

TABLE II  
CALCULATED STEREOCHEMICAL RESULTS IN THE BASE  
HYDROLYSIS OF *cis*-[Co(en)<sub>2</sub>LX]<sup>n+</sup> ASSUMING THE  
MECHANISM SHOWN IN FIGURE 1

L	X	% B	% retention for B <sup>a</sup>
OH	Cl	50	26
OH	Br	60	..
Cl	Cl	34	53
Cl	Br	26	..
Br	Cl	40	..
N <sub>3</sub>	Cl	44	..
NCS	Cl	16	~0
NH <sub>3</sub>	Cl	33	27
NO <sub>2</sub>	Cl	64	69

<sup>a</sup> % 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.<sup>6</sup> This rule is followed except for [Co(en)<sub>2</sub>NCSCl]<sup>+</sup>, 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,<sup>7</sup> 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.<sup>8</sup>

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(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).

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## 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 <sup>1</sup>T<sub>1</sub> state for the monoacidopentaammine, CoA<sub>5</sub>X, to a good approximation, may be written<sup>1</sup>

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

$$\begin{aligned} E(^1E^a) - E(^1A_1) &= \frac{5}{2}(Dq^X - Dq^A) \\ &= \frac{1}{4}(\Delta^X - \Delta^A) \\ &= \frac{1}{4}\delta\Delta \end{aligned}$$

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<sup>2</sup> and McClure<sup>3</sup> 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<sub>5</sub>X. We prefer to refer the splittings to the parent compounds CoA<sub>6</sub> and CoX<sub>6</sub> since chemists commonly think of the ligand field strength as characteristic of a given metal-

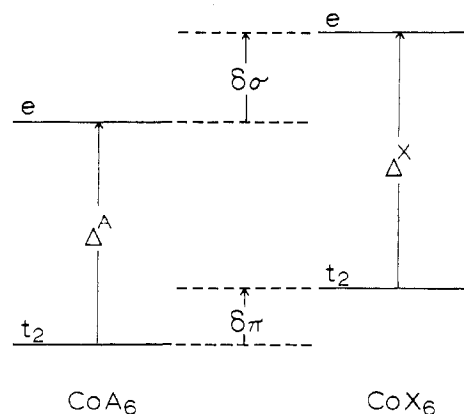


Figure 1.—A qualitative comparison of the splitting of the one-electron d levels for CoA<sub>6</sub> and CoX<sub>6</sub> where ligand X is a stronger  $\sigma$  and  $\pi$  bond than ligand A. Note that  $\delta\Delta = \delta\sigma - \delta\pi$ .

ligand interaction in a symmetric octahedral arrangement. Furthermore, this technique provides hope that not only splittings, but also band shifts, can be interpreted.

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

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

$$\delta\sigma = E(e_g, \text{CoX}_6) - E(e_g, \text{CoA}_6)$$

$$\delta\pi = E(t_{2g}, \text{CoX}_6) - E(t_{2g}, \text{CoA}_6)$$

whose significance is illustrated in Figure 1.<sup>4</sup> Clearly, one of these is redundant. Therefore, we have chosen to express our results in terms of  $\delta\Delta$  and  $\delta\pi$  since the former is readily available<sup>1</sup> and the latter should be the smaller effect. The energies of the singlet states are then

$$E(^1E^a) - E(^1A_1) = E(^1T_1, \text{CoA}_6) + \frac{1}{4}\delta\Delta$$

$$E(^1A_2) - E(^1A_1) = E(^1T_1, \text{CoA}_6)$$

$$E(^1E^b) - E(^1A_1) = E(^1T_2, \text{CoA}_6) + \frac{1}{12}\delta\Delta - \frac{1}{6}\delta\pi$$

$$E(^1B_2) - E(^1A_1) = E(^1T_2, \text{CoA}_6) + \frac{1}{3}\delta\Delta + \frac{1}{3}\delta\pi$$

(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  $\delta\pi$  it has the opposite sign to that of Yamatera.

