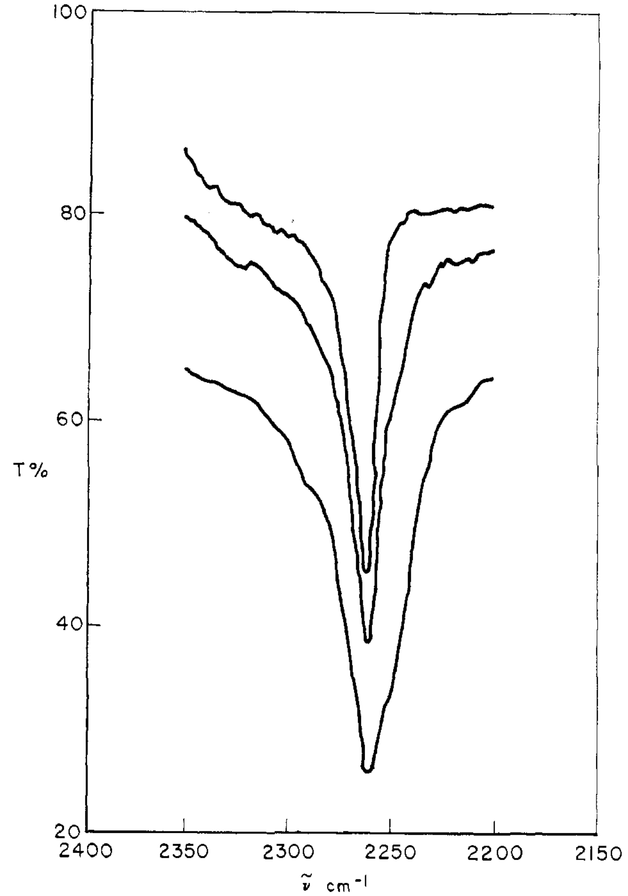

Figure 2.—Infrared C–D band of $CDCl_3$ in CCl_4 with added $Mn(DIBM)_3$: upper curve, no $Mn(DIBM)_3$, ~10% $CDCl_3$; middle curve, $CDCl_3$ to Mn(III) ratio ~10; lower curve, $CDCl_3$ to $Mn(DIBM)_3$ ratio ~2.5.

visible or near-infrared. Hydrogen-bonding solvents might be expected to perturb such a transition strongly through interaction with the oxygens, increasing the energy of the transition.

The size of the β-ketoenol ligand used in this study suggests a bulky solvent has some difficulty approaching closely to hydrogen bond with the ligands. When *n*-butyl and *t*-butyl alcohols are compared (Figure 1) a steric effect appears to be operative. Studies are currently in progress to observe the extent of the hydrogen-bond formation between various β-ketoenolates and several hydrogen-bonding solvents. For example, in the infrared only H-bonded OH is observed when $Mn(DIBM)_3$ is added to CCl_4 initially saturated with H_2O. In fact, CCl_4 solutions containing $Mn(DIBM)_3$ take up considerably more water than is dissolved without the complex being present. Also, infrared studies of $Co(AA)_3$, $Cr(AA)_3$, $Fe(AA)_3$, and $Be(AA)_2$ in $CDCl_3$ show these complexes, too, D-bond to the $CDCl_3$.

Chemical evidence suggests low energy "charge transfer" to be feasible in manganese(III) β-ketoenolates. 3-Chloroacetylacetone appears to reduce manganese(III). The tris chelate extracted into hexane decomposes with a half-life which appears to be of less than 15 min. duration. $Mn(AA)_3$ long has been known to decompose in the presence of light[3] and the hexafluoroacetylacetone and 3-cyano-2,4-pentanedione derivatives cannot be prepared by the usual oxidative procedures from manganese(II). The former complex appears to decompose when moist, the manganese being reduced in the process.

At this time it is unknown whether the hydrogen-bond interaction between the solvent and the complex involves primarily the chelate oxygens or the chelate ring itself. The oxygens certainly are basic, as indicated by the polymerization of nickel(II) and cobalt(II) acetylacetonates.[12] However, interaction between silver ion[13] and the chelate rings and bond formation by platinum[14] to the α-carbon suggests the ring itself (or the α-carbon) may be basic enough to form hydrogen bonds. Benzene is known to form weak hydrogen bonds[15] to $CHCl_3$. The extent of hydrogen-bond formation between complexes of β-ketoenols generally and various solvents is not yet known, but it is believed that this possible interaction has been badly neglected and may lead to considerable re-evaluation of data, particularly for studies conducted in $CHCl_3$ or MeOH.[16]

Acknowledgments.—The support of the National Science Foundation is gratefully acknowledged.

