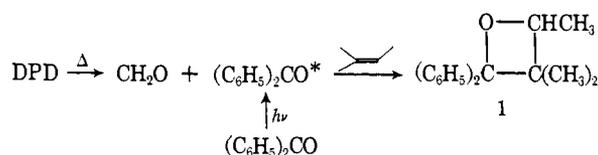


seen from Table I, α shows little variation with a tenfold change in *t*-S concentration as would be anticipated from this approximation. Also variation in the initial concentration of DPD indicates that at these low concentrations of dioxetane, induced decomposition of DPD by excited state species^{1n,x} is unimportant.

Based on a Boltzmann distribution of excitation energy^{1d,9} between benzophenone and formaldehyde, it is expected that excited state benzophenone should be produced almost exclusively from DPD. To assess this potential model, DPD ($1.9 \times 10^{-2} M$) was decomposed with 0.946 *M* 2-methyl-2-butene in degassed benzene to give $\Phi_{\text{A,DPD}} \cong 0.5 \times 10^{-2}$ (millimoles of **1** produced/millimoles of DPD decomposed) for **1** (Scheme II). The quantum yield for production of **1**

Scheme II



from 0.300 *M* benzophenone with 0.946 *M* 2-methyl-2-butene in degassed benzene, relative to 0.100 *M* benzophenone and 0.500 *M* benzhydrol actinometer in degassed benzene ($\Phi_{\text{Act}} = 0.91$),¹⁴ is 0.22.¹⁵ Assuming Φ_{ET} is unity, which is well approximated for stilbene isomerization, α is calculated from eq 1 to be approximately 2% for production of excited state benzophenone from DPD.

Considering experimental error, there is probably no significant difference between the total efficiency of excited state carbonyl formation and the production of excited state benzophenone, which would be in accordance with the Boltzmann distribution of excitation energy.¹⁸ Anomalous quenchers of excited state carbonyl products from DPD, to give low α values, are unlikely. The relative quantum yield for the formation of **1** from authentic reactants and from a decomposed sample of DPD with 2-methyl-2-butene is approximately unity in degassed benzene solutions. It is also unlikely that there is a "hidden" excitation of formaldehyde in the decomposition of DPD. The lifetime of triplet formaldehyde in the gas phase is estimated to be

(9) Triplet energies for benzophenone in solution and formaldehyde in the gas phase are reported to be 69¹⁰ and 72.5¹¹ kcal/mol, respectively. The corresponding singlet (S₁) energies are 74¹² and 81¹³ kcal/mol, respectively.

(10) P. S. Engel and B. M. Monroe, *Advan. Photochem.*, **8**, 245 (1971).

(11) G. W. Robinson and V. E. DiGiorgio, *Can. J. Chem.*, **36**, 31 (1958).

(12) Reference 6, p 78.

(13) J. C. D. Brand, *J. Chem. Soc.*, 858 (1956).

(14) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962).

(15) The minor isomer of **1**, 2,2-diphenyl-3,4,4-trimethyloxetane (**2**), is formed with a quantum yield of 0.032. Analyses for both of these isomers were performed by glc (3% SE-30 on Varaport-30, 5 ft \times 1/8 in., 130°, flow 30 ml H₂/min, FID; *t_r*(min) **1** (8.0) and **2** (6.4). Irradiations were performed with a 100-W medium-pressure Hanovia lamp on a merry-go-round¹⁶ with a potassium dichromate-carbonate filter solution to isolate the 302.5–313.0-nm region.¹⁷

(16) R. S. N. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

(17) P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 7480 (1972).

(18) Although the Boltzmann energy distribution model is consistent with the data, only the final energy distribution between the carbonyl products can be evaluated. It is possible that energy transfer between the carbonyl products in the solvent cage could occur so that the initial and final energy distribution is not the same.