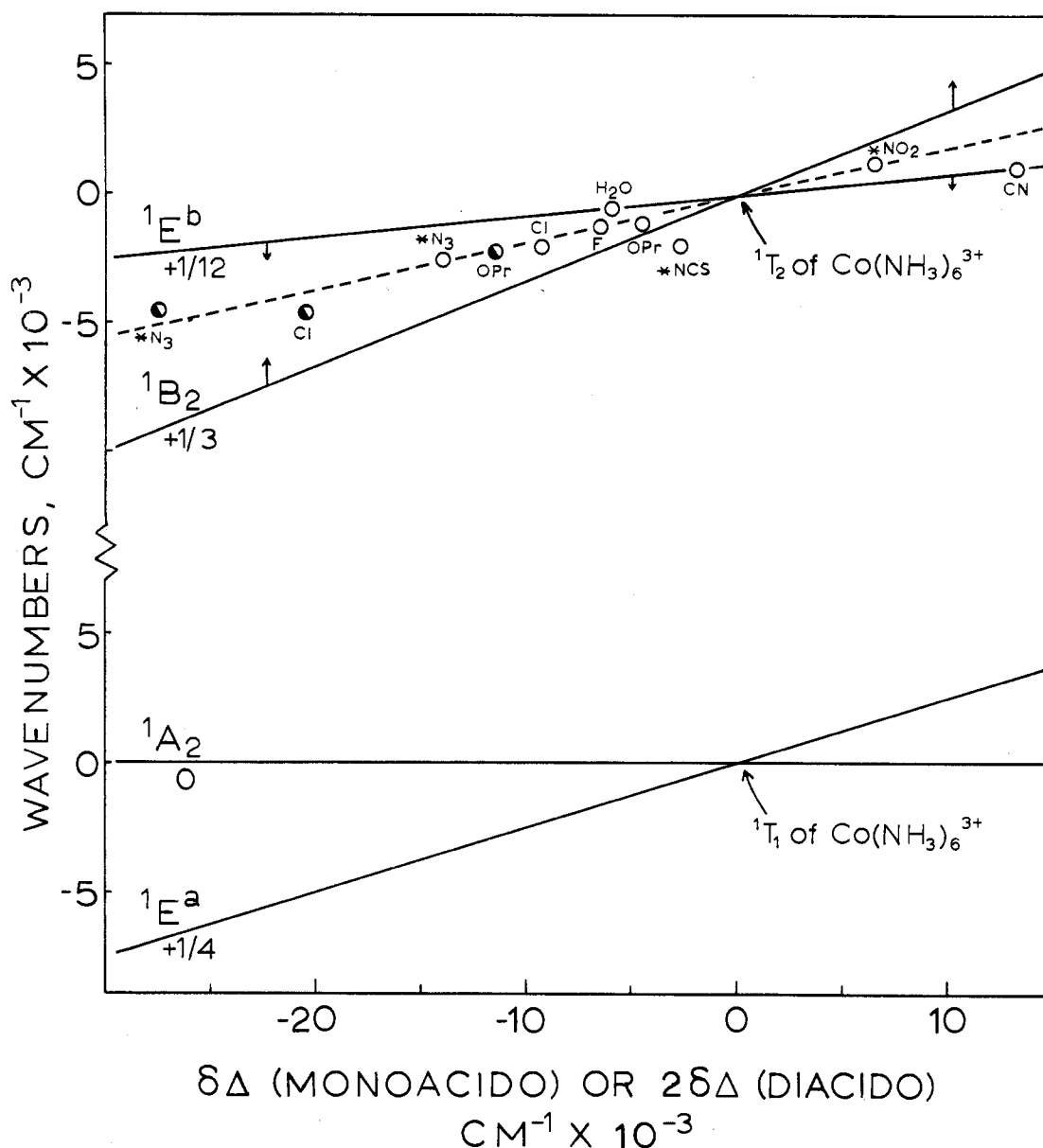


Figure 2.—The splitting of the tetragonal states of monoacidopentaamminecobalt(III) and diacidotetraamminecobalt(III) as a function of  $\delta\Delta$  with  $\delta\pi = 0$ . The effect of the  $\delta\pi$  contribution is indicated by the arrows. The values of  $\delta\Delta$  were taken from the splitting of the  ${}^1T_1$  band.<sup>1</sup> The open circles represent the band maxima of the  ${}^1T_2$  band for monoacidopentaammines while the half-filled circles are those for the diacidotetraammines. The asterisks indicate that this band appears as a poorly resolved shoulder. The dashed line indicates the linear dependence of the  ${}^1T_2$  band maximum *vs.*  $\delta\Delta$  followed by most of these compounds. All data are taken from references given previously.<sup>1</sup>

where we have assumed that the contribution to the energy from interelectronic mutual repulsions remains essentially unchanged in  $\text{CoA}_5\text{X}$ , which is an excellent approximation.<sup>1</sup> Furthermore, an analogous treatment of *trans*- $\text{CoA}_4\text{X}_2$  shows that it is only necessary to multiply all contributions of  $\delta\Delta$  and  $\delta\pi$  by 2, in agreement with Yamatera and McClure. The results are plotted in Figure 2 as a function of  $\delta\Delta$  with  $\delta\pi = 0$ . The  $\delta\pi$  contribution to the splitting of the  ${}^1E^b$  and  ${}^1B_2$  states is indicated by the arrows.

We turn our attention to the shifting of band II with respect to the same band for  $\text{Co}(\text{NH}_3)_6^{3+}$ . We previously have shown that with  $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$  a decrease in wave numbers is caused by the tetragonal perturba-

