$\nu C = O$ band near 1740 cm.$^{-1}$. This has not been observed; the most important features of the H$_4$Y spectrum are the presence of a single $\nu C = O$ band near 1690 cm.$^{-1}$, the absence of any νOH band above 2000 cm.$^{-1}$, and the presence of an almost continuous absorption between 1600 and 300 cm.$^{-1}$ on which sharper bands are superimposed. A probable explanation of these features is that there is a symmetrical hydrogen bond of the type
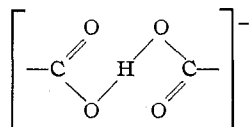
in the H$_4$Y crystal. This centered bond would make the carboxylic and carboxylate groups equivalent, giving rise to a single $\nu C = O$ band, and it would lower the νOH frequency below 2000 cm.$^{-1}$.[11,12] Similar spectra have been observed[11] for acid salts of carboxylic acids of the general formula MH(RCOO)$_2$ containing symmetrical hydrogen bonds, (COOH-OOC)$^-$. The spectrum of KH(CCl$_3$COO)$_2$ shown in Figure 1d is a typical example of a symmetrically hydrogen-bonded acid salt; its most important features are the same as those of H$_4$Y, *i.e.*, a single $\nu C = O$ band, no νOH band above 2000 cm.$^{-1}$, and the broad 1600–400 cm.$^{-1}$ absorption due to symmetrically hydrogen-bonded OH groups.

Ethylenediaminetetraacetic acid is then not a normal acid containing four COOH groups but it should have both nitrogen atoms protonated while the remaining acidic protons should form very strong, probably symmetrical, hydrogen bonds of the type (COOHOOC)$^-$. The NH$^+$ groups are also hydrogen-bonded, as indicated by the frequency and the breadth of the NH$^+$ stretching bands; however, it does not seem possible at present to specify this interaction.

Similar conclusions about protonation sites on nitrogen atoms are reached also for solid iminodiacetic and nitrilotriacetic acids. The details of this study will be published.

(11) D. Hadzi and A. Novak, *Spectrochim. Acta*, **18**, 1059 (1962).
(12) R. Blinc, D. Hadzi, and A. Novak, *Z. Elektrochem.*, **64**, 567 (1960).

LABORATOIRE DE SPECTROSCOPIE INFRAROUGE   A. NOVAK
LABORATOIRE DE CHIMIE PHYSIQUE   M. COTRAIT
FACULTÉ DES SCIENCES DE BORDEAUX   J. JOUSSOT-DUBIEN
BORDEAUX, FRANCE   J. LASCOMBE
RECEIVED NOVEMBER 9, 1964

Stereochemically Nonrigid Structures

Sir:

Chemists portray molecules in a rigid, point group formalism that ignores dynamics. Neglect of the effects of dynamics on stereochemistry can lead to serious misconceptions and, at the very least, is a step removed from reality. The dynamic processes critical to stereo-

chemistry are those which permute identical nuclei. Should the time scale of such processes for a given molecule be comparable to or shorter than that of a laboratory observation, then the molecule must be considered as a nonrigid structure for the purposes of the experiment. The consequences of the rigid approach can be rather serious, *e.g.*, incorrect spectroscopic assignments and failure to recognize intramolecular rearrangements.[1] Liehr[2] has previously presented elegant arguments against the rigid stereochemical approach, but a casual perusal of current literature shows that his admonitions unfortunately have been overlooked or ignored.

The question of conformation in isolated eight-coordinate species illustrates the inherent problems of point group formalism. As a specific example, consider the octacyanomolybdate ion, Mo(CN)$_8$$^{4-}$. In a crystalline potassium salt,[3] the anion has near D$_{2d}$ (dodecahedral) symmetry[4] with two equally-populated cyanide environments. The most plausible structural alternative is the D$_{4d}$ square antiprism with all cyanide groups equivalent, and some investigators[5] have concluded that the anion has this symmetry in the solution state although the data have also been interpreted[6] in terms of a dodecahedral configuration. Recently, we have found that the C^{13} n.m.r. absorption mode of Mo(CN)$_8$$^{4-}$ enriched[7] in C^{13} consists of a single sharp resonance (1.2 c.p.s. line width). The single absorption peak is literally without structural significance, but we believe that in the context of this note the stereochemical aspect is worthy of discussion. Our n.m.r. data are consistent with the following possibilities, (1) D$_{4d}$ point group symmetry, (2) D$_{2d}$ point group symmetry with very small chemical shift between nonequivalent sites, and (3) D$_{2d}$ or D$_{4d}$ symmetry with rapid intramolecular[8] exchange of cyanide groups. The last alternative is the only realistic one for the n.m.r. time scale because the energy difference between the two idealized geometries presumably is small and the distortion required to interconvert these structures is also small.[9] Point group symmetries should not be used to describe eight-coordinate structures if in the context of the description or the observa-

