in the kinetics and in the stereochemistry of these reactions.

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Table I. Stereochemical Data on the Spontaneous and Induced[a] Aquations of *cis*- and *trans*-$Co(en)_2AX^{n+}$ Complexes (X = Leaving Ligand)

cis complexes	method	% trans	% Λ	ref
Λ-$Co(en)_2(CN)Cl^+$	spont	0	100	4
Λ-$Co(en)_2(NO_2)Cl^+$	spont	0	100	5
Λ-$Co(en)_2(NH_3)Cl^+$	spont	0	100	6
Λ-$Co(en)_2Br_2^+$	spont	26.5 ± 1.5	70 ± 2	7
Λ-$Co(en)_2BrN_3^+$	NO^+ induc	27.5 ± 1.5	70.5 ± 1	7
Λ-$Co(en)_2Br(Me_2SO)^{2+}$	Cl_2 induc	29.5 ± 1.5	70.5 ± 1	7
Λ-$Co(en)_2Br_2^+$	Hg^{2+} induc	38.5 ± 1.5[b]	60 ± 1	7
Λ-$Co(en)_2Cl_2^+$	spont	25 ± 1.5	75 ± 1.5	7
Λ-$Co(en)_2Cl_2^+$	Hg^{2+}	24 ± 1.5	76.5 ± 1	8
Λ-$Co(en)_2ClN_3^+$	NO^+ induc	25 ± 1.5	77.5 ± 1	7
Λ-$Co(en)_2N_3Br^+$	spont	15 ± 2	85.5 ± 2	7
Λ-$Co(en)_2N_3Cl^+$	spont	14 ± 4	82 ± 3	7
Λ-$Co(en)_2N_3(Me_2SO)^{2+}$	spont	14 ± 4	84 ± 3	7
Λ-$Co(en)_2N_3Br^+$	Hg^{2+} induc	18 ± 1.5	83.5 ± 1	7
Λ-$Co(en)_2N_3Cl^+$	Hg^{2+} induc	17 ± 1.5	83.5 ± 1	7
Λ-$Co(en)_2(OH_2)Cl^{2+}$	Hg^{2+} induc	4.5 ± 1	93 ± 1	7
Λ-$Co(en)_2(OH_2)N_3^{2+}$	NO^+ induc	5	95	7
Λ-$Co(en)_2(OH_2)Br^{2+}$	Hg^{2+} induc	5 ± 1.5	94 ± 1	7
Λ-$Co(en)_2(OH)Cl^+$	spont	16 ± 1	84.5 ± 1	7
Λ-$Co(en)_2(OH)Br^+$	spont	15 ± 1	85 ± 1	7

trans complexes	method	% cis	ref
trans-$Co(en)_2(CN)Cl^+$	spont	0	9
trans-$Co(en)_2(CN)Br^+$	spont	0	10
trans-$Co(en)_2(NO_2)Cl^+$	spont	0	5
trans-$Co(en)_2(NH_3)Cl^{2+}$	spont	0	11
trans-$Co(en)_2(NH_3)Br^{2+}$	spont	0	11
trans-$Co(en)_2Br_2^+$	spont	15.5 ± 1.5	12
trans-$Co(en)_2Cl_2^+$	spont	26 ± 1.5	12
trans-$Co(en)_2Cl(Me_2SO)^{2+}$	spont	29.5 ± 1.5	13
trans-$Co(en)_2Cl(Me_2SO)^{2+}$	Cl_2 induc	30.5 ± 0.5	13
trans-$Co(en)_2Cl_2^+$	Hg^{2+} induc	28 ± 5	8
trans-$Co(en)_2ClN_3^+$	NO^+ induc	27 ± 0.5	14
trans-$Co(en)_2N_3(Me_2SO)^{2+}$	spont	8 ± 1	15
trans-$Co(en)_2N_3(DMF)^{2+}$	spont	8 ± 2	15
trans-$Co(en)_2N_3Cl^+$	spont	9 ± 2	15
trans-$Co(en)_2N_3Br^+$	spont	9 ± 1	15
trans-$Co(en)_2(OH_2)Cl^{2+}$	Hg^{2+} induc	38.0 ± 0.5	14
trans-$Co(en)_2(OH_2)N_3^{2+}$	NO^+ induc	37.5 ± 0.5	14
trans-$Co(en)_2(OH_2)Br^{2+}$	Hg^{2+} induc	38.0 ± 0.5	14

[a] In the induced aquations, the addition of Hg^{2+} replaces the anionic leaving ligands (Cl^- or Br^-) by a neutral or cationic species ($HgBr^+$), thereby facilitating the substitution process. [b] The fact that the steric course of the Hg^{2+}-induced aquation of Λ-$Co(en)_2Br_2^+$ is inconsistent with the other data has been explained by assuming that the Hg^{2+} ion attaches to both Br^- ions of the complex.[7]

Table II. Rate Constants for the Cis–Trans Isomerization[a] of $Co(en)_2A(H_2O)^{m+}$ and the Racemization of *cis*-$Co(en)_2A(H_2O)^{m+}$ Complexes

A	$k_{t\to c}$	$k_{c\to t}$	K	k_{rac}	ref
NH_3	1.8×10^{-8}	$\simeq 0$		3×10^{-8}	22
NCS^-	6.6×10^{-7}	1.44×10^{-7}	4.56	2.2×10^{-7}	17, 23
N_3^-	11.1×10^{-5}	5.2×10^{-5}	2.13	4.3×10^{-5}	7
H_2O	6.84×10^{-6}	1.2×10^{-7}	58	1.5×10^{-7}	24, 25
Cl^-	8.2×10^{-5}	2.2×10^{-5}	3.73	2.4×10^{-5}	13, 18
Br^-	1.7×10^{-4}	5.7×10^{-5}	3.0	4.6×10^{-5}	7, 12
OH^-	2.95×10^{-3}	2.05×10^{-3}	1.44		18

[a] For some of the A ligands (N_3^-, Cl^-, Br^-), the cis–trans isomerization reaction was reexamined recently, and the table shows only the most recent values; since these values are not dramatically different from the older results,[16,18,19] the values for the other A ligands can probably be maintained. The rate constants refer to room temperature (25 °C) and are given in s^{-1}; the equilibrium constant $K = k_{t\to c}/k_{c\to t}$.

renounce any attempt to describe specific solvent effects.[3] In all cases, the leaving ligand X (Cl^-, Br^-, H_2O) is replaced by an incoming water molecule. It is our intention to find out whether or not ligand field theory can offer a proper description of the role of the inert ligand A.