[12] See, for example, J. P. Fackler, Jr., *Inorg. Chem.*, **2**, 266 (1963), and refer ences therein.

[13] C. H. Oestreich, Ph.D. Thesis, Ohio University, 1961.

[14] A. G. Swallow and M. Truter, *Proc. Roy. Soc.* (London), **254**, 205 (1960).

[15] C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962).

[16] F. R. Clark, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **26**, 1311 (1964).

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Paratungstate Ion

Sir:

No general principle has yet been noted for the structures of the several isopoly- and heteropolyanions: $Nb_6O_{14}^{-8}$ and $Ta_6O_{14}^{-8}$,[1,2] $Mo_7O_{24}^{-6}$ and $Mo_8O_{26}^{-4}$,[3-5] $TeMoO_{24}^{-6}$,[6,7] $V_{10}O_{28}^{-6}$,[8-10] $MnMo_9O_{32}^{-6}$,[11] $W_{12}O_{40}^{-8}$,[12] $W_{12}O_{46}^{-20}$,[13] $PW_{12}O_{40}^{-3}$,[12,14] and $P_2W_{18}O_{62}^{-6}$.[14] Aside from tetrahedral coordination around P in the two phosphotungstate ions, all of these structures are based

[1] I. Lindqvist, *Arkiv Kemi*, **5**, 247 (1953).

[2] I. Lindqvist and B. Aronsson, *ibid.*, **7**, 49 (1954).

[3] I. Lindqvist, *Nova Acta Regiae Soc. Sci. Upsaliensis*, [4] **15** (1950).

[4] I. Lindqvist, *Acta Cryst.*, **3**, 159 (1950); *Arkiv Kemi*, **2**, 325 (1950).

[5] I. Lindqvist, *Acta Chem. Scand.*, **4**, 551 (1950); *Arkiv Kemi*, **2**, 349 (1950).

[6] J. S. Anderson, *Nature*, **140**, 850 (1937).

[7] H. T. Evans, Jr., *J. Am. Chem. Soc.*, **70**, 129 (1948).

[8] H. T. Evans, Jr., M. E. Mrose, and R. Marvin, *Am. Mineralogist*, **40**, 314 (1955).

[9] F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, **10**, 957 (1956).

[10] H. T. Evans, Jr., A. G. Swallow, and W. H. Barnes, *J. Am. Chem. Soc.*, **86**, 4209 (1964).

[11] J. L. T. Waugh, D. P. Shoemaker, and L. Pauling, *Acta Cryst.*, **7**, 438 (1954).

[12] J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, 575 (1935); also J. F. Keggin, *Proc. Roy. Soc.* (London), **A144**, 75 (1934).

[13] I. Lindqvist, *Acta Cryst.*, **5**, 667 (1952).

[14] B. Dawson, *ibid.*, **6**, 113 (1953).

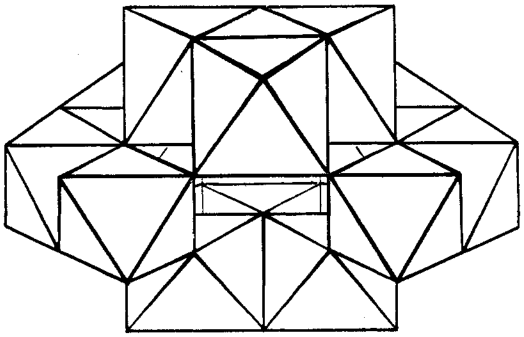
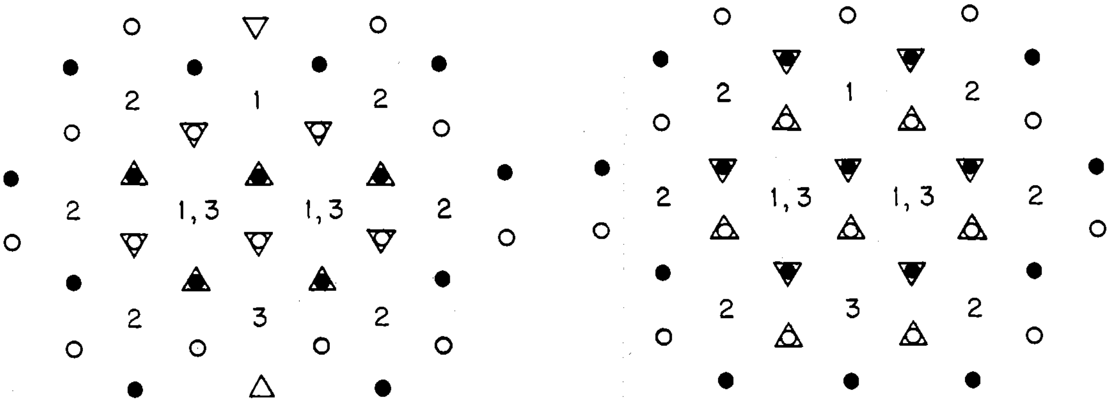


