Substitution Reactions of Inorganic Complexes. Concerning the Prediction of Activation Energies and Reaction Mechanisms by Crystal Field Theory[1,2]

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Abstract: The substitution reactions of octahedral or nearly octahedral inorganic complexes are briefly reviewed. If it is assumed that the observed activation energies for these reactions depend primarily upon the energy required for the particular complex to proceed to an intermediate of either enhanced or reduced coordination, then these observed activation energies may be compared to calculated crystal field stabilization energies (CFSE) for various geometries to see which model best fits the experimental data. The results of these calculations for a number of d^3 and d^6 systems indicate that a model with enhanced coordination number (CN) and C_{2v} symmetry fits the data best for Cr(III) complexes while a model with reduced CN and C_{4v} symmetry fits the data for Co(III) complexes best. Of course this analysis does not prove what the nature of the intermediate is in a particular case because many important factors have been omitted, but the results strongly suggest that the observed activation energies depend upon the CFSE in the fundamental way shown and that data available can be rationalized with one simple model.

Crystal field theory (CFT), or perhaps better, ligand field theory (LFT), has enjoyed tremendous success in predicting the properties of coordination compounds. In particular, the electronic spectra and magnetism of complexes seem especially amenable to theoretical studies.[5-8] However, in the field of reaction kinetics very few applications have been made. We believe the approach outlined below should be useful in considerations about reaction mechanisms.

Basolo and Pearson[9] first pointed out how CFT might be used to rationalize the variations observed in the substitution reactions of numerous coordination compounds. This suggestion has been elaborated upon by Pearson,[10] Hush,[11] and Olliff and Odell.[12a] We will take a more extreme view and will predict the probable intermediate or transition state for a number of d^3 and d^6 octahedral systems on the basis of the correlation between the crystal field stabilization energy (CFSE) and the observed activation energies.

(1) This paper was partially formulated in the Ph.D. Dissertation of S. T. S. in 1961. Since it is rather speculative the paper was not offered for publication then, but continuing interest and publications by others in a similar vein prompts us to submit it now.

(2) Presented in part at the Werner Centennial Symposium of the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

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(4) (a) Mellon Institute; (b) University of Southern California.

(5) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(6) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961.

(7) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962.

(8) L. E. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand Field Theory," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1966.

(9) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, Chapters 2 and 3.

(10) R. G. Pearson, *J. Chem. Educ.*, **38**, 164 (1961).

(11) N. S. Hush, *Australian J. Chem.*, **15**, 378 (1962).

(12) (a) R. W. Olliff and A. L. Odell, *J. Chem. Soc.*, 2417 (1964); (b) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 3.

In studies of reaction kinetics with transition metal complexes, two points are significant regarding the activated intermediate, the nature of the species and its geometrical shape. Substitution reactions are usually thought of in terms of whether bond breaking or bond formation is energetically most favorable. Thus if the reactant is a six-coordinated species, bond rupture would result in a pentacoordinated intermediate whereas the formation of an additional bond would yield a heptacoordinated intermediate. Actually, it has been very difficult to provide unequivocal experimental evidence for such a clear-cut mechanism as either bond rupture or bond formation.[12b] If the coordination number of the intermediate could be established, the next question of interest would concern its geometry, *i.e.*, the probable arrangement of the ligands in the intermediate. For example, a five-coordinated intermediate could have either square-pyramidal or trigonal-bipyramidal geometry. Similarly, a seven-coordinated intermediate could assume either a pentagonal bipyramid form or a trigonal prism with the seventh ligand bonded through one of its rectangular faces. One of the factors then that may contribute significantly to the activation energy of a particular reaction is extra CFSE required to attain such an intermediate.

Theoretical Model

While the calculations below are based upon CFT, the reasons for the particular electronic configurations used for the intermediates are based upon molecular orbital theory. We suppose that (1) an intermediate is preferred with a particular geometry which is stabilized by an electronic configuration in which the d electrons of the primary metal atom occupy the lowest energy d-like antibonding (σ or π, or both) molecular orbitals of the complex. Such an electronic configuration will be achieved even if the electrons are necessarily paired up in the lower energy d-like molecular orbitals in order to avoid the occupancy of higher antibonding orbitals. (Allocation of electrons to higher antibonding orbitals
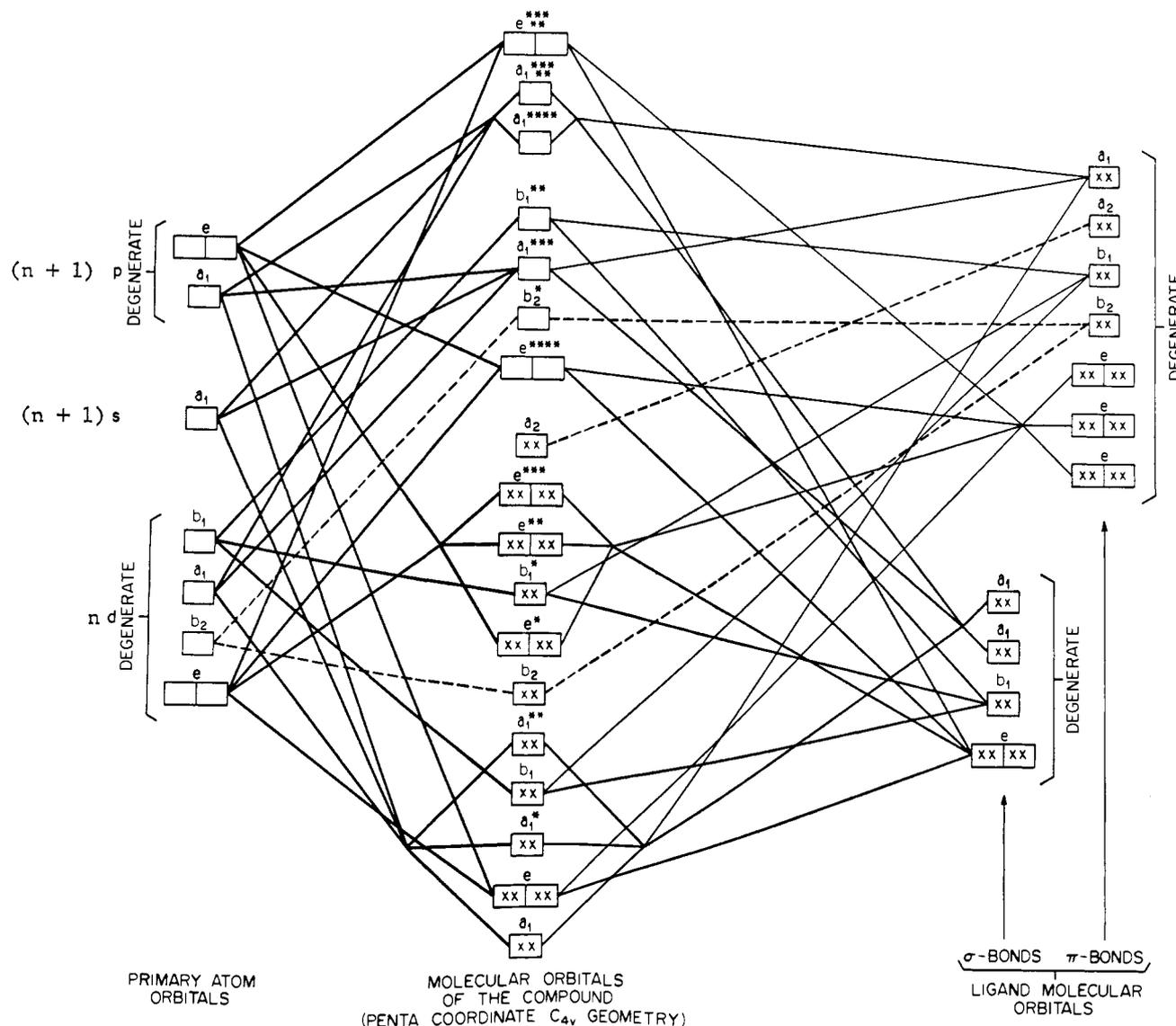
Figure 1a. Schematic molecular orbital energy level diagram for a five-coordinated complex of square-pyramidal (C_{4v}) geometry. [The various types of connecting lines in the diagram have the following meaning. On the right side of the diagram the σ orbitals of the ligands are connected with the molecular orbitals of the compound by medium-weight solid lines. Those π orbitals of the ligands which have common partners (*i.e.*, the same symmetry designation) among the σ orbitals are joined by light solid lines, and those which do not have common partners, by light dashed lines, so that the molecular orbitals of the compound on the right are connected by the light dashed lines alone, medium solid lines alone, or by both light solid lines *and* medium solid lines. As a result, on the left we respectively have either light dashed lines alone (signifying that those orbitals of the compound are only of π-antibonding character), or by medium solid lines alone (representing that they are only of σ-antibonding character) or by heavy solid lines arising because of the combination of both medium solid lines and light solid lines on the right. These latter lines then signify both σ- and π-antibonding character.]