Tables I and II list most of the experimental data that will be discussed in the later sections. Table I shows the stereochemical data on the aquation—both spontaneous and induced—of a number of *cis*- and *trans*-$Co(en)_2AX^{n+}$ complexes.[4-15]

$$trans\text{-}Co(en)_2AX^{n+} \xrightarrow{H_2O} cis,trans\text{-}Co(en)_2A(H_2O)^{m+}$$

$$\Lambda\text{-}cis\text{-}Co(en)_2AX^{n+} \xrightarrow{H_2O} \Lambda,\Delta\text{-}cis,trans\text{-}Co(en)_2A(H_2O)^{m+}$$

The A ligands of Table I can clearly be subdivided into two distinct categories: For certain ligands, A′, the reaction is completely stereoretentive for all leaving groups, both for cis and trans complexes. For other ligands, A″, the reaction is partly stereomobile, but without optical inversion for the cis complexes. Table I shows that the stereochemical product ratio is independent of the nature of the leaving group but is determined exclusively by the *nature* of the *position* (cis or trans) of the A ligand. The absence of leaving group effects on the stereochemistry implies that X dissociation from $Co(en)_2AX^{n+}$ is well advanced toward pentacoordination in the transition state. It is also well to observe that the product ratio depends on the structure of the reactants: in general, trans complexes yield more trans product than cis product and cis complexes yield more cis product than trans product. So the results cannot be simply explained by the production of one common intermediate, characterized by a well-defined stereochemistry.

It should be stressed here that the clear-cut picture offered by Table I is of rather recent date. The literature contains many reports of stereochemical data conflicting with those of Table I; it is true that these earlier studies were generally carried out with rather crude experimental techniques. The most notorious erroneous result has been the original report of complete stereoretentivity for the cis complexes.[16-20] As a matter of fact, these reports have obscured the issue for many years; they led to Basolo and Pearson's π-bonding hypothesis,[21] relating the supposed stereoretention of the cis complexes to the role of the π interactions between the A ligand and the metal 4p orbitals. The more recent reexamination of the stereochemical data has obviously rendered this π-bonding hypothesis out of date, since the results of Table I show that the A ligand essentially plays the same role in the aquation of both cis and trans complexes.

However, one has to admit that most experiments of Table I have been carried out at only one temperature (T = 25 °C); therefore, hardly any information is available on the tem-

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perature dependence of the stereochemistry or on the value of the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Clearly, more experimental data are needed before the detailed mechanism and the role of A in these aquation reactions can be elucidated completely. Hopefully, the present considerations can offer some constructive guidelines in setting up these experiments.

Table II shows the value of the rate constants $k_{t\rightarrow c}$ and $k_{c\rightarrow t}$ for the cis–trans isomerization of $Co(en)_2A(H_2O)^{m+}$, and k_{rac} for the racemization of *cis*-$Co(en)_2A(H_2O)^{m+}$. The results of Table II are more pure and, therefore, not quite comparable to the results of Table I; indeed, in the water-exchange reactions, the trans → trans and cis → cis substitutions remain unobserved, and a quantity such as the percentage of stereomobility cannot be obtained from the experimental data. Yet, it is well to stress that the A ligands of Table II, giving rise to a cis–trans isomerization reaction, are all of the earlier defined A″ type.[26] It is also interesting to note that K—as far as known—is independent of temperature.[18,19,28] Apparently the activation energies for the two opposite processes are equal, and the difference between $k_{c\rightarrow t}$ and $k_{t\rightarrow c}$ is due to a difference between the preexponential factors in the Arrhenius equation. Except for A = NH_3 and A = H_2O, $k_{t\rightarrow c}$ and $k_{c\rightarrow t}$ are of the same order of magnitude, but in all cases $k_{t\rightarrow c} > k_{c\rightarrow t}$ and, hence, $K > 1$.

For all A ligands except for NH_3, the racemization rate of the cis complexes, within experimental error, equals the cis → trans isomerization rate, suggesting that in each case racemization proceeds exclusively by isomerization to the inactive trans species.[7,29] One might consider NH_3 as an exception, where no cis → trans isomerization is observed, whereas the racemization does take place. But because of the very small value of the racemization constant, this observation hardly affects the general picture.

As a conclusion, the body of experimental data shows that the inert A ligand is indeed a major factor, determining the steric course of the substitution reactions of $Co(en)_2AX^{n+}$ complexes. The most recent studies on the aquation reactions suggest that the role of the A ligand can be described by means of a few simple rules. The available data on the cis–trans isomerizations and on the racemizations apparently fit into this picture. They confirm on the one hand that cis–trans stereomobility is only possible for A″ type ligands and, on the other hand, that there is no direct reaction path for optical inversion of the cis complexes.

Choice of the Reaction Path

In a purely dissociative mechanism, the hexacoordinated complex loses one ligand, thereby giving rise to a pentacoordinated fragment. If the dissociation is not accompanied by a simultaneous distortion, this fragment is a square pyramid (SP); reassociation of a solvent molecule into the vacant site yields a stereoretent aquation product. The occurrence of stereomobility depends on the nonrigidity of the square pyramid. The most plausible pentacoordinated structure giving rise to stereomobile reactions is the trigonal bipyramid (TBP). Figure 1 shows how the transitions SP → TBP requires only relatively small geometric distortions.