tion and not unexpectedly large changes in the mutual repulsion parameters. In Figure 2 we illustrate that the difference in energies for a wide range of tetragonal ammine complexes is very nearly linearly related to  $\delta\Delta$  for  $\text{Co}(\text{NH}_3)_5\text{X}$  and  $2\delta\Delta$  for *trans*- $\text{Co}(\text{NH}_3)_4\text{X}_2$ . It is interesting to note when  $\delta\Delta < 0$  the effect of the  $\delta\pi$  contribution will be to decrease the energy difference between these states and perhaps give rise to an unresolved band in the spectra,<sup>1,2</sup> which seems to be the case with all known complexes although the onset of charge transfer hampers a clear interpretation in many instances. The linear relation between the band position and  $\delta\Delta$ , however, indicates that the splitting of the  ${}^1E^b$  and  ${}^1B_2$  states is small for all of these cases, *i.e.*,  $\delta\pi$  must be ap-

preciable, and that not only  $\delta\Delta$ , but  $\delta\pi$ , varies monotonically throughout this region of the spectrochemical series, which is not unreasonable.

When  $\delta\Delta > 0$ , as with  $\text{NO}_2^-$  and  $\text{CN}^-$ , the effect of the  $\delta\pi$  contribution ought to increase the separation between the states in question. The value for  $\text{NO}_2^-$  remains linear with  $\delta\Delta$ , indicating that the  $\delta\pi$  contribution must be small. However, with  $\text{CN}^-$  the linear relation is no longer observed. In fact, the observed band maximum at  $30,600 \text{ cm.}^{-1}$  is at just the predicted wave number for the  ${}^1\text{E}^b$  state when  $\delta\pi = 0$ . The transition  ${}^1\text{A}_1 \rightarrow {}^1\text{B}_2$  is then expected at about  $34,000 \text{ cm.}^{-1}$ . From the solution spectra, the separation of the maximum of band II from the onset of transfer is about  $10,000 \text{ cm.}^{-1}$  with no indication of another band within this interval. We conclude that (1) the split component  ${}^1\text{B}_2$  must be of very low intensity and be

buried in the high energy tail of the observed band and (2)  $\delta\pi$  must be very close to zero. In support of this argument, a recent e.s.r. study<sup>5</sup> of  $\text{Cr}(\text{CN})_6^{3-}$  indicated that the  $t_{2g}$  set is only slightly antibonding.