results in a highly unstable intermediate.) (2) Changes in the CFSE and the interelectronic repulsion energy terms between the reactant and the hypothetical intermediate should be sufficient to give an estimate of the activation energy needed for the substitution reaction. Other factors which influence activation energies as the changes in solvation energies, bond lengths, etc., going from the reactant to the intermediate are not included. (3) The value of $10Dq$ does not change much on going from the hexacoordinated reactant to either the penta- or heptacoordinated intermediate.

Two possible geometries have been realized for a five-coordinated complex. One is the square pyramid, C_{4v} (*e.g.*, IF_5 molecule), obtained by eliminating one of the ligands in an octahedral complex and another is the tri-gonal bipyramid of D_{3h} symmetry (*e.g.*, PCl_5, $NbCl_5$,

$TaCl_5$, $Fe(CO)_5$, etc.). In the case of a seven-coordinate complex, three possible arrangements are found in na-ture: (1) pentagonal bipyramid, D_{5h} symmetry (*e.g.*, IF_7 (distorted), K_3ZrF_7, K_3UF_7, etc.); (2) trigonal prism with the seventh ligand along one of its square faces with some subsequent distortion, C_{2v} symmetry (*e.g.*, K_2NbF_7 and K_2TaF_7); and finally (3) octahedron with the seventh ligand added above the center of one of the faces which is distorted chiefly by separating the atoms at the corners of this face, C_{3v} symmetry (*e.g.*, A modification of the rare earth sesquioxides M_2O_3 such as La_2O_3, etc.). The latter two arrangements of the seven coordination are not much different from a geometry that is obtained by adding two ligands to a symmetrical square pyramid in such a way that they occupy two positions either in the $(x + y)z$ or $(x - y)z$ plane symmetrically along the z
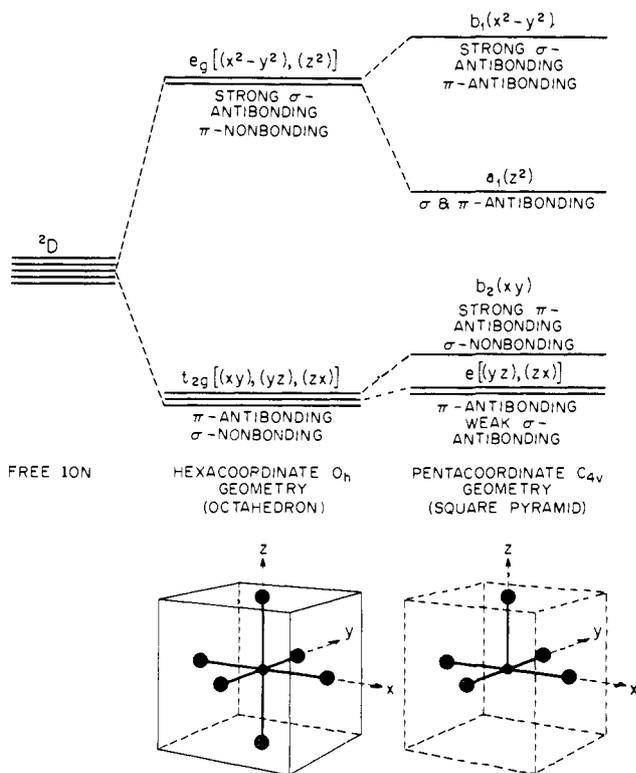
Figure 1b. Correlation of the octahedral (O_h) and square-pyramidal (C_{4v}) "d" orbital molecular energy levels.

axis on the other side of the axial ligand (the four ligands of the xy plane are along the x and y axes). Such an arrangement which could be called a trapezoidal octahedron[13] is shown in Figure 4b. In such an arrange-