In order to make the model as simple as possible, it will be assumed in what follows that the reaction is purely dissociative. The justification of this point of view appears to be evident from the experimental data discussed in the previous section.

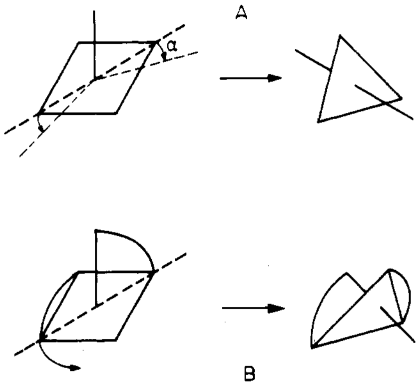

Figure 1. (A) Transition from the square pyramid to a trigonal bipyramid achieved by letting α vary from 0 to $\pi/6$. (B) Rotation of one ligand over $\pi/4$ to yield an approximate TBP, when a bidentate ligand prevents the simple movement of Figure 1A.

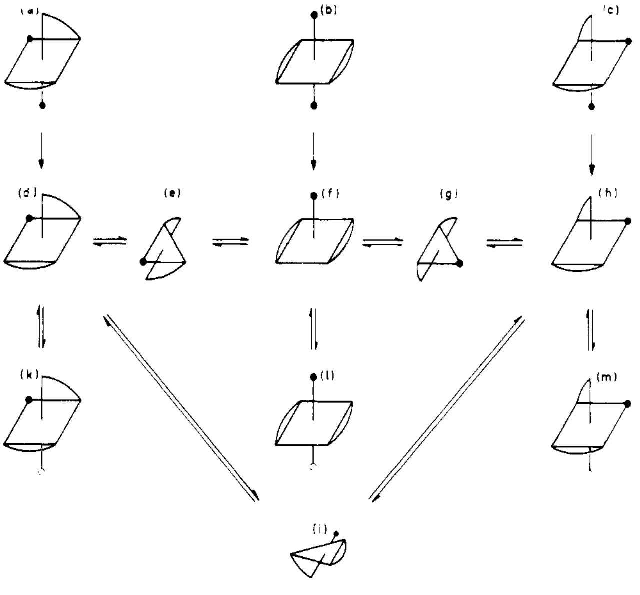

Figure 2. Hexa- and pentacoordinated species involved in the substitution reaction. Black circles indicate the A and X ligands, while open circles indicate the solvent molecules. a, b, and c are the initial complexes, and k, l, and m are the reaction products.

As a next simplification, we will assume that the rearrangement of the pentacoordinated fragment is simply a second consecutive step of the reaction. In this way, the conditions for stereomobility will be determined by the relative energy of the different five-coordinated structures.

Figure 2 shows the different hexa- and pentacoordinated species supposedly involved in the dissociative substitution reactions. The trigonal-bipyramidal structures of a d^6 system have no favorable access possibilities for solvent addition;[30] their role in the stereochemistry of the substitution reactions is only to serve as an intermediate or an activated complex, rearranging into a different square pyramid.

In the trigonal bipyramid, the A ligand can be either in axial or in equatorial position. The trigonal bipyramid with A in axial position, TBP(A_{ax}) (structure i in Figure 2) can only be obtained from the cis complex. On the basis of Figure 2, a direct racemization process along the reaction path of Figure 1B, and involving the i intermediate, cannot be excluded a priori. It will be shown in what follows that the small deviation from an equilateral triangle in structure i is without significant energetic consequences in d^6 systems and may be ignored in discussing the distortion possibilities.

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(26) The exception is A = NH_3: *trans*-$Co(en)_2(NH_3)(H_2O)^{3+}$ has been found to isomerize, but the rate constant of 1.8×10^{-8} s^{-1} is negligibly small. Also, $Co(en)_2(NO_2)(H_2O)^{2+}$ does isomerize but via a completely different mechanism, namely an intramolecular rearrangement involving the nitro group.[27]

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Table III. Ligand Field Parameters of Co(III) Ligands[a]

ligand	10*Dq*	σ	π	$\sigma - 2\pi$
CN^-	34.89	12.15	0.39	11.37
NH_3	23.43	7.81	0	7.81
en	23.77	7.92	0	7.92
N_3^-	18.98	6.76	0.32	7.16
H_2O	15.44	6.60	1.08	4.44
Cl^-	13.71	6.29	1.29	3.71
OH^-	10.67	9.61	4.54	0.53

[a] All parameters are given in units of 10^3 cm^{-1}.

The trigonal bipyramid with A in equatorial position TBP(A_{eq}) can be obtained both from the cis and trans complex. Within the framework of our mechanistic hypothesis, any cis–trans isomerization necessarily takes place via a structure of this type. However, the TBP itself is a chiral body: the structures e and g are optical antipodes. From a given (chiral) $Co(en)_2AX^{n+}$ molecule, only one of the two possible TBP(A_{eq}) can be obtained; via this route, direct optical inversion is impossible.[31] From *trans*-$Co(en)_2AX^{n+}$ both structures e and g are obtained in equal amounts; therefore, any trans → cis isomerization will necessarily lead to a racemic cis mixture.

The Hydroxo and Cyano Cases: Two Example Calculations

On the basis of ligand field theory,[32] energy correlation diagrams were calculated for the relevant structures of Figure 2, with A = OH^- (a typical A″ ligand) and A = CN^- (a typical A′ ligand). The ligand field parameters were taken from Table III and are based on published data.[33] The Racah parameters were kept constant for the two sets of calculations at $B = 0.6 \times 10^3$ cm^{-1} and $C = 3.7 \times 10^3$ cm^{-1}. The results are shown in Figures 3 and 4.

