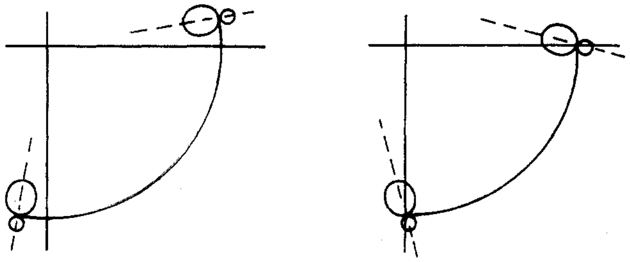
Stereochemistry of Tris(ethylenediamine)-copper(II) and Models for the Optical Activity of Tris(ethylenediamine)metal Ions[1,2]

Sir:

Several models have been proposed for the optical activity of metal tris(ethylenediamine) complexes. The predominant 3d character of the chromophoric electrons must be modified by introduction of some dissymmetry. We have focused attention on the six nitrogen nuclei in the first coordination sphere and proposed that these are displaced from octahedral points so as to have D_3 symmetry. Then we have adopted an ionic model[3,4] and more recently a molecular orbital model[5] in which the nitrogen σ-orbital directed toward the metal ion interacts with the $3d_\sigma$ orbitals (model I). Liehr[6a] has used a molecular orbital model with undisplaced nitrogens but with nitrogen σ-orbitals canted to the metal–nitrogen internuclear axis (model II). These models are illustrated in Figure 1. As an illustration of this second model Liehr calculated the dipole and rotational strengths for the transition E → T_2 of optically active $Cu(en)_3^{2+}$ ion.[6b] We here report some experimental results and theoretical calculations on this cation and then discuss the two models.



Displaced ligand model

Bent orbital model

Figure 1.—Models for the metal–ethylenediamine cycle.

We have measured the spectrum of $Cu(en)_3^{2+}$ ion diluted in the hexagonal crystal $Zn(en)_3(NO_3)_2$[7] with light polarized with respect to the C_3 molecular axis. The measured decadic extinction coefficients are 15 ($\epsilon_\parallel$) and 19 ($\epsilon_\perp$) ± 5 in units of M^{-1} cm.$^{-1}$ at the band maximum of 15,400 cm.$^{-1}$. This is to be compared with the extinction in pure ethylenediamine solution of 114 M^{-1} cm.$^{-1}$ at 16,500 cm.$^{-1}$. In the crystal the molecule is constrained to adopt D_3 symmetry at the zinc atom site[7]; this idea is confirmed by the fact that this ion does have undistorted D_3 symmetry in the pure crystal $Cu(en)_3SO_4$[8] despite the strong Jahn–Teller forces. However, the solution results can be understood only in terms of a highly distorted configuration probably involving complete dissociation of an amino group of one ethylenediamine molecule as has been postulated by Bjerrum and Nielson[9] on the basis of formation constants and comparison of the spectrum to pentaamminecopper(II) ion. From these results and the well-known lability of $Cu(en)_3^{2+}$ it is certain that it will not be possible to resolve this ion and measure its optical activity as a D_3 species in solution.

Although we cannot test the proposed models with experimental rotational strengths, we can use the dipole strengths or related transition moment lengths q_0, q_1, and q_2 previously defined[5] for one-electron transitions. In Table I we give experimental results and some theoretical calculations on the two models.

TABLE I

TRANSITION MOMENT LENGTHS. ABSOLUTE VALUES IN mÅ.

	Model I	Model II	Exptl.
q_1	6.6	0.09	13
$(q_0^2 + q_2^2)^{1/2}$	7.4	0.16	20

Liehr's calculation, illustrative of his model (Table I, model II), was carried out with nitrogen atoms at octahedral points 2.00 Å. from the copper and with a 5° cant of the σ-orbitals.[6] However, the crystal structure[8] of $Cu(en)_3SO_4$ proves there are sizable distortions from "octahedral" symmetry: a cartesian displacement of each nitrogen atom of 0.20 Å. in the plane of the chelate so as to expand the N–Cu–N angle and a smaller displacement 0.047 A. perpendicular to this plane; the experimental Cu–N bond distance is 2.17 Å. In order to facilitate comparisons we have adopted Liehr's bond distance, his orbital parameters, and a nitrogen displacement of 0.20 Å. in the chelate plane in calculating q values with our model (Table I, model I).

It is seen that model II gives very small transition moments as compared to those of model I which are in fair accord with experiment.[10] Increasing the angle of orbital cant to 15° in model II will triple these values. However, such a large angle is highly unlikely inasmuch as the experimental Cu–N–C angle[8] is close to tetrahedral (107°) and therefore essentially unstrained. We conclude that in the case of $Cu(en)_3^{2+}$ the contribution of the displaced ligands to the transition moment lengths and of course the rotational strength will be an order of magnitude greater while the contribution to the extinction coefficients will be two orders of magnitude greater than those of any possible bent orbitals.

---

(1) Supported by The National Science Foundation.

(2) Taken in part from the Ph.D. thesis of A. G. Karipides, University of Illinois, 1964.

(3) T. S. Piper and A. G. Karipides, *Mol. Phys.*, **5**, 475 (1962).

(4) A further study of the ionic model: M. Shinada, *J. Phys. Soc. Japan*, **19**, 1607 (1964).