Table I. Energy Levels of the d Orbitals in Various Symmetries

Symmetry	d orbitals	Energy, Dq
C_{4v}	$(x^2 - y^2)$	7.43
	(z^2)	2.57
	(xy)	−2.57
	$(yz), (xz)$	−3.71
D_{3h}	(z^2)	6.21
	$(x^2 - y^2), (xy)$	0.04
	$(yz), (xz)$	−3.14
D_{5h}	(z^2)	5.79
	$(s^2 - y^2), (xy)$	1.96
	$(yz), (xz)$	−4.86
C_{2v}	$(x^2 - y^2)$	6.10
	$(z^2, xy)^-$	1.48
	$(x + y)z$	0.16
	$(z^2, xy)^-$	−1.92
	$(x - y)z$	−5.81

ment, if the angle between the two ligands with the center is β, where β is the tetrahedral angle, 109° 28′, and if all the bond distances are equal, it becomes very close to case 2 described above. If the angle is $\beta/2$ and one of the two ligands occupy the sixth coordination position of the octahedron, i.e, along the z axis, this results in an arrangement which is very similar to the case of C_{3v} symmetry. Thus we could treat the C_{2v} and C_{3v} possibilities of seven coordination as special cases of the C_{2v} trapezoidal-octahedral configuration. The trap-

(13) The name "trapezoidal octahedron" has been kindly suggested to us by Dr. Andrew D. Liehr of the Mellon Institute.

Table II. Electronic Configurations and Corresponding Terms in Various Symmetries for the Intermediates for All the d^n, $n = 0$–10, Systems[a]

[Large multi-column table of electronic configurations and terms for O_h, C_{4v}, D_{3h}, D_{5h}, and C_{2v} symmetries]

[a] Based on our first postulate. [b] [CORE] represents all the filled molecular orbitals (formed from the σ and π orbitals of the ligands) below the d-like molecular orbitals in the molecular orbital energy level diagrams.

Figure 2a. Schematic molecular orbital energy level diagram for a five-coordinated complex of trigonal-bipyramidal (D_{3h}) geometry. (See the caption for Figure 1a for the meaning of connecting lines.)

ezoidal octahedron is similar to the model proposed by Hush.[11]

The values for the energy levels of the d orbitals in the various symmetries are given in Table I. These differ from those used by Basolo and Pearson for C_{4v}, D_{3h}, and D_{5h} symmetries and those given by Hush for C_{2v} symmetry because we set $\langle \rho_2(r) \rangle = \langle \rho_4(r) \rangle$ instead of $\langle \rho_2(r) \rangle = 2\langle \rho_4(r) \rangle$ as done by the workers above.[14]

We will now use our first postulate and derive the electronic configuration of the activated complex. In Figures 1a, 2a, 3a, and 4a, we give the schematic molecular orbital energy level diagrams[15] for complexes of five-

coordinated C_{4v} and D_{3h} and seven-coordinated complexes of D_{5h} and C_{2v} symmetries, respectively. Figures 1b, 2b, 3b, and 4b serially show only the d-like molecular orbitals, emphasizing their antibonding characteristics. We notice that in all cases we have "d" orbitals of either strongly σ antibonding or strongly π antibonding or both. According to our first postulate, a complete breakdown of Hund's rule of maximum spin multiplicity takes place and results in an electronic configuration with a minimum number of unpaired spins for the activated intermediate. Table II summarizes the terms arising from such electronic configurations in different symmetries for all the d^n ($n = 0-10$) systems. The energy differences between the ground terms of the octahedral complex and that of the active intermediates are given in Table III. In these equations, in addition to the crystal field parameter Dq, we have one other parameter P_n due to changes in interelectronic repulsion energies. The various P_n are given by the well-known Slater–Condon–Shortley parameters[16]

(14) For a discussion of this point, see S. T. Spees, J. R. Perumareddi, and A. W. Adamson, *J. Phys. Chem.*, **72**, 1822 (1968), and references therein. Changes in the value of ρ, the ratio of the radial parameters, from 2 to 1 do not seem to alter the general trend of the arguments that are derived from our model with the exception of the C_{2v} possibility, in which case the crystal-field d-orbital energy levels vary significantly. In fact, in the case of diamagnetic d^6 in Table III, only the value for the C_{2v} intermediate shows any change, being $8.86Dq$ for $\rho = 2$ and $3.10Dq$ for $\rho = 1$. Such a drastic variation in the case of C_{2v} is the result of the configuration interaction present in this symmetry alone. It is interesting to note that the over-all separation of the d orbitals in C_{2v} symmetry becomes comparable to that of D_{5h} symmetry when ρ is unity (see Table I and Figures 3 and 4).

(15) For construction and use of such schematic molecular orbital energy level diagrams read: (a) A. D. Liehr, *J. Chem. Educ.*, **39**, 135 (1962); (b) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963).

(16) (a) E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge University Press, Cambridge, 1953; (b) J. C. Slater, "Quantum Theory of Atomic Structure," Vol. 1 and 2, McGraw-Hill Book Co., Inc., New York, N. Y., 1960.
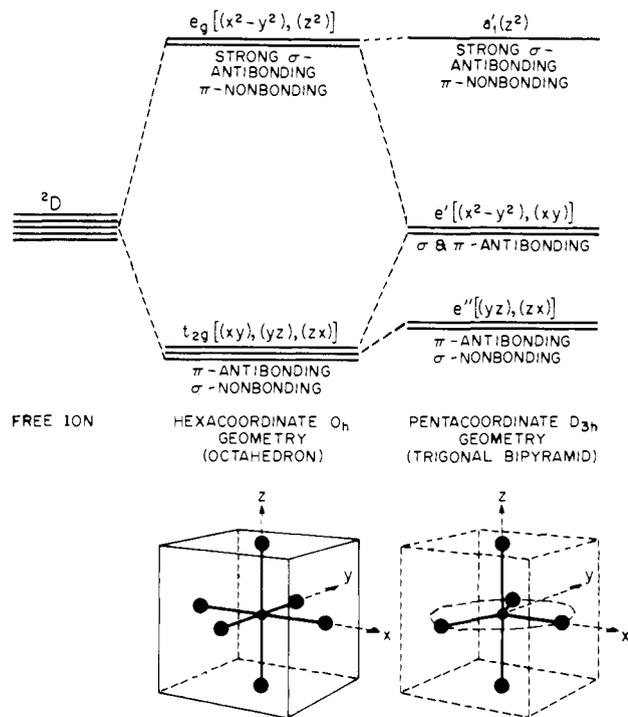
Figure 2b. Correlation of the octahedral (O_h) and trigonal-bipyramidal (D_{3h}) "d" orbital molecular energy levels.

