most intense peaks which presumably arose from the equatorial borons.

Although these results are of necessity more qualitative than quantitative, several interesting trends are apparent. All of the ten-membered cages give second-order or intermediate spectra whereas all the twelve-membered cages except one give first-order spectra. The quadrupole coupling is not independent of the cation present. The coupling constant is not therefore a reliable quantitative measure of the electron distribution within the boron cage. The unsymmetric cation $(C_2H_5)_3NH^+$ produces a sufficiently large field gradient at the boron of the twelve-membered cage to give rise to a second-order spectrum. In the twelve-membered cages with the small coupling constants the introduction of a substituent (iodine) distorts the electron distribution sufficiently to produce a significant increase in coupling. If, however, the symmetry is maintained, as in $B_{12}Cl_{12}^{2-}$, a small coupling again results.

The most interesting of these observations is the pronounced difference between the ten-membered and twelve-membered cages. This difference is of the same order as the difference between boron in a tetrahedral environment (*eqQ* ranges from $\sim$0 in $NaBH_4$[4] to 104 kc./sec. in $NaBF_4$[4] and up to 570 kc./sec. for BO_4^- in some glasses[2,12,13]) and boron in a planar environment (*eqQ* is 2.96 Mc./sec. in boron nitride[4] and 2.76 Mc./sec. for BO_3 in glasses[2,12,13]). These results are usually discussed in terms of the occupancy of the boron 2p orbitals. Thus, in a symmetric tetrahedral environment all three 2p orbitals are equally occupied, giving rise to zero field gradient at the nucleus so that in the absence of fields arising from external ions *eqQ* will be zero. On the other hand, for a planar boron forming three sp^2 bonds two of the p orbitals (p_x and p_y) are occupied, but p_z is empty. It may be readily shown that the quadrupole coupling constant expected for this situation is just that of a free boron atom[2,14] (5.39 Mc./sec.). The observation of lower values than this (in boron nitride, for example) has been rationalized in terms of donation of electrons into the p_z orbital by π bonding. It is of interest therefore to see whether these results for boron cage compounds can be similarly interpreted in terms of inequalities in the populations of the boron 2p orbitals. With this in view, extended Hückel calculations similar to those reported by Hoffman and Lipscomb[15] on these cage compounds have been made. These calculations indicate a difference of about 0.03 in the populations of the different p orbitals of the twelve-membered cage borons and of about 0.17 for the equatorial borons of the ten-membered cages. These population differences would give quadrupole coupling constants agreeing in order of magnitude with the experimental results. There are several reasons why this type of calculation cannot be regarded as being particularly reliable. The most important of these are the well-known inadequacy of the Hückel type of approximation for predicting charge distributions and the uncertainty regarding the directions of the principal axes of the quadrupole coupling tensor. The results may, however, be taken as providing at least a suggestive indication of the nature of the differences in boron bonding in the two types of cage compound.

Experimental

All spectra were obtained at 14.2 Mc./sec. using a Varian broad-line instrument. The samples were examined in the form of compressed pellets. The preparation of these compounds has been described previously.[7,9]

Acknowledgments.—The author is indebted to Dr. W. R. Hertler, who kindly provided the boron cage compounds used in this study, and to Mr. Lee Stone of the Engineering Department for computing facilities.

---

[12] P. J. Bray and J. G. O'Keefe, *Phys. Chem. Glasses*, **4**, 37 (1963).

[13] P. J. Bray, M. Leventhal, and H. O. Hooper, *ibid.*, **4**, 47 (1963).

[14] G. Wessel, *Phys. Rev.*, **92**, 1581 (1953).

[15] R. Hoffman and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2872 (1962).

Correspondence

Stereochemistry of the Base Hydrolysis of Cobalt(III) Complexes

Sir:

There is now considerable evidence in support of the conjugate base dissociation mechanism (SN1CB) for the base hydrolysis of halogenoamminecobalt(III) complexes.[1-3] However, the most detailed attempt to explain the stereochemistry of this reaction was done on the basis of a bimolecular displacement (SN2) mechanism.[4] We wish to show that the available stereochemical data can be better explained on the basis of a dissociation process and to propose two stereochemical rules that must be obeyed if the mechanism postulated is correct.