(5) A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).

(6) (a) A. D. Liehr, *J. Phys. Chem.*, **68**, 665 (1964). (b) The octahedral disposition of the ligand nuclei is not a necessary part of his theory of "misdirected" orbitals but it was chosen for simplicity in the calculations. In his recent paper on lower symmetry complexes, *J. Phys. Chem.*, **68**, 3629 (1964), he points out in qualitative terms that relaxation of this pseudo-octahedrality will lead to enhanced electric dipole transition moments.

(7) This compound is isomorphous to $Ni(en)_3(NO_3)_2$, the crystal structure of which has been determined by L. N. Swink and M. Atoji, *Acta Cryst.*, **13**, 639 (1959).

(8) M. Cola, G. Giuseppetti, and F. Mazzi, *Atti Accad. Sci. Torino*, **96**, 381 (1962).

(9) J. Bjerrum and E. J. Nielson, *Acta Chem. Scand.*, **2**, 297 (1948).

(10) The question remains as to what fraction of the q values calculated from experimental intensities is to be ascribed to vibronic intensity. Reference 2 gives evidence that only a moderate fraction may be due to this mechanism.

Further evidence is provided by our experimental results[5] on $(-)$-Co(en)$_3{}^{3+}$. We have shown that the only q value sets $(q_0:q_1:q_2)$ which are consistent with experiment are $+2.8:+25:+45$ or $-45:+25:-2.8$ in mÅ. Our interpretation of the optical activity of the near-ultraviolet band provides reason to give strong preference to the first set. Our molecular orbital model gives $+1.3:+8.2:+10.0$[2] in mÅ. and our ionic model gives the relative values $+1:+3:+4$, whereas the bent orbital model gives the relative values $-2.34:+1.34:-1.00$[6] (these values calculated for Cu(en)$_3{}^{2+}$; corresponding values for cobalt are not available but their ratios would not differ appreciably from those for the copper). These comparisons lend further support to the idea of displaced ligands.

One serious problem remains for the model of displaced ligands. In order to fit the absolute sign of the optical activity we have had to assume an expansion of the N–Co–N bond angle. The experimental results indicate that in Co(en)$_3{}^{3+}$ this bond angle is very close to 90°,[11] and indeed the whole ring is quite strain free.[12] Further, if there is any slight distortion of the bond angle it seems more likely to be a contraction. Thus our model appears to give the incorrect absolute sign. However, it should be borne in mind that only very small distortions are required and the available crystal structures do not provide bond distances of high accuracy.

---

[11] K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 158 (1957), and earlier papers.

[12] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[13] Fellow of the Alfred P. Sloan Foundation.

Department of Chemistry
University of Illinois
Urbana Illinois

T. S. Piper[13]
A. G. Karipides

Received February 8, 1965

Book Review

Annual Review of Physical Chemistry. Edited by H. Eyring. Volume 15. Annual Reviews, Inc., Palo Alto, Calif. 1964. 15.5 × 22.5 cm. vii + 577 pp. $8.50.

The topics reviewed in the 1964 edition have been selected within the following general areas: (a) *Reaction Kinetics*—"Fast Reactions in Solutions" by G. G. Hammes, "Chemical and Electrochemical Electron-Transfer Theory" by R. A. Marcus; (b) *Properties of Solutions*—"Solutions of Nonelectrolytes" by A. G. Williamson, "Solutions of Electrolytes" by J. N. Agar; (c) *Statistical Mechanics*—"The Theory of Liquids and Dense Gases" by D. Henderson, "Statistical Mechanics—A Selected Review" by I. Oppenheim; (d) *Thermodynamics and Other Macroscopic Properties*—"Cryogenics, Helium Three" by J. G. Daunt and D. O. Edwards, "The Solid State: Intermetallic Compounds" by W. E. Wallace, "Surface Chemistry" by R. L. Burwell, Jr., and J. A. Peri, "High Pressure Chemistry" by S. D. Hamann, "Thermochemistry and Bond Dissociation Energies" by H. A. Skinner; (e) *Spectroscopy and Quantum Theory*—"Electron Spin Resonance" by D. Kivelson and C. Thomson, "Microwave Spectroscopy" by D. R. Lide, Jr., "Quantum Theory of Atoms and Molecules" by Oktay Sinanoğlu and D. Fu-tai Tuan, "Optical Rotation" by D. J. Caldwell and H. Eyring,. "High Resolution Nuclear Magnetic Resonance" by David M. Grant; (f) *Biophysical Chemistry*—"Quantum Processes in Photosynthesis" by G. Wilse Robinson, "Nucleic Acids" by I. Tinoco, Jr., and D. N. Holcomb, "Contractile Process in Fibrous Macromolecules" by L. Mandelkern. All but two of the contributions ("Optical Rotation" and "High Pressure Chemistry") fall in categories which have also been the subject of related articles in the Annual Reviews of Physical Chemistry within the past 5 years. The present contributions, therefore, represent for the most part the most recent developments within the titled fields. Two introductory chapters by W. F. Libby on "Thirty Years of Atomic Chemistry" and "Berkeley Radiochemistry" are also included. The high quality of previous editions of this series is maintained in the present volume.

Department of Chemistry
University of Colorado
Boulder, Colorado 80304

Stanley J. Gill