(F_2 and F_4) or the equivalent Racah parameters (B and C: $B = F_2 - 5F_4$; $C = 35F_4$) as follows.

$$P_2 = P_4 = 9B + 3C$$
$$P_3 = 12B + 4C$$
$$P_4' = 15B + 8C$$
$$P_5' = 15B + 10C$$
$$P_6 = 3C$$
$$P_6' = 5B + 8C$$
$$P_6'' = 5B + 5C$$
$$P_7' = 4B + 4C$$
$$P_8 = 12B + 3C$$

It should be remarked, however, that the equations in Table III will be true for d^0, d^1, d^2 (excepting C_{2v}), d^5 (low spin), d^6 (low spin), d^7 (low spin), d^9, and d^{10} regardless of our assumption (first postulate) in deriving the electronic configurations of the intermediates.

A few observations emerge from Table III and eq 1 for activation energies. According to these observations we may expect octahedral complexes with electronic configuration d^0, d^1, d^2, high-spin d^4, high-spin d^5, high-spin d^6, low-spin d^7, d^9, and d^{10} to be labile, whereas complexes with configurations d^3, low-spin d^4, low-spin d^5, low-spin d^6, and d^8 will be inert. And in the latter case low-spin d^4, low-spin d^5, and d^8 configurations result in more lability compared to the inert d^3 and low-spin d^6 configurations. These observations are in good agreement with the empirical correlations that have been noticed in the past regarding the reactions of transition-metal complexes.[9,17] We

(17) (a) J. R. Perumareddi, unpublished results; (b) H. Taube, *Chem. Rev.*, **50**, 69 (1952).

refer particularly to the correlation based on the "criterion of antibonding" which may be stated as follows. If the electronic configuration of the reactant is such that the electrons occupy orbitals of antibonding nature, such a complex will be labile in its reactions compared to the one in which the antibonding orbitals are not occupied. The latter will be inert. Thus we may arrive at a qualitative conclusion that high-spin d^4, high-spin d^5, high-spin d^6, high-spin d^7, low-spin d^7, d^8, d^9, and d^{10} configurations in octahedral symmetry result in labile reactions, and the d^0, d^1, d^2, d^3, low-spin d^4, low-spin d^5, and low-spin d^6 configurations result in inertness. Among these latter configurations we may further conclude that d^3 and diamagnetic d^6 (because of the half-filled and filled molecular orbital configurations) will be more inert compared to the d^0, d^1, d^2, low-spin d^4, and low-spin d^5. Another conclusion that can be drawn from our Table III and eq 2 is the probable path of the reaction itself. Thus octahedral complexes with d^1, d^2, d^3, and d^4 (low spin and high spin) configurations probably proceed by a process in which bond making is important and complexes with d^7 (low spin and high spin), d^8, and d^9 configurations by a bond-breaking process; complexes with d^0, d^5 (low spin and high spin), d^6 (low spin and high spin), and d^{10} seem to be explained by both bond-rupture and bond-formation processes.

In order to test these qualitative inferences quantitatively, we choose the d^3 and diamagnetic d^6 electronic configurations as exemplified respectively by trivalent chromium and trivalent cobalt complexes as they provide most of the data on substitution reactions. Let us begin with Cr(III) complexes which have a d^3 configuration. To estimate the energy difference between the initial octahedral complex and the various possible intermediates, we need to know the Dq, B, and C parameters. Here we use our postulates 2 and 3 and evaluate these parameters from the spectral data.[18] In chromium(III) complexes, the first spin-allowed ligand field band ($^4A_{2g} \rightarrow {}^4T_{2g}$) directly gives the value of $10Dq$. Although the pairing energy P_3 is given by $(12B + 4C) = {}^4/_3(9B + 3C)$ (see eq 2), we directly use the value of the energy of the first spin-forbidden transition ($^4T_{2g} \rightarrow {}^2E_g$, $^2T_{1g}$) which is actually given by $(9B + 3C)$. This does not affect our results since the term P_3 is present in all four cases of symmetry considered, and we are interested in relative probability of a particular geometry for the activated intermediate. Table IV shows the observed and calculated activation energies for some aquation reactions of Cr(III) complexes for the various intermediates. Since the calculated energies for the reduced coordination are so high, it seems that the reactions of Cr(III) complexes probably proceed *via* an intermediate with an enhanced coordination number, and the probable geometry of the intermediate is either the pentagonal bipyramid or the trapezoidal octahedron.

Next, consider Co(III) complexes, which have in general a low-spin d^6 configuration. In this case, it is interesting to note that the parameters due to interelectronic repulsions are present only for the intermediates with trigonal-bipyramidal and pentagonal-