The symmetry of the fragment is specified for each segment of the reaction path; if necessary, the holohedron symmetry and symmetry labels are given in parentheses.[30,34] The orbitals d_{y^2}, d_{x^2}, etc., abbreviated as y^2, x^2, etc., are defined by

$$(x^2 \quad y^2 \quad x^2 - z^2 \quad y^2 - z^2) = (z^2 \quad x^2 - y^2)\begin{pmatrix} -1/2 & -1/2 & -3^{1/2}/2 & -3^{1/2}/2 \\ 3^{1/2}/2 & -3^{1/2}/2 & 1/2 & -1/2 \end{pmatrix}$$

x^2 and y^2 represent functions with the same shape as d_{z^2}, but with rotation symmetry about the *x* or *y* axis; $x^2 - z^2$ and $y^2 - z^2$ have the same shape as $d_{x^2-y^2}$ but are situated essentially in the *xz* or the *yz* planes. The designation ~ means that the components of the relevant orbital are close to, but not quite equal to, the elements of the 2 × 4 matrix.

In the state correlation diagrams, the zero of energy was taken to be the ground-state energy of the square pyramid with A in the apical position: $^1A_{1g}$[SP(A_{ap})]. The SP(A_{eq}) ground state has virtually the same energy, but the ^1A energy increases very sharply under the influence of the small distortions resulting in a trigonal-bipyramid TBP(A_{ax}) or TBP(A_{eq}). Obviously, a stereomobile substitution cannot possibly take place on the ^1A potential surface but has to proceed along a low-lying surface crossing the ^1A level.[1] It is reasonable to assume that, of the different levels crossing ^1A, the lowest one will play the most important role; this level corresponds to the ground state of the trigonal bipyramids. Comparison of Figures 3 and 4 show that the multiplicity of the TBP ground state depends on the heteroligand A. For the hydroxo complex, the TBP ground states are quintets: $^5A_2$ for TBP(A_{eq}) and ^5E for TBP(A_{ax}). For the cyano complex, the TBP ground states are triplets: $^3B_2$ for TBP(A_{eq}) and $^3A_2$ for TBP(A_{ax}).

The rearrangement of the square pyramid is competitive with the direct stereoretent addition of a solvent molecule. Therefore, for stereomobility to be possible, one would expect an activation energy in the neighborhood of zero. In fact, for the cis–trans isomerization reaction, one obtains an energy of 29 kcal/mol for the cyano complex and 4 kcal/mol for the hydroxo complex. For the other A ligands, one would obtain intermediate values. A direct racemization process via TBP(A_{ax}) requires a very high energy for both complexes: 22 kcal/mol for the cyano complex and 18 kcal/mol for the hydroxo complex. It is true that the thus calculated values do not account for the differential ligand–ligand repulsion. Kepert[35] has shown that the interligand repulsion is smaller for TBP than for the SP structure; therefore, this additional term in the activation energy would tend to make the isomerization process more accessible. Yet, the most important factor, favoring a stereomobile reaction, appears to be the value of the activation entropy. It has long been recognized by Tobe and co-workers[36] that the activation entropy is correlated with the steric course of the aquation reactions of *cis*- and *trans*-$Co(en)_2AX^{n+}$ complexes: steric change, and hence the formation of a trigonal bipyramid, is always associated with a much higher entropy of activation than is retention of the configuration. It has been stressed before[1] that the entropy increase on going to a trigonal bipyramid can be traced back to two independent effects: the multiplicity increase on the one hand and the flatness of the quintet surface on the other hand.

No recent information is available on the value of the activation entropy for the aquation reactions under consideration. However, in the light of the present considerations, it seems reasonable to conjecture that a reexamination of the aquation reactions as a function of temperature will confirm Tobe's original correlation between $\Delta S^{\ddagger}$ and the steric course of the reactions.

Considering the influence of interligand repulsion, as well as the role of the activation entropy, the numerical results of Figures 3 and 4 become quite acceptable: the hydroxo fragment will be nonrigid and will give rise to cis–trans stereomobility. Racemization via a direct path is, however, impossible. For the cyano fragment, the activation energy for both processes is so high that it will remain rigid even if interligand repulsion and entropy effects are accounted for. As will be shown in the next section, OH^- and CN^- are the prototypes of stereomobility and stereoretention-inducing ligands, while the behavior of the other A ligands is intermediate.

Analysis of the Results: Role of the A Ligand

The state function of the ^1A ground state of the SP can be described by the single determinant $[(xy)^2(xz)^2(yz)^2]$, corresponding to the full occupation of the three π orbitals. One of the π orbitals has its main density in a plane containing only amine ligands (*xy* in SP(A_{ap}) and *xz* in SP(A_{eq})) and can therefore be characterized by zero energy ($\pi_N = 0$ in Table III). The other two orbitals are degenerate at π_A.

Any rotation of two equatorial ligands leading to a TBP modifies the character of the one π orbital that is situated in the plane of rotation. Indeed, along the rearrangement path,

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(31) This implies that the lifetime of the TBP(A_{eq}) is insufficient to racemize. This is true in aqueous solution but not necessarily in other solvents. For instance, in methanol[17] the racemization of *cis*-$Co(en)_2Cl_2^+$ is faster than cis–trans isomerization and, quite probably, takes place via a TBP(A_{eq}).

(32) L. G. Vanquickenborne and A. Ceulemans, *J. Am. Chem. Soc.*, **100**, 475 (1978).

(33) L. G. Vanquickenborne and A. Ceulemans, *Coord. Chem. Rev.*, **48**, 157 (1983).

(34) In the determination of the symmetry of a fragment, the ethylenediamine bridges of the chelate ligands were neglected.

(35) D. L. Kepert, "Inorganic Stereochemistry", Springer-Verlag: New York, 1982.

(36) M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).