The energies and splittings which we have presented also apply to the split components of the  ${}^4\text{T}_1$  and  ${}^4\text{T}_2$  states for  $\text{Cr}(\text{III})$  and those of the  ${}^3\text{T}_2$  and low energy  ${}^3\text{T}_1$  for  $\text{Ni}(\text{II})$ .

(5) H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, **41**, 3802 (1964).

(6) (a) Fellow of the Alfred P. Sloan Foundation. (b) The financial support of the National Science Foundation and Alfred P. Sloan Foundation is gratefully acknowledged. We thank E. I. du Pont de Nemours and Co., Inc., for a grant-in-aid.

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## Book Review

**Molecular Orbital Theory.** By C. J. BALLHAUSEN and HARRY B. GRAY. W. A. Benjamin, Inc., New York, N. Y. 1964. ix + 273 pp.  $16 \times 23.5 \text{ cm.}$  \$9.00 (clothbound); \$4.95 (paperback).

This is another Benjamin quasi-book, with some 135 pages of text and a skimpy reprint collection of 130 pages (R. G. Parr's "Quantum Theory of Molecular Electronic Structure" by the same publisher contains 340 pages of reprint + 160 of text). Of the twelve reprints, three are by the authors, and four, one each by Mulliken and co-workers and Van Vleck and two by Walsh, are extremely important. The text itself is a rather good introduction to qualitative molecular orbital theory, stressing the importance of symmetry and overlap considerations and eventually directed toward inorganic applications. The spirit of the book is commendable; to quote the final paragraph: "Thus, although we feel it is useful to do simple MO calculations to *help* in interpreting and classifying electronic spectra, it is certainly clear that the calculated MO's must be consistent with a goodly amount of experimental information before they can be taken seriously." The treatment clearly will not appeal to nihilistic purists but it is the only reasonable approach to molecules of some complexity.

The best part of the volume is the discussion of the shapes and spectra of diatomics, triatomics, and some small molecules. Less satisfactory is the last chapter, the most detailed, which describes the kind of Wolfsberg-Helmholz calculations the authors do. There are some bad points in earlier chapters. For instance, a figure, (4-3), claims to show an energy diagram for  $\text{Li}_2$  and two Li atoms with and without hybridization. This is clear nonsense; there exist the real energy levels of two Li atoms and those of a  $\text{Li}_2$  molecule. If one wants to look for hybrids *after* one obtains the correct  $\text{Li}_2$  wave function one may do so; but there is nothing real about hybrids interacting. (Perhaps the point should not be stressed; the authors make excellent

and consistent use of MO arguments, and the hybridization chapter is mercifully short.) Throughout the book there are representations of p and d orbitals which purport to be "boundary surfaces" but which are the end products of artistic license applied to polar diagrams. I wish to recommend in this respect a beautiful extended article in a source probably not familiar to inorganic chemists: C. A. Coulson and E. T. Stewart in "The Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964. Or perhaps Benjamin might harness a computer to produce a useful non-book containing contour diagrams of atomic and molecular orbitals in various stages of approximation.

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### BOOKS RECEIVED

August 1965

- RONALD RICH. "Periodic Correlations." W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1965. v + 159 pp. \$8.00.
- WILLIAM L. JOLLY, Editor. "Preparative Inorganic Reactions." Volume 2. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1965. vii + 378 pp. \$14.50.
- GEORGE G. LIBOWITZ. "Solid-State Chemistry of Binary Metal Hydrides." W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1965. v + 139 pp. \$7.25.
- TIBOR S. LASZIO. "Image Furnace Techniques." Technique of Inorganic Chemistry, Volume V. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1965. v + 195 pp. \$12.00.