(18) The spectral data for Cr(III) complexes are collected from ref 7 and also from the following: (a) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **266**, 49 (1951).
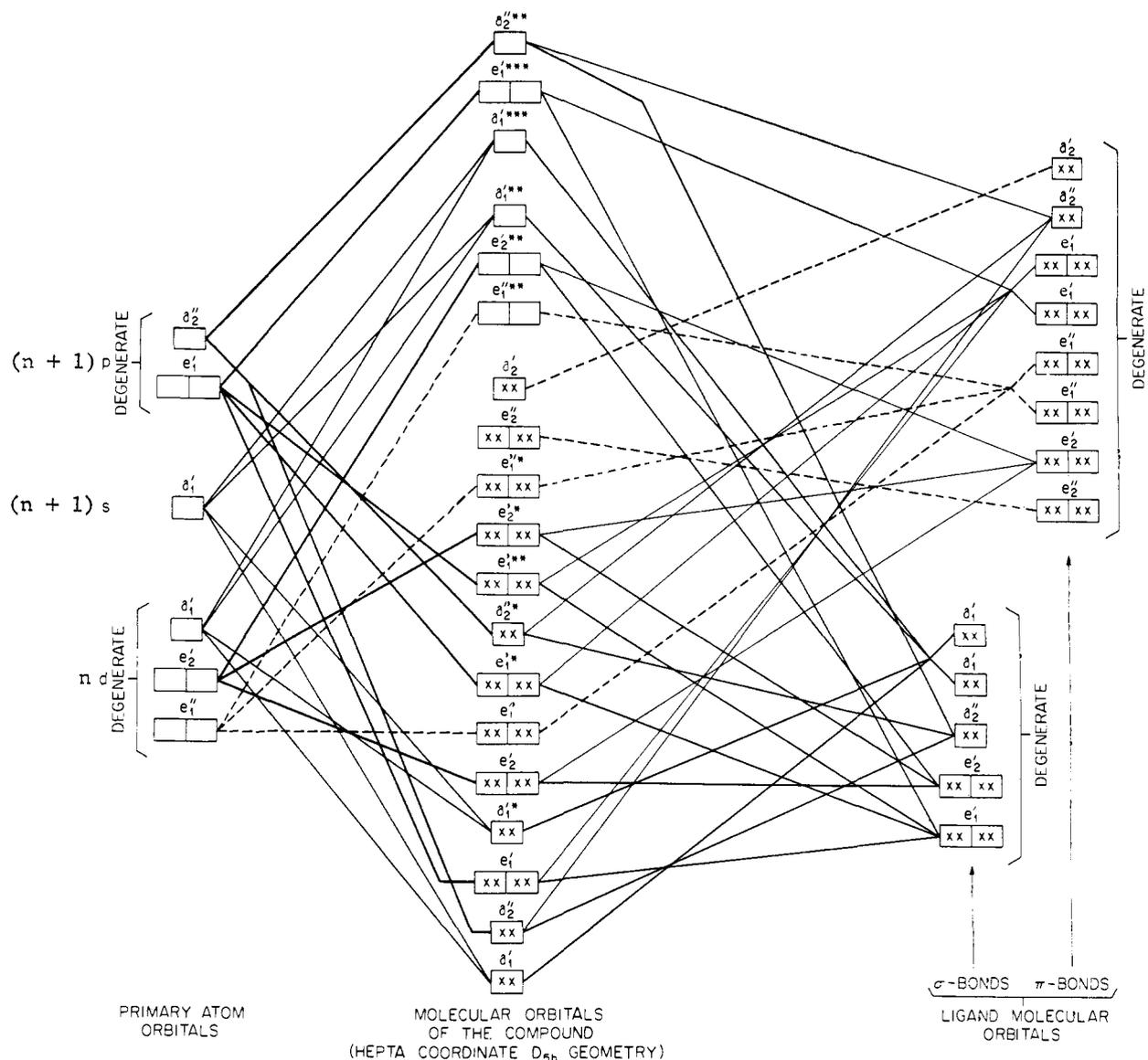
PRIMARY ATOM
ORBITALS

MOLECULAR ORBITALS
OF THE COMPOUND
(HEPTA COORDINATE D_{5h} GEOMETRY)

LIGAND MOLECULAR
ORBITALS

σ-BONDS π-BONDS

Figure 3a. Schematic molecular orbital energy level diagram for a seven-coordinated complex of pentagonal-bipyramidal (D_{5h}) geometry. (See the caption for Figure 1a for the meaning of connecting lines.)

Table III. Equations for the Energy Differences between the Ground Terms of the Octahedral Configuration and That of the Intermediate Configurations (Based on Table II) for All the d^n, n = 0–10, Systems[a]

d^n	C_{4v}	D_{3h}	D_{5h}	C_{2v}
d^0	0	0	0	0
d^1	$0.29Dq$	$0.86Dq$	$-0.86Dq$	$-1.81Dq$
d^2	$0.58Dq$	$1.72Dq$	$-1.72Dq$	$(-3.62Dq + P_2)$
d^3	$(0.87Dq + P_3)$	$(2.58Dq + P_3)$	$(-2.58Dq + P_3)$	$(-1.54Dq + P_3)^b$
d^4 (low spin)	$(1.16Dq + P_4)$	$(3.44Dq + P_4)$	$(-3.44Dq + P_4)$	$(0.54Dq + P_4)^b$
d^4 (high spin)	$(-8.84Dq + P_4{}')$	$(-6.56Dq + P_4{}')$	$(-13.44Dq + P_4{}')$	$(-9.46Dq + P_4{}')^b$
d^5 (low spin)	$2.59Dq$	$7.48Dq$	$2.52Dq$	$4.70Dq^b$
d^5 (high spin)	$(-17.41Dq + P_5{}')$	$(-12.52Dq + P_5{}')$	$(-17.48Dq + P_5{}')$	$(-15.30Dq + P_5{}')^b$
d^6 (low spin)	$4.00Dq$	$(11.52Dq - P_6)$	$(8.48Dq - P_6)$	$8.86Dq^b$
d^6 (high spin)	$(-16.00Dq + P_6{}')$	$(-8.48Dq + P_6{}'')$	$(-11.52Dq + P_6{}'')$	$(-11.41Dq + P_6{}')^b$
d^7 (low spin)	$0.59Dq$	$5.56Dq$	$4.44Dq$	$4.34Dq^b$
d^7 (high spin)	$(-9.41Dq + P_7{}')$	$(-4.44Dq + P_7{}')$	$(-5.56Dq + P_7{}')$	$(-5.66Dq + P_7{}')^b$
d^8	$(-2.84Dq + P_8)$	$(0.40Dq + P_8)$	$(0.40Dq + P_8)$	$(-0.18Dq + P_8)$
d^9	$-1.41Dq$	$-0.19Dq$	$0.19Dq$	$-0.08Dq$
d^{10}	0	0	0	0

[a] The ratio, ρ, of the radial parameters is taken to be unity. [b] In these cases the equations given for pairing energies are obtained with the assumption that $(z^2, xy)^+ \sim xy$ and $(z^2, xy)^- \sim z^2$, i.e., by not including the interaction between the z^2 and xy orbitals which both transform as a_1 representation.
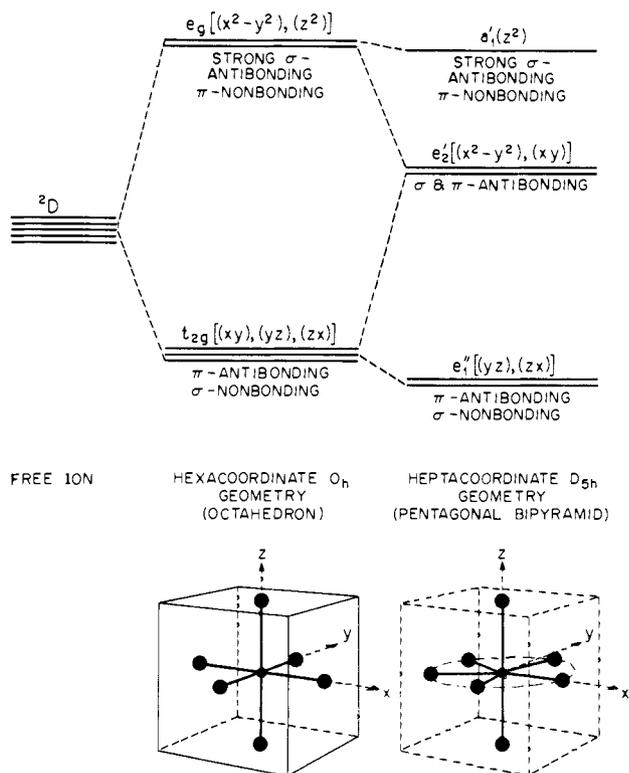
Figure 3b. Correlation of the octahedral (O_h) and pentagonal-bipyramidal (D_5h) "d" orbital molecular energy levels.