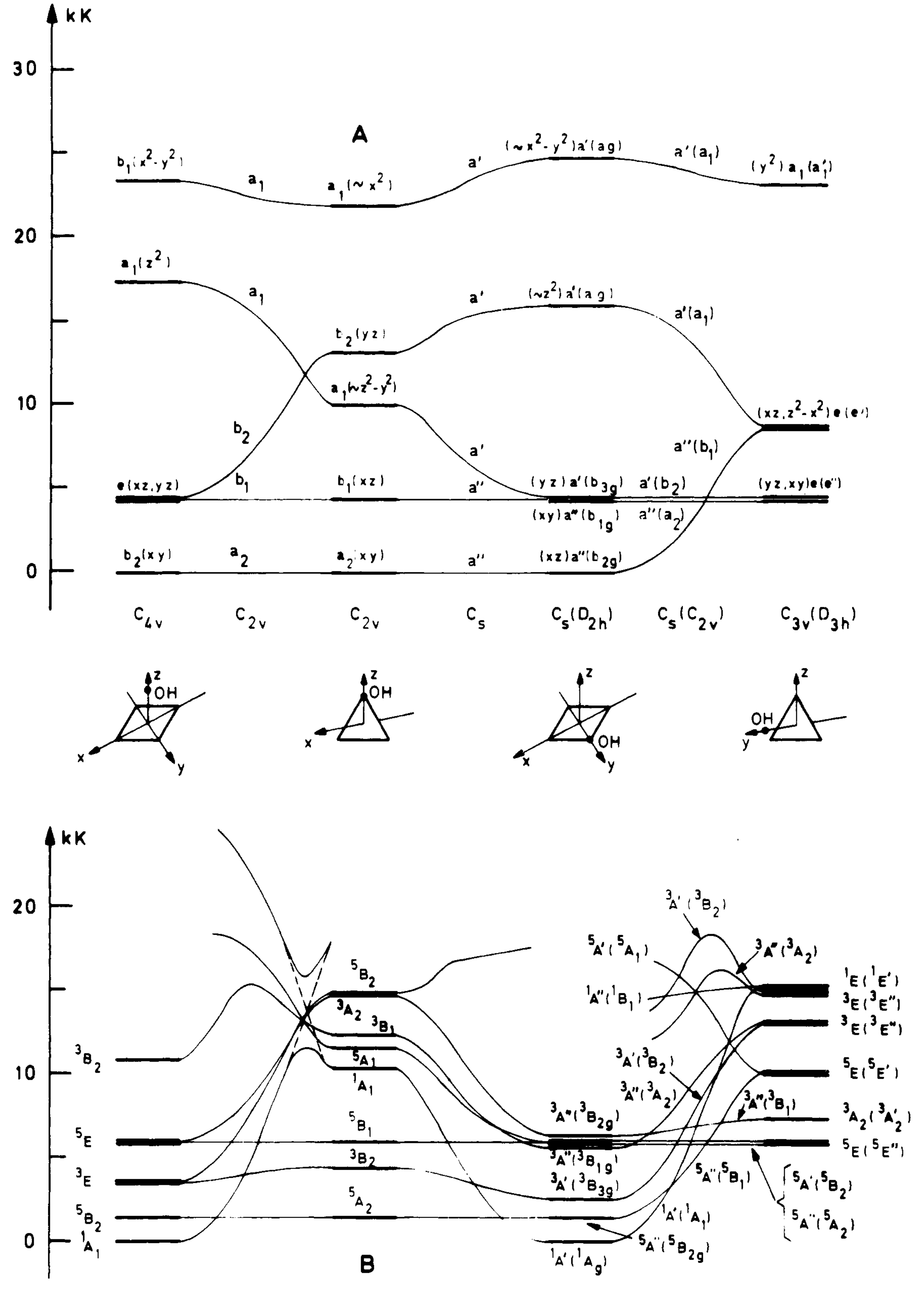

Figure 3. Orbital (A) and state (B) correlation diagrams for the rearrangement of the pentacoordinated hydroxotetraaminecobalt(III) complex.

this π orbital acquires σ character and, correspondingly, a much higher energy. This energetic evolution is at the basis of the steep increase of the ^1A energy along the reaction coordinates of Figures 1.

(a) TBP(A_{eq}) as a Transition State. The relevant orbitals and their energies are given by the expressions[37]

$$\sim x^2\text{: } \tfrac{5}{2}\sigma_N + \tfrac{1}{4}\sigma_A \qquad xz\text{: } \pi_A \qquad yz\text{: } \tfrac{9}{8}\sigma_N + \pi_A \qquad xy\text{: } 0$$

$$\sim z^2 - y^2\text{: } \tfrac{3}{8}\sigma_N + \tfrac{3}{4}\sigma_A$$

The two possible ground states of the TBP, $^3B_2$ and $^5A_2$, correspond either to a one-electron excitation or to a two-

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(37) In the analytical expressions for the orbital and state energies, the π_N parameter was assumed to be equal to zero, and it was dropped throughout. If another ligand L were used, the ligand field expressions could be readily generalized. For instance, to the right side of eq 1a one should add $-2\pi_L$; in eq 1b, one should add $-4\pi_L$. Similarly for the quintet energy difference of eq 2, one would need an additional term of $-{}^{11}/_2\pi_L$.

electron excitation in the SP structures:

$$\Psi(^3B_2) = |(xy)^2(xz)^2(yz)^1(\sim z^2 - y^2)^1|$$

$$\Psi(^5A_2) = |(xy)^2(xz)^1(yz)^1(\sim z^2 - y^2)^1(\sim x^2)^1| = |(xy)^2(xz)^1(yz)^1(z^2)^1(x^2 - y^2)^1|$$

With respect to the SP ground state, the energy differences are[37,38]

$$E(^3B_2(\mathrm{TBP})) - E(^1A(\mathrm{SP})) = {}^3\!/_2\sigma_N + {}^3\!/_4\sigma_A - \pi_A - 3C \quad (1a)$$

$$E(^5A_2(\mathrm{TBP})) - E(^1A(\mathrm{SP})) = 4\sigma_N + \sigma_A - 2\pi_A - 5B - 8C \quad (1b)$$

Both TBP states increase in energy as σ_A increases and π_A decreases, thus roughly as $10Dq$ increases. But in an energy–Dq curve, the slope of the $^5A_2$ state is considerably larger than the slope of the $^3B_2$ curve. Therefore, for weak A ligands, the ground state is $^5A_2$; for strong ligands, the ground state is $^3B_2$. Figures 3 and 4 of the previous section show an example of each case. The crossover of the two states takes place approximately[38] at NH_3.