10^{-8} to 10^{-9} sec.¹⁹ Considering eq 2, it should be possible to effect energy transfer from excited state formaldehyde to *t*-S at the quencher concentrations that were employed (Table I). Furthermore, when DPD was decomposed in toluene the expected "photoreduction" products of excited state formaldehyde, methanol, and ethylene glycol were not observed. Finally, the type I products from excited state formaldehyde, carbon monoxide, and hydrogen^{19,20} were not observed from the decomposition of DPD in degassed benzene. We are actively pursuing the effect of structure on α and on the distribution of excitation energy between two dissimilar carbonyl products for other substituted 1,2-dioxetanes.

Acknowledgments. We thank the Army Research Office (Durham) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(19) B. A. DeGraff and J. G. Calvert, *J. Amer. Chem. Soc.*, **89**, 2247 (1967).

(20) S. G. Thomas, Jr., and W. A. Guillory, *J. Phys. Chem.*, **77**, 2469 (1973).

William H. Richardson,* Frederick C. Montgomery
Mary B. Yelvington, Gregory Ranney

Department of Chemistry, San Diego State University
San Diego, California 92115

Received January 17, 1974

The Relationship between Metal-Donor Distance and Ring Size in Macrocyclic Complexes

Sir:

The significance of macrocyclic ligands and their metal complexes is most obvious as it relates to such natural products as the metalloporphyrins, vitamin B₁₂, and chlorophyll; however, other special aspects of such ligands have been found which will doubtless lead to a continued growth in the importance of these structurally distinctive materials.¹⁻³ The relationship between the size of the metal ion and the opening in the middle of the ring clearly must be important, because, for example, the iron porphyrins involve a 16-membered ring while the cobalt in vitamin B₁₂ occupies a 15-membered ring. Also, Pedersen's cyclic polyfunctional ethers show sharp selectivities toward alkali metal ions as a function of ring size.⁴ Early observations on complexes with substituted 14-membered tetraaza macrocyclic ligands led to the suggestion that a constrictive effect might be responsible for their surprisingly large ligand field strengths.⁵ We wish to report a quantitative assessment of the metal ion ring size relationship that is both experimental and theoretical in origin. We have demonstrated that there is an ideal ring size for any metal ion having a given metal-donor atom distance and that ring sizes slightly smaller (0.1–0.2 Å in terms of M–N distance) than the best fit ring show abnormally strong metal-donor bonds while

(1) D. H. Busch, K. Farmery, V. L. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, No. 100, 44 (1971).

(2) J. J. Christenson, J. O. Hill, and R. M. Izatt, *Science*, **174**, 459 (1971).

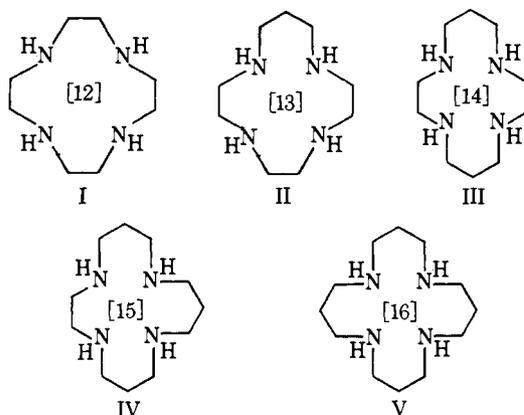
(3) J. M. Lehn, *Struct. Bonding (Berlin)*, **16**, 69 (1973).

(4) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 386, 391 (1970).

(5) D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, No. 100, 60 (1971).

rings that are slightly oversized show substantially decreased metal-donor interactions. It has previously been realized that in cases where the mismatch in size is more extreme, distortions from square planar coordination occur, common distortions being ring folding to form cis-octahedral⁶ structures, ring folding to form trigonal bipyramidal structures,⁷ and extrusion of the metal ion from the donor atom plane to form a tetragonal pyramidal structure.⁸

The ideal ligands for the demonstration of these newly realized relationships are a series of unsubstituted, fully saturated, cyclic, tetraaza hydrocarbons such as those given in structures I-V below. We have synthesized the new members of this series by modifications of the method used by Koyama and Yoshino⁹ in the preparation of a related series of cyclic triaza ligands. Characterization: II, mass spectrum m/e