taken into consideration in the earlier discussions on activation energies.[9] The first spin-allowed ligand field band ($^1A_{1g} \rightarrow {}^1T_{1g}$) in the spectra of cobalt(III) complexes is given by ($10Dq - C$). We have added a reasonable value of C for the energy of the first spin-allowed band[19] to obtain a value of $10Dq$ for d[6] configuration. Since, on the average B has a value of 500 cm^{-1} and $C = 6B$ in the cobalt(III) spectra, a constant value of 9000 cm^{-1} is used for $3C$ in all the calculations on d[6]. Tables V–VIII show the observed and calculated activation energies for the aquation of a number of Co(III) complexes. Although the square-pyramidal C_{4v} geometry seems to be preferred in the intermediate, the seven-coordinate D_{5h} geometry also comes close to the observed activation energies. So it seems it is rather difficult to decide definitely any preferred geometrical arrangement for the intermediate in the reactions of trivalent diamagnetic cobalt complexes.

Conclusion

To recapitulate, what do we need to know in order to calculate the activation energy for a reaction? We need a theory of energetics and bonding such that differences between the initial state and excited state may be estimated. Our model simply assumes that

Table IV. The Observed and Predicted Activation Energies for the Aquation of Some Cr(III) Complexes

No.	Complex	Activation energy, kcal/mole Calculated C_{4v}	D_{3h}	D_{5h}	C_{2v}	Observed[a]
1	$Cr(NH_3)_6{}^{3+}$	49.1	59.6	27.9	34.3	26.0
2	$Cr(NH_3)_5Cl^{2+}$	47.3	56.8	28.2	33.9	22.4[b]
3	$Cr(NH_3)_5Br^{2+}$	47.1	56.5	28.4	34.1	21.5[b]
4	$Cr(NH_3)_5I^{2+}$	47.0	56.0	28.8	34.3	21.4[b]
5	$Cr(NH_3)_5(SCN)^{2+}$	46.6	59.6	29.0	35.2	25.0
6	$trans$-$Cr(NH_3)_2(SCN)_4{}^-$	43.1	52.6	24.1	29.8	27.0[c]
7	$Cr(en)_3{}^{3+}$	48.1	58.7	26.5	33.0	24.6
8	$Cr(en)(C_2O_4)_2{}^-$	46.1	55.4	27.6	33.2	19.5[d]
9	cis-$Cr(en)_2(H_2O)_2{}^{3+}$	48.3	58.5	28.0	34.1	23.7[e]
10	cis-$Cr(en)_2Cl_2{}^+$	45.9	55.1	27.3	33.2	21.1[f]
11	$Cr(H_2O)_6{}^{3+}$	47.3	55.7	30.1	35.2	28.0
12	$Cr(H_2O)_5F^{2+}$	47.1	55.2	30.6	35.5	28.7[g]
13	$Cr(H_2O)_5Cl^{2+}$	46.3	54.2	30.2	35.0	24.3[g]
14	$Cr(H_2O)_5(SCN)^{2+}$	47.1	54.6	28.9	32.3	28.0
15	$Cr(urea)_6{}^{3+}$	45.4	58.9	29.5	34.2	27.0
16	$Cr(C_2O_4)_3{}^{3-}$	45.4	54.0	28.1	33.3	22.1[h]
17	$Cr(H_2O)_5I^{2+}$	44.6	52.3	29.7	34.2	23.0[g]

[a] Except where noted, data from D. R. Stranks, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkens, Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 2. [b] M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, **83**, 2453 (1961). [c] A. W. Adamson, *ibid.*, **80**, 3183 (1958). [d] H. L. Schlafer, O. Kling, L. Mahler, and H. P. Optiz, *Z. Physik. Chem.* (Frankfurt), **24**, 307 (1960). [e] H. L. Schlafer and R. Kollrack, *ibid.*, **18**, 348 (1958). [f] J. Selbin and J. C. Bailar, *J. Am. Chem. Soc.*, **79**, 4285 (1957). [g] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965). [h] K. V. Krishnamurty and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960).

bipyramidal geometry. This is the result of the presence of a degenerate orbital doublet e' and e_2' respectively of D_{3h} and D_{5h} symmetries. As has been already pointed out, regardless of our postulate (1), this situation remains, as the electronic configurations for our d[6] system will be $(t_{2g})^6$ in octahedral symmetry, $(e'')^4(e')^2$ in trigonal-bipyramidal symmetry, and $(e_1'')^4(e_2')^2$ in pentagonal-bipyramidal symmetry. The respective terms are singlet A_{1g}, triplet A_2', and triplet A_2' as given in Table II. This point has not been