Figure 1.—Coordination of octahedra in the proposed structure of paratungstate ion, $W_{12}O_{42}^{-12}$. This ion has a center of symmetry, and consists of four distinct units assembled by sharing of corners. The four units are of two types, each type consisting of three octahedra sharing common edges. In the type at the top and bottom, adjacent edges are shared, and in the central octahedron of the type at the left and right nonadjacent, but nonopposite, edges are shared.

upon MO_6 octahedra which share edges or corners in such a way that the total charge of O^{-2} is shared among the highly positively charged cations. The radii[15] of the M^{+n} ions are 0.54 Å. for Mn^{+4}, 0.56 Å. for Te^{+6}, 0.59 Å. for V^{+5}, 0.62 Å. for Mo^{+6}, *ca.* 0.65 Å. for W^{+6}, 0.70 for Nb^{+5}, and *ca.* 0.7 Å. for Ta^{+5}. In octahedral coordination with O^{-2} (radius 1.40 Å.) these ions may be unsymmetrically displaced, thus localizing the lines of force to reduce the number of M^{+n}–O^{-2} bonds. Thus, we note that these MO_6 octahedra polymerize in aqueous solution to give stable ions in which no octahedron terminates in three or more unshared O^{-2} ions, *with the single exception of the paratungstate ion,* $W_{12}O_{46}^{-20}$.

In the X-ray diffraction study[13] of the salt $5Na_2O \cdot 12WO_3 \cdot 28H_2O$, the positions of the W atoms were located unambiguously, but neither the Na nor the individual O atoms were found, aside from strong evidence of multiple W–O vectors which support a close-packed array of O atoms within the paratungstate ion. The centrosymmetric $W_{12}O_{46}^{-20}$ ion was derived[13] from these results; therefore the formula requires 10 H^+ ions which protonate either the $W_{12}O_{46}^{-20}$ ion or H_2O molecules or a corresponding total of both species. The isolation[16] of this material from a solution at pH about 5.2 had led earlier to the formulation[16] of the ion as $W_{12}O_{41}^{-10}$, but this formula requires an O atom at the center of symmetry and is therefore inconsistent with the W arrangement of the X-ray diffraction study.



(a) (b)

Figure 2—(a) The 42 oxygen atoms of the proposed paratungstate ion showing hexagonal close packing. The layers parallel to the plane of the paper are stacked in the order ∇, ●, ○, Δ. The W atoms which lie in the same plane are designated by the same number. (b) A similar description of the $W_{12}O_{46}^{-24}$ formulation[13] of paratungstate ion.

It is here proposed that paratungstate ion is neither of the previous formulas, but $W_{12}O_{42}^{-12}$ or a protonated version such as $H_2W_{12}O_{42}^{-10}$. First, it has been possible to construct a molecular model (Figure 1) which satisfies all of the X-ray results so far obtained: in particular the W atom arrangement is identical with that proposed earlier for the $W_{12}O_{46}^{-20}$ formula, and the O atoms are still in a hexagonal close packed array (Figure 2). Second, this structure is completely consistent with the termination of all octahedra by two or less unshared O^{-2} ions and therefore follows the same structural principles as those of all other large polyanions based upon MO_6 octahedra. Third, the formula seems a bit more consistent with the isolation from weakly acidic rather than strongly acidic aqueous solutions. Fourth, the consistency of structural principles followed by the $W_{12}O_{42}^{-12}$ structure and all other known structures implies the existence of only a few additional species (*e.g.*, $Mo_5O_{18}^{-6}$ of C_{4v} symmetry and $Mo_{10}O_{32}^{-4}$ of C_{2v} symmetry), whereas the extended structural principles required by the $W_{12}O_{46}^{-20}$ structure would imply the existence of an exceedingly large number of new isopolyanions. A detailed and careful X-ray diffraction study is required, and further considerations of these structural principles will probably lead to only a very limited number of predictions for the topology of these iso- and heteropolyanions. Metal ion to metal ion interactions may indeed be important in detailed stabilization of some ground states, and particularly in electronic

(15) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 437 ff., 514 ff., 540 ff.