Since a tetragonal pyramidal structure with water entering at the position vacated by the leaving group can only result in retention of configuration, the initial assumption is that the five-coordinated intermediate has a trigonal-bipyramidal structure. This is in accord with the hypothesis that this structure is stabilized by the π bonding of the electron pair on the amido nitrogen, which must be in the same trigonal plane as the vacant $d_{x^2-y^2}$ orbital on Co(III).[5] Assuming that a

---

[1] For discussion and references see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 124; F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 25 (1960).

[2] M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).

[3] R. B. Jordan and A. M. Sargeson, *ibid.*, **4**, 433 (1965).

[4] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **194**, 344 (1962).

[5] R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, **78**, 4878 (1956).

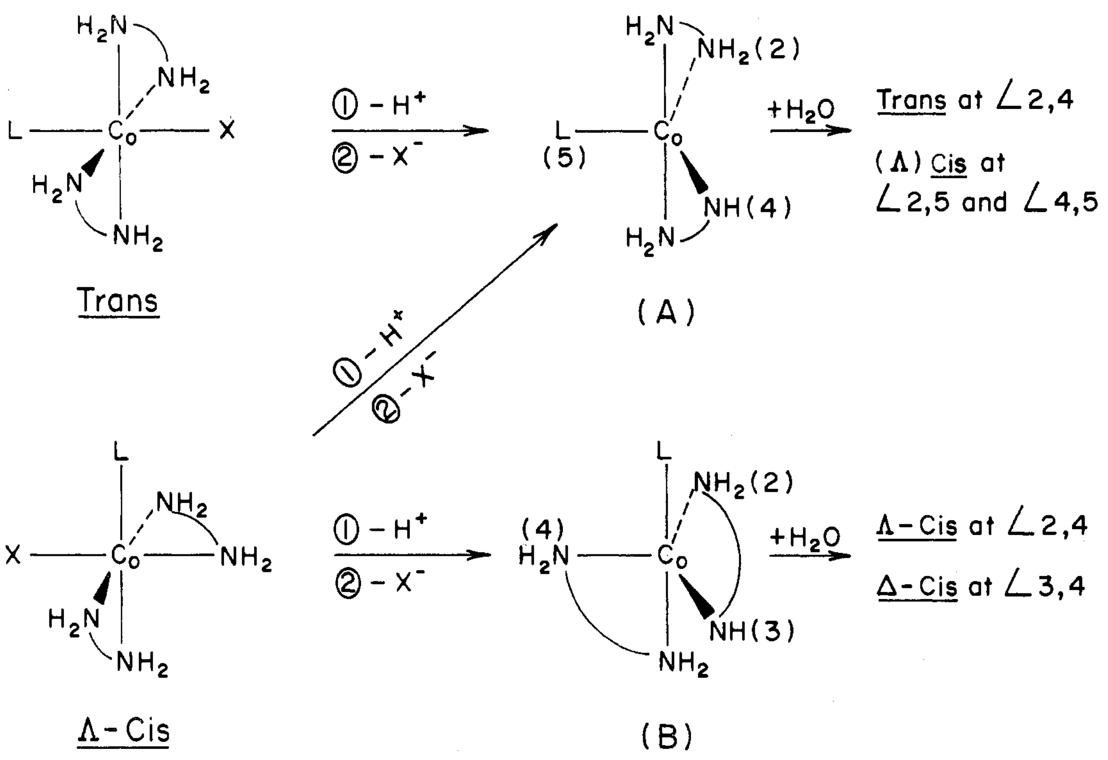

Figure 1.—Mechanism of reaction proposed for the base hydrolysis of $[Co(en)_2LX]^{n+}$.

minimum of atomic motion takes place in the formation of an intermediate, then it follows that *trans*-$[Co(en)_2LCl]^{n+}$ can readily form only structure A shown in Figure 1. This same structure and also structure B can be formed by the *cis* isomer. The addition of water in the trigonal plane of A may result in rearrangement. Furthermore, if the addition of water is fast compared to proton transfer, then B is asymmetrical and can give rise to a net retention or inversion of configuration. If proton transfer is faster than the addition of water, then racemic *cis* product must form from B. In any event, B can only form the *cis* isomer, whereas A can yield both *cis* and *trans* isomers.

Since the common intermediate A is the only one for the *trans* isomer, this permits the statement of the first rule, which is that for base hydrolysis *the cis isomer must never give less cis product than does the trans form.* An examination of the data in Table I shows that this rule is obeyed.