the changes in σ bonding due to the s and p metal

(19) The spectral data for Co(III) complexes are gathered from ref 7 and also from the following: (a) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **271**, 101 (1952); (b) H. Taube and F. A. Posey, *J. Am. Chem. Soc.*, **75**, 1463 (1953); (c) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956); (d) R. S. Nyholm and M. L. Tobe, *ibid.*, 1707 (1956); (e) M. L. Tobe, *ibid.*, 3776 (1959); (f) M. E. Baldwin and M. L. Tobe, *ibid.*, 4275 (1960); (g) P. J. Stables and M. L. Tobe, *ibid.*, 4812 (1960); (h) R. C. Brasted and C. Hirayama, *J. Phys. Chem.*, **63**, 780 (1959); (i) F. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952); (j) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950); (k) F. Basolo, *ibid.*, **75**, 227 (1953).
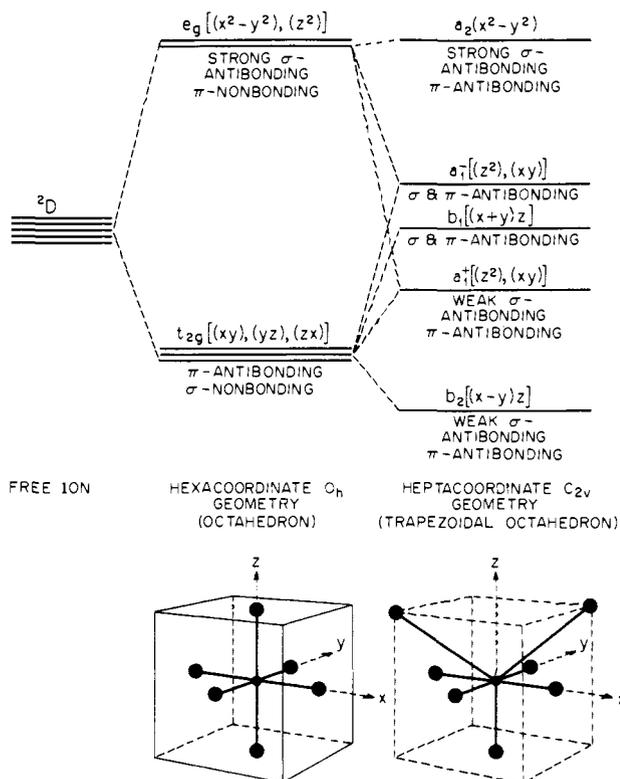
Figure 4a. Schematic molecular orbital energy level diagram for a seven-coordinated complex of trapezoidal-octahedral (C_{2v}) geometry. [As this system is somewhat complicated regarding the placement of bonding π orbitals, the guidelines have been the descent from octahedral symmetry and other factors such as qualitative configuration interaction and overlap considerations. Hence, their locations in the diagram should not be taken too literally. Since in this case all the molecular orbitals of the compound are of both σ- and π-antibonding character, the connecting lines are differentiated only according to the type of the symmetry designation of the orbitals.]

Figure 4b. Correlation of the octahedral (O_h) and trapezoidal-octahedral (C_{2v}) "d" orbital molecular energy levels.

orbitals[20] should nearly cancel in a series of similar reactions. Gray and Langford[21] have made a similar assumption when they suggest that the reactivities of the first-row transition metals are dominated by d-orbital

Table V. The Observed and Predicted Activation Energies for the Aquation of Some $[Co^{III}(NH_3)_5X]^{n+}$ Complex Cations

| | Activation energy, kcal | | | | |
| | Calculated | | | | |
X	C_{4v}	D_{3h}	C_{2v}	D_{5h}	Observed[a]
H_2O	27.0	52.0	59.7	31.6	27.0
Cl^-	26.8	51.5	59.3	31.1	23.0
Br^-	26.7	50.9	58.8	30.8	24.0
NCS^-	27.7	51.4	59.2	31.1	26.8
SO_4^{2-}	26.2	49.9	58.0	30.0	19.0

[a] Data from J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 129.

bonding. Therefore, the simplest theory that might accomplish this purpose would be the electrostatic theory taking account of crystal field stabilization energies. The variables considered were (1) the nature of the metal ion, (2) the nature of the ligands, (3) the nature of the external reagent, (4) the geometry of the complex, and (5) the coordination number of the complex.

(20) It might be pointed out that in all the cases considered here there is no change in the p-orbital participation. This is not always the case, e.g., the changes involved when a square-planar complex (dsp²) adds a ligand to become either trigonal bipyramidal (sp³d) or square pyramidal (sp³d).

(21) H. B. Gray and C. H. Lanford, Chem. Eng. News, 46 (15), 68 (1968).

Table VI. The Observed and Predicted Activation Energies for the Aquation of Some cis-$[Co^{III}(en)_2X_2]^{n+}$ Complex Cations

| | Activation energy, kcal | | | | |
| | Calculated | | | | |
X_2	C_{4v}	D_{3h}	C_{2v}	D_{5h}	Observed[a]
Cl_2	25.4	47.6	56.3	28.2	22.0
$(NO_2)Cl$	26.9	51.9	59.6	31.4	22.0
$(N_3)Cl$	25.8	48.7	57.1	29.1	21.7[b]
$(H_2O)_2$	27.3	53.0	61.2	32.3	28.8[c]
$(OH)_2$	26.0	49.3	57.6	29.5	27.4[c]
F_2	26.6	51.0	58.9	31.5	30.0
$(NCS)Cl$	26.9	51.9	59.6	31.4	20.8[d]
$(NCS)Br$	26.9	51.9	59.6	31.4	23.1[d]

[a] Except where noted, data from J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 129. [b] M. L. Tobe, J. Chem. Soc., 3776 (1959). [c] W. Kruse and H. Taube, J. Am. Chem. Soc., 83, 1280 (1961). [d] M. E. Baldwin and M. L. Tobe, J. Chem. Soc., 4275 (1960).

Table VII. The Observed and Predicted Activation Energies for the Aquation of Some $trans$-$[Co^{III}(AA)_2X_2]^{n+}$ Complex Cations

| | Activation energy, kcal | | | | |
| | Calculated | | | | |
$(AA)_2X_2$	C_{4v}	D_{3h}	C_{2v}	D_{5h}	Observed[a]
$(en)_2F_2$	26.6	51.1	59.0	30.9	29.0
$(en)_2Cl_2$	25.9	49.1	57.5	29.4	27.0
$(en)_2Br_2$	25.0	46.3	55.3	27.3	26.0
$(en)_2(NCS)Br$	23.7	42.7	52.5	24.6	30.1[b]
$(en)_2(NCS)Cl$	24.6	45.2	54.5	26.6	30.4[b]
$(Pn)_2Cl_2^c$	22.7	39.8	50.3	22.5	28.0
$(i\text{-bn})_2Cl_2^d$	22.6	39.6	50.1	22.4	26.0
$(en)_2(H_2O)_2$	27.3	53.0	60.5	32.3	30.6[e]
$(en)_2(OH)_2$	25.8	48.8	57.2	29.1	30.4[e]

[a] Except where noted, data from D. R. Stranks, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 2. [b] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, J. Chem. Soc., 1691 (1956). [c] pn represents 1,2-diaminopropane. [d] i-bn represents 2,3-diaminobutane. [e] W. Kruse and H. Taube, J. Am. Chem. Soc., 83, 1260 (1961).