In a number of experimental series (Tables I and II), $Co(en)_2(NH_3)X^{n+}$ is also found at the pivotal position, separating stereomobility from stereoretention. The borderline position of the NH_3 ligand is illustrated by the fact that cis–trans isomerization does take place, but with a very small rate constant; on the other hand, the aquation of *cis*- and *trans*-$Co(en)_2NH_3Cl^{2+}$ proceeds much faster, but in a completely stereoretentive way. Apparently, stereomobility is only possible for weak A ligands, where the $TBP(A_{eq})$ has a quintet ground state. Whenever the TBP has a triplet ground state, its energy is too high to be accessible from the SP.

The relevant part of the activation energy is then given by eq 1b: as far as A is concerned, the parametric expression is simply $\sigma_A - 2\pi_A$. This value can also be taken directly from the energy difference between the lowest quintet state and the singlet ground state in either SP. Indeed, once this quintet state has been reached, no further energy is required, since the quintet energy is independent of the angular position of the ligands.[39]

To some extent then, our treatment joins the older π-bonding theory of Basolo and Pearson in stressing the role of the π interactions of the A ligand. But obviously, the σ_A interactions play a role that is probably even more important, and the dichotomy between A′ and A″ type ligands can be understood quite nicely from the $\sigma_A - 2\pi_A$ values shown in Table III.

Moreover, the activation energy for stereomobility is calculated (eq 1b) to be independent of the position of the A ligand (cis or trans). Our treatment is therefore supportive of the experimental results of Table I, suggesting that the role of A is identical for cis and trans complexes.

The conservative behavior of the aquating complexes (cis yields more cis than trans and vice versa) can also readily be explained, if we assume that the aquation proceeds via two competing reaction paths, taking place simultaneously and with comparable rates: a stereoretentive path characterized by low values of both activation energy and activation entropy and a stereomobile path characterized by higher values of both activation energy and activation entropy. In this respect, our views are in marked contrast to the prevailing ideas[2,15] of one single reaction path proceeding via a five-coordinated intermediate that is then supposed to be different for cis and for trans complexes.

The model presented here implies that the fraction of stereomobility increases with increasing temperature. Indeed, increasing the temperature will favor the reaction path characterized by the largest activation energy. In order to verify this conclusion, additional experimental data are badly needed: so far, only one case has been analyzed in detail.[40] In the aquation of *cis*-$Co(en)_2Br_2^+$, the trans product fraction increases from 23% at 15 °C to 35% at 40 °C, in agreement with our predictions.

Very good agreement between theory and experiment is obtained for the cis–trans isomerizations of $Co(en)_2A(H_2O)^{n+}$. The stereoretentive reaction path is unobserved in this case, and we expect an increasing isomerization rate with decreasing values of $\sigma_A - 2\pi_A$.[41] Figure 5 shows the value of $\Delta G^{\ddagger}$ (derived from Table II) for the cis–trans isomerization of $Co(en)_2A(H_2O)^{n+}$ as a function of $\sigma_A - 2\pi_A$. The linear relationship obtained both for cis → trans and trans → cis reactions is a strong indication of the validity of the proposed mechanism.

For the cis → trans and the trans → cis processes we predict the same activation energy—in agreement with the observed fact that K is independent of temperature. On purely statistical grounds, we expect a [cis]/[trans] ratio of 4 at equilibrium. From Table II, it is clear that $K < 4$ in most cases. A partial rationalization of this deviation from simple statistics is based on the consideration of spin–orbit coupling effects. Indeed, somewhere along the reaction path, a singlet–quintet transition has to take place, and since spin–orbit coupling is described by a one-electron operator, one needs a triplet to render the singlet–quintet transition possible. Now it can readily be shown that the relevant triplet–quintet matrix element is twice as large for a cis complex than for a trans complex. This is at least one of the factors favoring cis → trans over the opposite process and, hence, leading to $K < 4$.

(b) $TBP(A_{ax})$ as a Transition State. The orbitals and the associated one-electron energies are given by[37]

$$y^2\colon \sigma_A + {}^7\!/_4\sigma_N \qquad xz,\ z^2 - x^2\colon {}^9\!/_8\sigma_N \qquad yz,\ xy\colon \pi_A$$

Here again, the ground state can be a triplet or a quintet:

$$\Psi(^3A_2) = |(yz)^2(xy)^2(xz)^1(z^2 - x^2)^1|$$

$$\Psi(^5E) = |(yz,xy)^3(xz)^1(z^2 - x^2)^1(y^2)^1| = |(yz,xy)^3(xz)^1(z^2)^1(x^2 - y^2)^1|$$

The energy difference between these states and the $^1A'$ ground state of the $SP(A_{eq})$ is given by[37,38]

$$E(^3A_2(\mathrm{TBP})) - E(^1A'(\mathrm{SP})) = {}^9\!/_4\sigma_N - 3C = {}^3\!/_4(10Dq)_N - 3C \quad (2a)$$

$$E(^5E(\mathrm{TBP})) - E(^1A'(\mathrm{SP})) = 4\sigma_N + \sigma_A - \pi_A - 5B - 8C \quad (2b)$$

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(38) Equations 1 and 2 given in the text are only first-order formulas. A rigorous calculation of the energy levels, including configuration interaction (CI) within the d^6 manifold (see Figures 3 and 4) will move the singlet and triplet states under consideration to a lower energy but will have no influence on the energy of the quintet surface. So the CI effects will tend to cancel in eq 1a and 2a, giving the energy difference between a triplet and a singlet level, but not in eq 1b and 2b, giving energy differences that are too small. For example, for $A = NH_3$, eq 1a and 1b predict a quintet ground state. However, including of configuration interaction moves the triplet just below the quintet.