On the basis that the proposed mechanism is followed, it is also possible to calculate what fraction of A and what fraction of B are formed in the base hydrolysis of *cis*-$[Co(en)_2LX]^{n+}$. Thus, *trans*-$[Co(en)_2Cl_2]^+$ gives 95% *trans*-$[Co(en)_2ClOH]^+$ and 5% *cis*, which tells us the behavior of intermediate A. The 37% of *cis*-$[Co(en)_2ClOH]^+$ formed from *cis*-$[Co(en)_2Cl_2]^+$ must then come from the formation of 33.6% of B, which gives all *cis* product, and 66.4% of A, which gives (0.05)·(0.664) or 3.3% additional *cis* product. Table II shows the calculated fractions of trigonal bipyramids A and B formed from the other examples in Table I.

TABLE I

STERIC COURSE OF BASE HYDROLYSIS OF SOME COBALT(III) COMPLEXES

$[Co(en)_2LX]^{n+} + OH^- \rightarrow [Co(en)_2LOH]^{n+} + X^-$

		% *cis* product[a]							
Λ-*cis*-L	X	Λ		Δ	Ref.	*trans*-L	X	% *cis* product[a]	Ref.
OH	Cl	61		36	*b*	OH	Cl	94	*b*
OH	Br		96[c]		*b*	OH	Br	90	*b*
Cl	Cl	21		16	*b*	Cl	Cl	5	*b*
Cl	Br		30[c]		*b*	Cl	Br	5	*b*
Br	Cl		40[c]		*b*	Br	Cl	0	*b*
N_3	Cl		51[c]		*d*	N_3	Cl	13	*d*
NCS	Cl	56		24	*d*	NCS	Cl	76	*e*
NH_3	Cl	60		24	*f*	NH_3	Cl	76	*f*
NO_2	Cl	46		20	*g*	NO_2	Cl	6	*g*

[a] For Λ-*cis*-L the total % *cis* = % Λ + % Δ, whereas optically inactive *trans*-L yields *racemic-cis*. For both % *trans* product = 100 − % *cis*. [b] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962). [c] The starting material was *racemic-cis*-L. [d] P. J. Staples and M. L. Tobe, *ibid.*, 4803 (1960). [e] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *ibid.*, 1691 (1956). [f] R. S. Nyholm and M. L. Tobe, *ibid.*, 1707 (1956). [g] S. Asperger and C. K. Ingold, *ibid.*, 2862 (1956).

Also included in Table II are the modes of reaction of intermediate B when optically active *cis* isomers are used. For example, the data in Table I show that the base hydrolysis of Λ-*cis*-$[Co(en)_2NH_3Cl]^{2+}$ gives 60% Λ-*cis*- and 24% Δ-*cis*-$[Co(en)_2NH_3OH]^{2+}$. To explain this we note from Table II that intermediate A is formed 67% of the time and B is formed 33% of the time. Also A forms *cis* product 76% of the time and *trans* product 24% of the time. From the Λ-*cis* substrate the *cis* product *via* A must have the retained Λ configuration. This gives (0.67)(0.76) or 51% of Λ-*cis* product and the remaining 9% of this product must come *via* intermediate B. Therefore, B must add water with retention of configuration 27% of the time, (0.27)(0.33) giving 9%. In this way the results listed

Table II
Calculated Stereochemical Results in the Base Hydrolysis of *cis*-$[Co(en)_2LX]^{n+}$ Assuming the Mechanism Shown in Figure 1

L	X	% B	% retention for B[a]
OH	Cl	50	26
OH	Br	60	. .
Cl	Cl	34	53
Cl	Br	26	. .
Br	Cl	40	. .
N_3	Cl	44	. .
NCS	Cl	16	~0
NH_3	Cl	33	27
NO_2	Cl	64	69

[a] % inversion is 100% − % retention. If B became symmetric, each of these figures would be 50%.

in Table II for % retention by B were accumulated. A second rule that must be obeyed for base hydrolysis reactions through structures A and B is that *the % retention of configuration by a cis substrate must be greater than or equal to the % of intermediate A times the fraction of cis product from A.*[6] This rule is followed except for $[Co(en)_2NCSCl]^+$, where changes of only 2% in the various products, which is within the limit of experimental error, would also bring this system into accord with the rule.

Finally, it should be noted that because B may not be symmetrical, it can provide a path for the reaction of an optically active *cis* substrate to give an optically active product with the inverted configuration. Only two examples of inversion are known,[7] but if conditions can be found to minimize the reaction of an optically active *cis* isomer *via* intermediate A and/or maximize the desired stereospecific attack on B, then inversion should occur.[8]

Acknowledgment.—This research was supported by the U. S. Atomic Energy Commission under Grant COO-1087-90.