(1) Certainly, the static approach has led to an unreasoning and invalid reliance upon crystallographic data for characterization of solution, liquid, and vapor states of molecules.
(2) A. D. Liehr, *J. Phys. Chem.*, **67**, 471 (1963).
(3) It is conceivable that square antiprismatic (D$_{4d}$) geometry may prevail in other salts.
(4) J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.*, **61**, 2853 (1939).
(5) H. S. Stammreich and O. Sala, *Z. Elektrochem.*, **65**, 149 (1961).
(6) R. M. Golding and A. Carrington, *Mol. Phys.*, **5**, 377 (1962).
(7) This enriched complex was prepared by the procedure outlined in *Inorg. Syn.*, **3**, 160 (1950), from a commercial sample of KCN enriched in C^{13} to about 50%. Intensities of the C^{12}N and C^{13}N infrared stretching frequencies were approximately equal in the enriched cyanomolybdate sample. Measurements were made on a saturated aqueous solution of K$_4$Mo(CN)$_8$·2H$_2$O in a 5-mm. tube at 15 Mc. by Mr. H. Retcofsky of the U. S. Bureau of Mines, Pittsburgh, Pa. The chemical shift is +40.3 p.p.m. from carbon disulfide.
(8) Intermolecular cyanide exchange has been shown to be very slow; exchange is less than 2% in 7 days in the dark: A. W. Adamson, J. P. Welker, and M. Volpe, *J. Am. Chem. Soc.*, **72**, 4030 (1950). Exchange between Mo(CN)$_8$$^{4-}$ and CN$^-$ is photocatalyzed. The C^{13} n.m.r. spectrum of Mo(CN)$_8$$^{4-}$(aq) in the dark was identical with the spectrum obtained in the light.
(9) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

tion the time scale is relatively long, *ca.* 1 μsec. The accurate symmetry assay is the molecular symmetry as defined by Longuet-Higgins.[10]

Liehr[2] proposes that chemists deliberate stereochemistry in terms of the potential energy surface encompassing all possible geometries for a given molecular aggregate. This approach is highly recommended even though much guesswork is necessarily involved in such an assay for all but the very well-characterized nonrigid molecules such as ammonia and ethane. Such deliberations delineate structural interrelations, potential intramolecular rearrangements, and feasibility of separation of optical or geometrical isomers. Admittedly, tetrahedral and octahedral structures are stereochemically rigid in the context of virtually all experimental observations. However, inorganic chemistry is rich[11] in nonrigid structures, *e.g.*, five-,[12-13]

TABLE I
GROUND-STATE LIFETIMES FOR NONRIGID MOLECULES

Molecule or ion	Lifetime, sec.	Origin of data
NH_3	2.5×10^{-11}	Calcd.[a]
ND_3	2.7×10^{-10}	Est.[12]
PH_3	10^{-3}	Est.[12]
AsH_3	10	Est.[12]
CH_4	10^{15}	Est.[a]
PF_5	10^{-5}	Est.[12]
PCl_5	10^4	Est.[12]
PF_3Cl_2	$10^{-3} (-50°)$	N.m.r.[13]
IF_7	Between 10^{-3} and 10^{-12}	N.m.r.–infrared[14] est.
$ReH_9{}^{2-}$	Between 10^{-3} and 10^{-12}	N.m.r.–infrared[15] est.
$Mo(CN)_8{}^{4-}$	Between 10^{-3} and 10^{-12}	Est.
$PF_4N(CH_3)_2$	10^{-4}	N.m.r.[13]
$B_2Cl_4 (D_{2d})$	Between 10^{-3} and 10^{-12}	Infrared[b] est.

[a] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp. 223–225. [b] D. E. Mann and L. Fano, *J. Chem. Phys.*, **26**, 1665 (1957).

seven-,[14] eight-, and nine[15]-coordinate species. Some specific examples are listed in Table I with estimated lifetimes for the ground-state geometry. Nonrigidity was also correctly suspected for complex polyhedra such as $B_{10}H_{10}C_2H_2$, $B_{10}H_{10}{}^{2-}$, and $B_{12}H_{12}{}^{2-}$, but in these structures the barrier to intramolecular isomerization is rather high[16-20] and the polyhedra are nonrigid only for observations in the 250–500° range.

(10) H. C. Longuet-Higgins, *Mol. Phys.*, **6**, 445 (1963). See also A. J. Stone, *J. Chem. Phys.*, **41**, 1568 (1964).