Table VIII. The Observed and Predicted Activation Energies for the Aquation of Some $trans$-$[Co^{III}(en)_2AX]^{2+}$ Complex Cations

| | Activation energy, kcal | | | | |
| | Calculated | | | | |
AX	C_{4v}	D_{3h}	C_{2v}	D_{5h}	Observed[a]
$(NH_3)Cl$	27.3	53.0	57.1	32.3	23.6
$(NH_3)Br$	26.3	50.1	54.3	30.1	24.6
$(NH_3)NO_3$	28.0	55.0	60.0	33.7	25.5
$(N_3)Cl$	23.7	42.7	52.5	24.6	23.1[b]

[a] Except where noted, data from M. L. Tobe, J. Chem. Soc., 3776 (1959). [b] P. J. Stables and M. L. Tobe, ibid., 4803 (1960).

We want to emphasize that crystal field effects contribute only a small amount to the over-all bonding and that there is not necessarily any correlation between the crystal field energies and total bonding energies. A correlation between E_{act} and CFSE for a series of reactions might be fortuitous. The fact that CF effects are not the only ones of importance is shown by the large change in E_{act} for a small change in CFSE, e.g., the $Co(NH_3)_5X^{2+}$ series. Our principal point is that, if only the variables involved in the CFSE are considered, do the observed activation energies parallel the crystal field effects? We believe the answer is yes.

We have attempted to present a unified model based on crystal field theory and qualitative molecular orbital

theory to predict the activation energy of a particular reaction and hence assign a probable mechanism on the basis of these calculations. The results show that the reactions of complexes with a certain primary metal atom may not proceed always by the same mechanistic path. Moreover, the model does not definitely assign the probably geometry of the intermediate in cases where it predicts one type of mechanism. Crude as it now stands, we believe that as more data are accumulated on the precise measurement of the activation energies of a large number of reactions (and on the electronic spectra of the complexes) further refinements of this model will be able to correlate the data and, perhaps, predict the activation energy of a reaction yet to be carried out.

More recent experimental evidence and speculation about the mechanisms of substitution reactions for Cr-(III) and Co(III) reactions does not arrive at a consensus. Taking into account both entropies and enthalpies of activation for a number of Co(III) reactions, Tobe concludes that they are all essentially dissociative reactions with the probable intermediate being a trigonal bypyramid if the entropy is positive and a tetragonal pyramid if not.[22] However, the energy difference between these two is small so that a very small difference in the ligand, for example, can change the intermediate. Duffy and Earley[23] conclude that the anation of Cr-$(NH_3)_5OH_2^{3+}$ proceeds *via* an S$_N$1IP reaction, whereas on the basis of an nmr study of the aquation of Co-$(CH_3NH_2)_5Cl^{2+}$ Parris[24] concludes that an S$_N$1 mechanism is involved and suggests that the analogous Cr(III) complex probably proceeds *via* an S$_N$2-type mechanism.

(22) M. L. Tobe, *Inorg. Chem.*, 7, 1261 (1968).
(23) N. V. Duffy and J. E. Earley, *J. Am. Chem. Soc.*, 89, 272 (1967)
(24) M. Parris, *J. Chem. Soc., A*, 583 (1967).

Chelation of Uranyl Ions by Adenine Nucleotides. II. Proton Magnetic Resonance Investigation of the Uranyl Nitrate–Adenosine 5'-Monophosphate Chelate in D_2O at Basic pD[1]

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Abstract: Proton magnetic resonance spectra (100 MHz) of various mixtures of uranyl nitrate and adenosine 5'-monophosphate in D_2O at pD $\sim$10 have been obtained and analyzed. In 0.1 M equimolar solution all 5'-AMP proton resonances experience a downfield shift, specifically, H_8 (0.46 ppm), H_2 (0.31 ppm), $H_{1'}$ (0.03 ppm), $H_{2'}$ (2.87 ppm), $H_{3'}$ (0.74 ppm), $H_{4'}$ (2.35 ppm), $H_{5'}$ (1.04 ppm), and $H_{5''}$ (0.32 ppm). The uranium-induced purine proton shifts are attributed to destacking of the adenine rings plus complete elimination of the specific phosphate deshielding of H_8. The movement of the ribose proton signals is believed to result from the formation of a dinuclear sandwich-type chelate in which one uranyl group is chelated by the 2'- and 3'-ribose oxygen atoms of one 5'-AMP molecule and by a phosphate oxygen and the 3'-oxygen of a second AMP molecule, and a second uranyl group is chelated by the 2'- and 3'-oxygens of the second AMP molecule and a phosphate oxygen and the 3'-oxygen of the first AMP. This chelate structure is so strong that the free ligand resonances and the complexed ligand resonances appear simultaneously in the spectrum of a mixture containing excess AMP, with no difference in their purine proton peak widths being detectable. The compatibility of the proposed structure and its pmr spectrum is discussed.

This paper is a continuation of the investigation of the reaction of UO_2^{2+} with nucleotides. In the previous paper[4] we interpreted pH titrations of mixtures of adenine nucleotides and $UO_2(NO_3)_2$. For the present paper we have carried out a proton magnetic resonance investigation of the uranyl nitrate–adenosine 5'-mono-phosphate 1:1 chelate (U-AMP) in D_2O. Gelation and precipitation limited this pmr study to basic pD.

Experimental Section

Materials. All nucleotides were Sigma Chemical Co. Sigma grade used as received without further purification. They were standardized by titration. D_2O (99.82%) was purchased from Volk Radiochemical Co. Eastman grade aqueous 10% tetramethyl-ammonium hydroxide was purchased from Distillation Products Industries. Fisher Certified Reagent grade uranyl nitrate hexahydrate was used.

Preparation of Solutions. Each aqueous nucleotide solution was first made up to $\sim$0.05 M by direct weighing of the desired amount and then raising the pH with 10% $(CH_3)_4NOH$ to the desired value. The aqueous solution was then lyophilized overnight, and the residue

(1) (a) This paper is based on work performed under contract with the U. S. Atomic Energy Commission at the University of Rochester Atomic Energy Project and has been assigned Report No. UR-49-948; (b) presented in part at the Second International Symposium on Nuclear Magnetic Resonance, Sao Paolo, Brazil, July 1968.
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(4) I. Feldman, J. Jones, and R. Cross, *J. Am. Chem. Soc.*, 89, 49 (1967).