(39) In the quintet $^5A_2$, all orbitals are singly occupied, except for the lowest π orbital. Since the latter has a constant energy along the reaction path under consideration, the quintet energy is constant.

(40) C. G. Barraclough, R. W. Boschen, W. W. Fee, W. G. Jackson, and P. T. McTigue, *Inorg. Chem.*, **10**, 1994 (1971).

(41) Obviously, eq 1b gives only part of the total activation energy for the isomerization. The missing part, which is the dissociation energy of the leaving water ligand, can also be calculated in the framework of ligand field theory. See for instance L. G. Vanquickenborne and A. Ceulemans, *J. Am. Chem. Soc.*, **99**, 2208 (1977). The result of such a calculation is that the dissociation energy is given by $2\sigma_{H_2O}$, independent of the nature and the position of A.

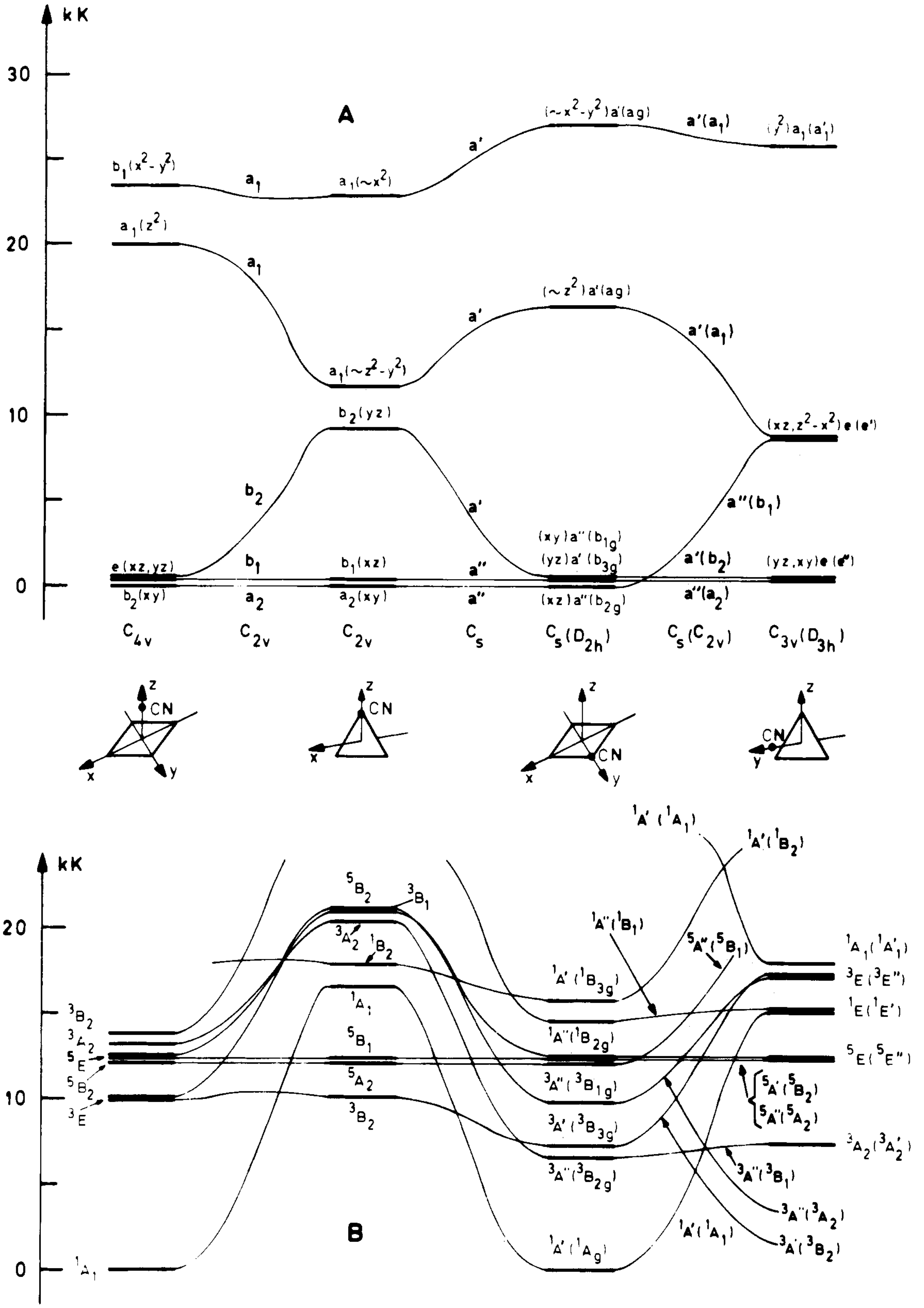

Figure 4. Orbital (A) and state (B) correlation diagrams for the rearrangement of the pentacoordinated cyanotetraaminecobalt(III) complex.

The above orbital and state energies refer to an ideal trigonal bipyramid, with equatorial angles of 120°. In fact, the equatorial plane of TBP(A_{ax}) contains a chelate ethylenediamine ligand, characterized by a bite angle that is closer to 90° than to 120°. The resulting distortion induces a first-order energy splitting of the e′ (xz, $z^2 - x^2$) level (Figure 3 and 4). But in the two TBP states under consideration ($^3A_2$ and ^5E), both orbitals are singly occupied and, consequently, the state energy differences of eq 2 do not depend on this orbital splitting.

With respect to the square-pyramidal ground state, the energy of $^3A_2$ is independent of A; its numerical value is 6.5 × 10^3 cm^{-1} from eq 2 and becomes 7.5 × 10^3 cm^{-1} = 21.5 kcal/mol if one allows for the configuration interaction within the d^6 manifold. This energy is too high to induce the racemization process to any significant extent.