[6] Operationally, the fraction of A is given by the ratio (% *trans* from *cis*)/(% *trans* from *trans*). The % of *cis* from A is equal to the % of *cis* from *trans*.

[7] J. C. Bailar, Jr., and W. Auten, *J. Am. Chem. Soc.*, **56**, 774 (1934); J. C. Bailar, Jr., J. H. Haslom, and E. M. Jones, *ibid.*, **58**, 2226 (1936).

[8] F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *ibid.*, **85**, 1215 (1963); L. J. Boucher, E. Kyuno, and J. C. Bailar, Jr., *ibid.*, **86**, 5716 (1964).

Department of Chemistry
Northwestern University
Evanston, Illinois

Ralph G. Pearson
Fred Basolo

Received June 7, 1965

An Empirical Molecular Orbital Treatment of Tetragonal Ammine Complexes of Cobalt(III)

Sir:

A theoretical treatment of the crystal field model and experimental evidence indicates that the splitting of the $^1T_1$ state for the monoacidopentaammine, CoA_5X, to a good approximation, may be written[1]

$$\begin{aligned} E(^1E^a) - E(^1A_1) &= {}^5/_2(Dq^X - Dq^A) \\ &= {}^1/_4(\Delta^X - \Delta^A) \\ &= {}^1/_4\delta\Delta \end{aligned}$$

This simple result suggests that it should be obtainable from a molecular orbital method, and when expressed in these terms could be considerably more useful.

We have found that the similar empirical molecular orbital treatments of Yamatera[2] and McClure[3] can indeed be recast to obtain this result. McClure's model in its original form focuses attention on the splitting of the one-electron energy levels of CoA_5X. We prefer to refer the splittings to the parent compounds CoA_6 and CoX_6 since chemists commonly think of the ligand field strength as characteristic of a given metal–ligand interaction in a symmetric octahedral arrangement. Furthermore, this technique provides hope that not only splittings, but also band shifts, can be interpreted.

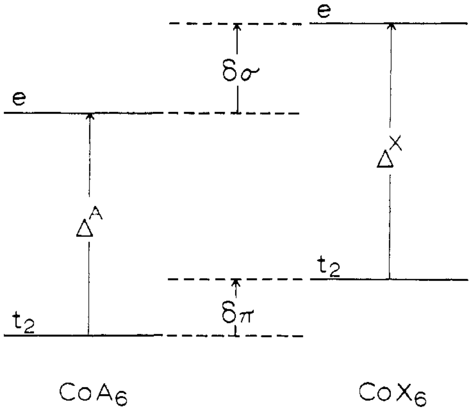

Figure 1.—A qualitative comparison of the splitting of the one-electron d levels for CoA_6 and CoX_6 where ligand X is a stronger σ and π bonder than ligand A. Note that $\delta\Delta = \delta\sigma - \delta\pi$.

The method of calculation follows closely to that of Yamatera. The results can be expressed in terms of three parameters

$$\delta\Delta = \Delta^X - \Delta^A = \delta\sigma - \delta\pi$$

$$\delta\sigma = E(e_g, CoX_6) - E(e_g, CoA_6)$$

$$\delta\pi = E(t_{2g}, CoX_6) - E(t_{2g}, CoA_6)$$

whose significance is illustrated in Figure 1.[4] Clearly, one of these is redundant. Therefore, we have chosen to express our results in terms of δΔ and δπ since the former is readily available[1] and the latter should be the smaller effect. The energies of the singlet states are then

$$E(^1E^a) - E(^1A_1) = E(^1T_1, CoA_6) + {}^1/_4\delta\Delta$$

$$E(^1A_2) - E(^1A_1) = E(^1T_1, CoA_6)$$

$$E(^1E^b) - E(^1A_1) = E(^1T_2, CoA_6) + {}^1/_{12}\delta\Delta - {}^1/_6\delta\pi$$

$$E(^1B_2) - E(^1A_1) = E(^1T_2, CoA_6) + {}^1/_3\delta\Delta + {}^1/_3\delta\pi$$

---

[1] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

[2] H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

[3] D. S. McClure, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 498.

[4] Note that as we have defined δπ it has the opposite sign to that of Yamatera.