(16) K. Saddington and R. W. Cahn, *J. Chem. Soc.*, 3526 (1950).

spectra, but the major aspects of these structures appear to a first approximation to be dominated by the localization of M^{+n}–O^{-2} bonding.

Acknowledgment.—It is a pleasure to acknowledge a conversation with Dr. H. T. Evans, Jr., whose recent study of the $V_{10}O_{28}^{-6}$ ion reawakened the author's interest in these polyanions. This research was supported by the Office of Naval Research.

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Book Review

Mathematical Methods of Physics. By JON MATHEWS and ROBERT L. WALKER. W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1964. x + 475 pp. 16 × 24 cm. Price, $12.50.

This book has evolved from the notes on a course which is intended primarily for first-year physics graduate students. As the authors put it in the preface, it is a book *about mathematics for physicists.* It contains chapters on "Ordinary Differential Equations," "Infinite Series," "Evaluation of Integrals," "Integral Transformations," "Application of Complex Variables," "Vectors and Matrices," "Special Functions," "Partial Differential Equations," "Eigenfunctions," "Eigenvalues and Green's Functions," "Perturbation Theory," "Integral Equations," "Calculus of Variations," "Numerical Methods," "Probability and Statistics," "Tensor Analysis and Differential Geometry," and "Introduction to Groups and Group Representations." There is a brief appendix on "Some Properties of Functions of a Complex Variable," a bibliography, and an index, the latter sufficiently detailed to make the book suitable as a reference to many definitions and equations although that is not its primary purpose. The reader is supposed to have some acquaintance with simultaneous linear equations and determinants, vector analysis (including differential operations in curvilinear coordinates), elementary differential equations, and complex variables (through Cauchy's theorem).

The above should make it very clear that this is not a book for the average chemist. On the other hand, this reviewer can strongly recommend it to students of chemical physics even if some sections will lie outside their field of interest and comprehension. The level of presentation is by no means uniform. Thus, the chapter "Vectors and Matrices" starts off immediately with the definition of linear vector spaces, with little or no mention of "ordinary" vector algebra. Later, in the same chapter, matrices are introduced "from scratch." The choice of material has generally been a fortunate one. Many of the mathematical aspects of quantum mechanics are particularly clearly presented. Of course there are omissions; for example, we have looked in vain for some topics from the mathematics of thermodynamics such as the Pfaff differential equation in conjunction with the Carathéodory derivation of the second law. But, as the authors point out, this book is intended as a text, not as a reference work. In this connection the inclusion of a considerable number of problems at the end of each chapter is to be lauded. It is to be hoped that in a future edition answers to these problems may be provided in an appendix, so that the book will be even more suitable for self study.

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November 1964

ARTHUR W. ADAMSON. "Understanding Physical Chemistry." Parts I and II. W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1964. xix + 489 pp. Clothbound $10; paperback (in two parts), $3.95 each.

N. F. MOTT and R. W. GURNEY. "Electronic Processes in Ionic Crystals." Dover Publications, Inc., 180 Varick St., New York 14, N. Y. 1964. xii + 275 pp. $2 (paperbound).

D. D. PERRIN. "Organic Complexing Reagents." John Wiley and Sons, 605 Third Ave., New York, N. Y. 1964. xi + 365 pp. $12.

LASZLO ERDEY. "Theorie und Praxis der Gravimetrischen Analyse." III. Band. Akademiai Kiado, Publishing House of the Hungarian Academy of Sciences, Budapest V. Alkotmany U. 21, Hungary. 1964. 340 pp. $13.

Y. K. SYKRIN and M. E. DYATKINA. "Structure of Molecules and the Chemical Bond." Dover Publications, Inc., 180 Varick St., New York 14, N. Y. ix + 509 pp. $2.75 (paperbound).

JOEL H. HILDEBRAND and ROBERT L. SCOTT. "The Solubility of Nonelectrolytes." Dover Publications, Inc., 180 Varick St., New York 14, N. Y. 1964. xiv + 488 pp. $2.50 (paperbound).