For weak ligands, the ^5E state drops below the triplet and the activation barrier becomes smaller. However, when eq 1

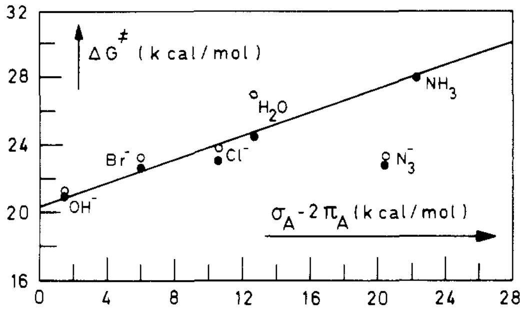

Figure 5. Linear relationship between the rate constants (Table II) for the cis → trans (○) and the trans → cis (●) isomerization reactions of $Co(en)_2A(H_2O)^{m+}$ and $\sigma_A - 2\pi_A$. The anomalous position of N_3^- is probably due to the fact that this ligand is characterized by π-acceptor as well as π-donor properties. The π-donor properties of N_3^- are therefore probably more important than would appear from the value $\pi = 324$ cm^{-1}; a larger π parameter would move the N_3^- result closer to the curve of Figure 5. The absence of NO_2^- and CN^- corresponds to the nonobservation of the isomerization process for those ligands (see also footnote 26).

and 2 are compared, it follows that ^5E is always π_A higher than $^5A_2$. Therefore, one expects the racemization to take place, not via TBP(A_{ax}) but rather via cis-trans isomerization. It is also clear now why the aquation of the cis complexes is never accompanied by racemization.

As stressed before, these expectations are borne out by the experimental data (Table II). The fact that $Co(en)_2NH_3(H_2O)^{3+}$ racemizes without cis-trans isomerization can hardly be considered as a counterexample. For A = NH_3, we predict the same activation energy for cis-trans isomerization and for racemization; the calculated value is very high though (7.5 kcal/mol), and therefore the racemization rate is very small. The difference in interligand repulsion alone might easily induce differences of the observed order of magnitude.

Conclusion

The simple reaction scheme of Figure 2 can be used to rationalize the role of the inert A ligand in the isomerizations and the substitutions of $Co(en)_2AX^{n+}$; it shows how the stereochemistry can be predicted and—for stereomobile reactions—how the reaction rate depends on the ligand field parameters of A.

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Contribution from the Department of Chemistry,
Georgetown University, Washington, D.C. 20057

Reinterpretations, Based on ^{183}W NMR Spectra, of Several Heteropolytungstates Derived from the Wells-Dawson "2:18" Structure. Preparation and Structure Proof for the First γ-Isomer of a 2:18 Complex[1]

RAFAEL ACERETE, CHARLES F. HAMMER, and LOUIS C. W. BAKER*

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^{183}W NMR spectra prove the following: (1) The first γ-isomer of the 2:18 Wells-Dawson heteropoly structure has been isolated. γ-$[As_2W_{18}O_{62}]^{6-}$ differs from the α-isomer by 60° rotations of *both* W_3O_{13} caps about their 3-fold axes. (2) α-$[P_2W_{12}Mo_6O_{62}]^{6-}$, obtained quantitatively by reaction of molybdate with the P_2W_{12} complex, does not, as previously supposed, contain all the W's in the two W_6 belts but has the W's in a boatlike arrangement derived from the α-$[P_2W_{18}O_{62}]^{6-}$ structure by stripping a W from the W_3O_{13} cap on one end of the complex and the eclipsed W from the cap on the other end, plus those two eclipsed W's from each belt that were immediately adjacent to the W's removed from the caps. It is highly probable that the unsaturated P_2W_{12} species has the W's in the same arrangement and that its formula is $[P_2W_{12}O_{48}H_x]^{(14-x)-}$. (3) The complex previously formulated as α-$[P_2W_{16}Mo_2O_{62}]^{6-}$ is really α-$[P_2W_{15}Mo_3O_{62}]^{6-}$, wherein one Mo_3O_{13} cap has replaced a W_3O_{13} cap of the Wells-Dawson structure. The complex is prepared quantitatively from what was heretofore taken to be "α-$[P_2W_{16}O_{59}]^{12-}$", which is probably really a 15-tungsto species. (4) The currently accepted formulation of Preyssler's 6-tungstophosphate, "$[P_3W_{18}O_{66}]^{9-}$", cannot be correct. The simple NMR spectrum could reconcile with more highly polymeric structures.

Introduction

In recent papers[2-4] we demonstrated the power of ^{183}W NMR for unambiguous elucidation of the structures of polytungstate complexes in solution. Besides discussion of factors involved in the origin of ^{183}W NMR chemical shifts, band assignments, use of quadrupolar nuclei as structure probes, and use of coupling constants, numerous spectra were presented in those papers including, of pertinence here, those of the α- and β-isomers of $[P_2W_{18}O_{62}]^{6-}$, α_2-$[P_2W_{17}O_{61}]^{10-}$, and α_2-$[P_2W_{17}VO_{62}]^{7-}$.

It is worth noting that essentially all of the conclusions that were commonly accepted prior to our ^{183}W NMR data, about the specific structures and isomerisms in the sizable series of complexes derived from the well-known 2:18 Wells-Dawson structure[5-7] (Figure 1), have been proven incorrect by a combination of the ^{183}W NMR spectra we reported previously[2-4] and those reported in the present paper.[1] The earlier con-

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(1) From portions of the June 1981 Georgetown University Ph.D. Dissertation of R.A., who was on leave from the Department of Chemistry, School of Pharmacy, University of Valencia, Spain. *Diss. Abstr. Int. B* **1982,** *42(9),* 3701; *Chem. Abstr.* **1982,** *56,* 192159*k*.

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