(11) Nonrigid structures are extremely common in biochemistry. Here potential energy surfaces have many minima with relatively small barriers. In these systems, it is mandatory that any description or any speculation based on physical measurements be qualified as to the time scale.

(12) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(13) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

(14) E. L. Muetterties and K. J. Packer, *J. Am. Chem. Soc.*, **86**, 293 (1964).

(15) S. C. Abrahams, A. P. Ginsburg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).

(16) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).

(17) D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

(18) R. Hoffman and W. N. Lipscomb, *ibid.*, **2**, 231 (1963).

(19) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962).

(20) W. R. Hertler, W. H. Knoth, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 5434 (1964).

TABLE II
TIME SCALE FOR STRUCTURAL TECHNIQUES

Technique	Approx. time scale, sec.
Elect. diffr.	10^{-20}
Neutron diffr.	10^{-18}
X-Ray diffr.	10^{-18}
Ultraviolet	10^{-15}
Visible	10^{-14}
Infrared–Raman	10^{-13}
Electron spin res.[a]	10^{-4}–10^{-8}
Nuclear mag. res.[a]	10^{-1}–10^{-9}
Quadrupole res.[a]	10^{-1}–10^{-8}
Mössbauer (iron)	10^{-7}
Molecular beam	10^{-6}
Exptl. sepn. of isomers	$>10^2$

[a] Time scale sensitively defined by chemical systems under investigation.

Any comparison or application of structural data for a nonrigid molecule must take into account the pertinent time scales (as well as the physical state), a point all too often ignored. In Table II, the time scales for the principal structural techniques are listed. It is important to note that all the new resonance techniques have time scale ranges comparable to those of ground-state geometries in nonrigid molecules (Table I). In fact, one of these resonance techniques, n.m.r., has detected a large number of low-energy, intramolecular rearrangements. An illustrative example is PF_3Cl_2, which has C_{2v} symmetry in the ground state. F^{19} n.m.r. shows the expected multiplicity for a C_{2v} model but only below $\sim110°$.[12,13] Above this temperature, the fluorine atoms are spectroscopically equivalent. Dilution studies identified this transition as an intramolecular process, and analysis of the transition region set a lifetime of about 10^{-3} sec. to the ground-state geometry at $-50°$.[13,21] This lifetime is still very long with respect to the vibrational time scale, and, consistently, the infrared and Raman data are in accord with C_{2v} symmetry.[22]

Experimentally there is much to be done with nonrigid molecules. Consider five-coordinate species[23] and specifically phosphorus pentafluoride. There is a good possibility that the ground-state structure will vary through the various physical states. Plausible geometries are trigonal bipyramid, tetragonal pyramid, and pentagon. Molecular models show the first two to be very similar. These should have comparable energy levels, whereas the pentagon should be a very high energy state. Furthermore, as pointed out by Berry,[12] there should be a facile interconversion of D_{3h} and C_{4v} models through vibrational excitation. However, there are no data to indicate whether the C_{4v} state is a minimum in the potential energy diagram. If the C_{4v} state is a minimum in the potential energy diagram, it is a detectable state. For example, a careful electron diffraction study over a temperature

(21) We are presently re-examining the n.m.r. transition region of PF_3Cl_2 to obtain a more accurate value of the exchange barrier and of fluorine atom lifetimes.

(22) J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964).

(23) A comprehensive review of five-coordinate structures will be published shortly, E. L. Muetterties and R. A. Schunn.

range could, providing the resolution problem is minimized, outline the potential energy surface of PF$_5$. Another, possibly better, approach to an analysis of the energy surface is through molecular beam studies. In the solution state, asymmetric solvation may favor the C$_{4v}$ state for PF$_5$; the stable adducts derived from PF$_5$ and strong donor molecules[24] represent the extreme case (actually octahedral structures). In the crystalline state, packing forces or intermolecular P–F–P

(24) E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 52 (1962).

interactions may lower the C$_{4v}$ state relative to D$_{3h}$. A single crystal X-ray study of PF$_5$ should be made.

Acknowledgment.—The author is indebted to Mr. H. Retcofsky of the U. S. Bureau of Mines for the C^{13} n.m.r. analysis of K$_4$Mo(CN)$_8$, and to Dr. W. D. Phillips and Dr. W. Mahler for helpful discussions.

CONTRIBUTION NO. 1053   E. L. MUETTERTIES
CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND CO.
WILMINGTON 98, DELAWARE
                                     RECEIVED DECEMBER 28, 1964

Book Review

Fused Salts. Edited by BENSON ROSS SUNDHEIM, Department of Chemistry, New York University. McGraw-Hill Book Co., Inc., 330 West 42 St., New York, N. Y. 1964. ix + 435 pp. 14.5 × 22.5 cm. $18.50.