186; mp 40–41°; nmr (MH100, CDCl₃-TMS) δ 1.68 (quintet, 2 H, $J \sim 6$ Hz), 2.20 (s, 4 H), 2.78 (complex multiplet, 16 H); overall yield 58%. IV, m/e 214; mp 98–99°; nmr δ 1.71 (quintet, 6 H, $J \sim 6$ Hz), 1.94 (s, 4 H), 2.74 (complex multiplet, 16 H); overall yield 56%. V, m/e 228; mp 82–83°; nmr δ 1.70 (quintet, 8 H, $J \sim 6$ Hz), 1.82 (s, 4 H), 2.72 (triplet, 16 H, $J \sim 6$ Hz); overall yield 54%. Compositions were verified by analysis of ligand or its metal-ion derivatives. Cyclam (III) and cyclen (I) have, of course, been known for a long time.^{10–12} The ligands are identified here by their systematic abbreviations.¹³

The complexes of cobalt(III) and nickel(II) have been prepared and characterized by common methods and their electronic spectra have been measured in solution at room temperature and in solid mulls at room temperature and at the boiling point of liquid nitrogen. The values for the ligand field parameter Dq^{2v} appropriate to the square planar coordinated macrocyclic ligands^{14,15} are given in Table I, along with values for the unconstrained reference ligand ethylenediamine. The

(6) J. P. Collman and P. W. Schneider, *Inorg. Chem.*, **5**, 1380 (1966).
(7) V. L. Goedken, J. Molin-Case, and G. G. Christoph, *Inorg. Chem.*, **12**, 2894 (1973).

(8) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Amer. Chem. Soc.*, **87**, 2312 (1965).

(9) H. Koyama and T. Yoshino, *Bull. Chem. Soc. Jap.*, **45**, 481 (1972).

(10) J. van Alphen, *Recl. Trav. Chim. Pays-Bas*, **56**, 343 (1937).

(11) K. H. Mayer and H. Stetter, *Chem. Ber.*, **94**, 1410 (1961).

(12) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).

(13) J. C. Dabrowiak, P. H. Merrell, and D. H. Busch, *Inorg. Chem.*, **11**, 1979 (1972).

(14) Details of the calculations for Ni complexes are contained in R. Sperati, Thesis, The Ohio State University.

(15) Calculations for Co complexes are based on R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

Table I. Ligand Field Splitting Parameter for *trans*-Diacidotetraammine Complexes of [Co([13–16]aneN₄)Cl₂]⁺ and [Ni([13–16]aneN₄)Cl₂]

Ligand	Dq^{2v} , cm ⁻¹	
	Co ³⁺	Ni ²⁺
[13]aneN ₄	2750	<i>b</i>
[14]aneN ₄	2480 ^a	1480 ^c
[15]aneN ₄	2360	1250
[16]aneN ₄	2250	1110
en	2530 ^a	
Me ₂ en		1215 ^d

^a N. Sadasivan, J. A. Kernohan, and J. T. Endicott, *Inorg. Chem.*, **6**, 770 (1967). ^b Ligand folds on metal producing cis complex. ^c R. C. Sperati, Ph.D. Thesis, 1971. ^d D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **7**, 795 (1968).

Co(III) derivative of the 14-membered ring shows very nearly the same Dq value as the reference ligand (en). We believe that this occurs because the normal Co(III)-N distance is most easily accommodated by this ring size in the case of the fully saturated macrocycles. Note also that the Ni(II) derivative of the 15-membered ring exhibits a Dq value very close to that of the unconstrained reference ligand. This is to be expected since high spin Ni(II)-N distances are generally about 0.1 Å greater than Co(III)-N distances. We return to this point below.

Dq values for both Co(III) and Ni(II) deviate from the unconstrained values as ring size either exceeds or falls below the *best fit* value. This is a consequence of the effects of increased strain energy on the metal-ligand bonds as demonstrated by our calculations.