The proliferation of research with and on fused salts in recent years has made the appearance of a second book on the subject welcome. Before the publication of this volume (and "Molten Salt Chemistry," edited by M. Blander, Interscience Publishers, New York, N. Y., 1964) the only compilations of research in the field were a few scattered review articles and published proceedings of symposia. Since fused salt research has many aspects ranging from the most highly theoretical to the almost entirely technological, an exhaustive treatise on the subject would have been a formidable task and the editor has wisely avoided the attempt. Instead, the book consists of seven independent essays on seven aspects of fused salt research. Each chapter is intended to be a critical review, rather than a compilation of references, by authors who have made original contributions in the fields on which they write.

The first chapter, "Structural Aspects of Ionic Liquids," is by H. Bloom and J. O'M. Bockris. The authors discuss the various conceptual models of ionic liquids—the quasi-lattice, hole, crystallite, polyhedral hole, liquid free-volume, and significant structure models. Attempts to evaluate the distribution function from intermolecular force laws are dismissed as having given little indication of the nature of a liquid. Transport properties are discussed briefly and a qualitative comparison is given of predictions from various models of the volume change on fusion, entropy of expansion, and diffusion parameters. The remainder of the chapter deals largely with the evidence for the existence of complex species in ionic melts from Raman spectra, conductance, viscosity, surface tension, thermodynamic activity, ultraviolet spectra, and potential–time transients at electrodes.

The longest chapter of the book is by T. Førland on "Thermodynamic Properties of Fused Salt Systems." Following a discussion of the fusion process, in relation to disorder in solids, and a brief discussion of theories of the liquid state, the author presents derivations of classical and statistical thermodynamic equations for binary fused salt mixtures and reciprocal salt mixtures, including mixtures of ions with different numbers of charges. Brief mention is made of the formation of complex species in fused salt mixtures. A section on experimental methods for the determination of thermodynamic properties, and thermodynamic calculations associated with the methods, follows. Phase diagrams are treated here, but no attempt is made to present a systematic compilation of the multitude of types of phase diagrams found for multicomponent salt systems. This section contains diagrams of apparatus used for filtration, cryoscopic measurements, electromotive force measurements,

calorimetry, and measurements of surface tension and density. The final section is a discussion of thermodynamic data for one- and two-component systems, reciprocal mixtures, metal–slag equilibria, complex formation, and polyanionic systems, such as silicates, borates, and beryllium fluoride.

B. R. Sundheim has contributed a chapter entitled "Transport Properties of Liquid Electrolytes." In the first section, he develops the phenomenological equations of irreversible thermodynamics for the description of conductance, transference, diffusion, thermoelectricity, and thermal diffusion in fused salts. Experimental methods are described for determining the above transport properties and extensive tables of results are included. The transference numbers reported for pure fused salts are attributed to the properties of the salt alone with little discussion of admonitions to the contrary.[1] Transport results are discussed in terms of statistical mechanical and phenomenological theories of transport.

H. A. Laitinen and R. A. Osteryoung have written "Electrochemistry in Molten Salts." They deal with dynamic rather than static measurements. The equations and some experimental details of chronopotentiometry are outlined, with particular reference to molten salts. The application of chronopotentiometry to the measurement of diffusion coefficients and complex association constants is reviewed. The need for rapid transient techniques in the determination of electrode overpotentials is pointed out. The evaluation of parameters of electrode kinetics is described from impedance measurements, the voltage-step method, the double-pulse method, and the Faradaic-rectification method. Polarography of a number of cations in molten salt solvents with a variety of stationary, rotating, and dipping solid microelectrodes is described, as well as the results obtained at low temperatures (in nitrate mixtures) with dropping electrodes. A good representation of the Russian literature is included.

D. M. Gruen has contributed "Spectroscopy of Transition Metal Ions in Fused Salts," which deals with the electronic spectra of these ions. Following an introductory section on the effect of melting and temperature changes on the ultraviolet absorption spectra of pure salts, Gruen reviews the results of electronic absorption spectra of dilute solutions of 3d, 4f, and 5f ions in fused salt solvents, to which he and his co-workers have contributed significantly. The results are interpreted in terms of the coordination numbers of the ions and the associated crystal field splitting. Experimental methods are not discussed, nor are vibrational spectra reviewed.

J. D. Corbett has contributed "The Solution of Metals in Their Molten Salts." The section on experimental methods is particularly desirable in a chapter on these unusual systems. The most extensive studies have been of the alkali metals and

(1) G. Scatchard, *Ann. Rev. Phys. Chem.*, **14** (1963).