Our calculation scheme and minimization technique¹⁶ are analogous to those employed recently by others.^{17,18} In order to estimate the optimal M-N bond distance we began with a planar trial structure having a four-coordinate metal ion in the center of the ring. The M-N stretching force constant was then set to 0.0 mdyn/Å so that the M-N bond length would be determined solely by the various other strain energy requirements of the macrocyclic ligand. In effect this permits the determination of the minimum energy conformation of the ligand in the correct stereochemistry for approximately planar chelation but with no metal ion present. The minimized strain energy terms for these calculations are given in Table II. The specific

Table II. Minimized Strain Energies for the "Free" Macrocycles

Ring size	<i>R</i>	<i>NB</i>	θ	ϕ	<i>H</i>
[12]	0.52	-1.70	6.75	3.04	8.61
[13]	0.67	-1.94	4.47	3.52	6.72
[14]	0.81	-0.79	3.68	1.36	5.06
[15]	0.98	0.10	4.85	3.20	9.12
[16]	1.17	1.05	5.71	5.71	13.63

conformations used were: [12]aneN₄, $\delta\lambda\delta\lambda$; [13]aneN₄, $\delta\lambda\delta\lambda$; [14]aneN₄, $\delta\gamma\lambda\gamma$; [15]aneN₄, $\delta\gamma\lambda\gamma$; [16]aneN₄, $\delta\gamma\lambda\gamma$, where δ and λ refer to chiralities while γ indicates a chair form six-membered ring. Although the matter has not been explored thoroughly for

(16) L. J. DeHayes and D. H. Busch, *Inorg. Chem.*, **12**, 1505, 2010 (1973).

(17) R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968).

(18) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3617 (1970).

15- and 16-membered rings, these are presumed to be the lowest energy conformations.

We find a minimum in strain energy for the 14-membered ring. The greater strain energies of the 12- and 16-membered rings parallel the observed resistance of these rings toward coordination in a planar fashion.^{6,19}

For a given size of macrocyclic ligand of this class, the idealized metal-nitrogen distance calculated by this method represents the hole size for which the strain energy in the ligand is at a minimum. A metal ion having this ideal M-N distance would chelate with minimum strain of the macrocyclic ligand. A larger or smaller metal ion would require readjustment of the M-N distance and an attendant increase in the strain energy of the ligand. The ideal metal-nitrogen bond distances calculated according to this scheme are given in Table III. Most transition metal-nitrogen linkages

Table III. Ideal Metal-Nitrogen Bond Lengths and Planarity of the Macrocyclic Ligands

Ring size	Average ideal bond length (Å)	Average deviation from the ideal N ₄ plane (Å)
[12]	1.83	0.41
[13]	1.92	0.12
[14]	2.07	0.00
[15]	2.22	0.14
[16]	2.38	0.00

fall within the 1.8–2.4 Å range spanned by the idealized values given in Table III, but the most distinctive feature of this data is the regular increase in ideal M-N distance as the number of ring members increases. This amounts to some 0.1–0.15 Å increase in M-N distance for each ring member added. Immediate significance is found in the fact that the metal ions for which we have experimental data (Co(III) and Ni(II)) differ in their M-N distances by just the amount calculated for best fits in rings that differ by one member. That is, the Co-N distance in Co(en)₃³⁺ is 2.00 Å, while the range of Co-N distances for many Co(III) complexes is 1.94–2.03 Å.²⁰ The larger high spin Ni(II) ion has a Ni-N distance of 2.12 Å in Ni(en)₃²⁺,²¹ and the difference of 0.1–0.15 Å between the Co(III)-N and Ni(II)-N distances is general. Thus our calculational model predicts that if the 14-membered ring provides the best fit for Co(III), the 15-membered ring will fit high spin Ni(II) best. It is apparent that the data of Table III can be used to make predictions in many other cases. The close correspondence between prediction and observation for the metal ions we have studied establishes the conformational strain energy as the source of the effects we have described.

A very important aspect of these results is the irrefutable demonstration that mechanical constraint, of molecular origin, on the metal-donor distance can have a profound effect on the strength of the metal-donor interaction. Thus, the rings that are smaller than those that fit best exert abnormally high *Dq* values for the given donor atoms because the distribution of strain energy over the whole complex results in shortening

(19) E. K. Barefield and D. H. Busch, *Inorg. Chem.*, **10**, 1216 (1971).

(20) Y. Saito, "Spectroscopy and Structure of Metal Chelate Compounds," K. Nakamoto and P. J. McCarthy, Ed., Wiley, New York, N. Y., 1968.

(21) L. N. Swink and M. Atoji, *Acta Crystallogr.*, **13**, 639 (1960).

the metal-donor distance. Similarly oversized rings result in markedly low ligand field strengths. In consequence, we caution against the easy assumption that the properties of a given metal-donor linkage are insensitive to the detailed structure of the ligand. It is possible that such mechanical effects may be used in natural systems to alter metal-donor interactions under appropriate conditions, e.g., by changes in the tertiary structure of a protein. An effect of mechanical pressure on ligand field strength has been found in spectroscopic studies on samples under very high pressure.²²

Acknowledgment. The financial support of the National Science Foundation is gratefully acknowledged.

(22) H. G. Drickamer, *Comments Solid State Phys.*, **3**, 53 (1970).

Ludmila Y. Martin, Louis J. DeHayes
Leverett J. Zompa, Daryle H. Busch*

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received February 21, 1974

Stereoelectronic Properties and Reactivity of the Tetrahedral Intermediate in Amide Hydrolysis. Nonempirical Study of Aminodihydroxymethane and Relation to Enzyme Catalysis

Sir:

We wish to report that an *ab initio* quantum chemical study of aminodihydroxymethane provides theoretical evidence for the operation of marked stereoelectronic effects on the properties of this species. Taking CH(OH)₂NH₂ as a model of the tetrahedral intermediate in amide hydrolysis, the results give insight into the conformational requirements for optimal reactivity and selectivity in this chemically and biologically most important reaction.

Recent experimental results led to the proposal that the selective cleavage of tetrahedral intermediates in ester and amide hydrolysis is controlled by trans-anti-periplanar (app) oriented electronic lone pairs.^{1,2} It has also been considered that orientational effects may play an important role in the catalytic configurations of biochemical reactions.^{3–6}

Our previous theoretical work on the hydroxymethanes^{7a} led to a coherent picture of the electronic and structural properties of these model tetrahedral species and of the resulting reactivity patterns in oxygen exchange, ester hydrolysis, and transesterification reactions.

Calculations (same method as in ref 7; see footnote 2 in ref 7b) were performed on the 15 different, fully

(1) P. Deslongchamps, P. Atlani, D. Fréhel, and A. Malaval, *Can. J. Chem.*, **50**, 3405 (1972).

(2) P. Deslongchamps, C. Lebreux and R. Taillefer, *Can. J. Chem.*, **51**, 1665 (1973).

(3) W. J. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969.

(4) M. L. Bender, "Mechanisms of Homogeneous Catalysis from Protons to Proteins," Wiley-Interscience, New York, N. Y., 1971.

(5) R. Henderson and J. H. Wang, *Ann. Rev. Biophys. Bioeng.*, **1**, 1 (1972).

(6) D. R. Storm and D. E. Koshland, Jr., *J. Amer. Chem. Soc.*, **94**, 5815 (1972); A. Dafforn and D. E. Koshland, Jr. *Biochem. Biophys. Res. Commun.*, **52**, 779 (1973) and references therein.

(7) (a) J. M. Lehn, G. Wipff, and H. B. Bürgi, *Helv. Chim. Acta*, **57**, 493 (1974); (b) H. B. Bürgi, J. M. Lehn, and G. Wipff, *J. Amer. Chem. Soc.*, **96**, 1956 (1974).