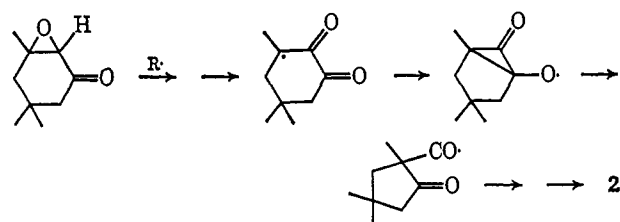


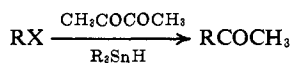
are readily eliminated in  $\beta$ -cleavage reactions such as suggested in (3) was well demonstrated by the work of Walsh, *et al.*,<sup>8</sup> who studied reactions of a large number of alkoxy intermediates analogous to **1** which were generated from the corresponding hypochlorite precursors. In fact, the previously published radical-catalyzed conversion of isophorone oxide to 2,4,4-trimethylcyclopentanone (**2**) is quite possibly an *intramolecular* acetylation as the authors suggest.<sup>9</sup> The



reaction of methyl radicals with 3-penten-2-one to give 2-butene and acetyl in the gas phase appears to be a closely analogous addition-elimination reaction.<sup>10</sup>

In contrast to the cited examples of attack at carbonyl carbon by alkyl radicals, *alkanoyl*<sup>11</sup> and *benzoyl*<sup>11b</sup> radicals have been shown to give products of *carbonyl oxygen attack* as illustrated by the reaction of butanoyl radicals with hexafluoroacetone to yield the hexafluoro ester.<sup>5</sup> These differences may reflect the influence of polar effects on the direction of attack or may have to do with the ease with which products of carbon or oxygen attack are trapped, since both processes may well be reversible. We are currently looking for products of acyl exchange in reactions of acyl radicals with biacetyl as evidence of carbonyl carbon attack.

We are also attempting to exploit the synthetic potential of these reactions by the selective generation of radicals at desired positions of more complex molecules through reaction of the chloride or bromide with trialkyltin hydride in the presence of biacetyl.



Reactions of radicals with various other carbonyl compounds which may potentially react by addition-

(8) E. J. Walsh, Jr., L. Witmer, M. McNeil, T. Wilcko, and B. Orwig, *Tetrahedron Letters*, 77 (1968).

(9) W. Reusch, C. K. Johnson, and J. A. Manner, *J. Am. Chem. Soc.*, **88**, 2803 (1966).

(10) J. N. Pitts, Jr., R. S. Tolberg, and T. W. Martin, *ibid.*, **79**, 6370 (1957).

(11) (a) L. Kaplan, *ibid.*, **88**, 1833, 4970 (1966); E. J. Walsh, Jr., and H. G. Kuivila, *ibid.*, **88**, 576 (1966); E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, **29**, 3690 (1964); (b) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 3258 (1948).

elimination to split out stable radicals other than acetyl are also being studied.<sup>12</sup>

**Acknowledgment.** Support of this work by the Petroleum Research Fund of the American Chemical Society through a research grant (PRF-2439-A4) is gratefully acknowledged.

(12) An apparently related reaction is chlorocarbonylation utilizing oxalyl chloride and a free-radical initiator (I. Tabushi, J. Hamuro, and R. Oda, *J. Org. Chem.*, **33**, 2108 (1968); E. Hedaya and L. M. Kyle, *ibid.*, **32**, 197 (1967); M. S. Kharasch, S. S. Kane, and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 1621 (1942); M. S. Kharasch, and H. C. Brown, *ibid.*, **64**, 329 (1942)).

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### A New Structural Type for Heteropoly Anions. The Crystal Structure of $(\text{NH}_4)_2\text{H}_6(\text{CeMo}_{12}\text{O}_{42}) \cdot 12\text{H}_2\text{O}$

As part of a continuing study of the isopoly- and heteropolyanions of molybdenum and tungsten, we wish to report the crystal structure of  $(\text{NH}_4)_2\text{H}_6(\text{CeMo}_{12}\text{O}_{42}) \cdot 12\text{H}_2\text{O}$ <sup>1</sup> which shows two significant features not previously reported in the crystal structures of related compounds.<sup>2-8</sup> First, the structure involves face sharing between  $\text{MoO}_6$  octahedra, and, second, the polyhedron formed by the molybdenum atoms is an icosahedron.

$(\text{NH}_4)_2\text{H}_6(\text{CeMo}_{12}\text{O}_{42}) \cdot 12\text{H}_2\text{O}$  was prepared by the method of Baker, *et al.*<sup>9</sup> The crystals are trigonal with rhombohedral dimensions:  $a = 10.589 \pm 0.004 \text{ \AA}$ ,  $\alpha = 78.108 \pm 0.004^\circ$ . There is one formula unit in the rhombohedral cell. With rhombohedral indexing, there are no systematic absences in the X-ray data, but Friedel<sup>10</sup> symmetry indicates space groups  $R\bar{3}$  or  $R\bar{3}$ .

X-Ray intensity data were collected by the stationary crystal-stationary counter method and peak heights were converted to integrated intensities by means of an experimental curve.  $\text{Mo K}\alpha$  X-radiation ( $\lambda 0.7107 \text{ \AA}$ ) was used and 2699 independent reflections were measured up to a  $2\theta$  angle of  $65^\circ$ . 1830 of the reflections had peak heights greater than twice the calculated standard deviation of peak height and are regarded as observed.

After application of the usual corrections, a sharpened Patterson map was calculated. While it is realized that the Patterson map would show only relatively large

(1) When the compound was prepared the major fraction of the product was monoclinic crystals analyzed as  $(\text{NH}_4)_2\text{H}_6(\text{CeMo}_{12}\text{O}_{42}) \cdot 10\text{H}_2\text{O}$ . These crystals proved unsuitable for accurate structural investigation, and the X-ray work was carried out on a very small quantity of rhombohedral crystals which were also present. The small quantity precluded analysis but the structural results indicate the formula  $(\text{NH}_4)_2\text{H}_6(\text{CeMo}_{12}\text{O}_{42}) \cdot 12\text{H}_2\text{O}$ .

(2) J. F. Keggin, *Proc. Roy. Soc. (London)*, **A144**, 75 (1934).

(3) A. Perloff, Ph.D. Dissertation, Georgetown University, Washington, D. C., 1966.

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

(5) B. Dawson, *ibid.*, **6**, 113 (1953).

(6) N. F. Yannoni, Ph.D. Dissertation, Boston University, 1961.

(7) H. T. Evans Jr., *J. Am. Chem. Soc.*, **70**, 1291 (1948).

(8) H. T. Evans, Jr., paper presented before Washington Crystal Colloquium, 1967.

(9) L. C. W. Baker, C. A. Gallagher, and T. P. MacCutcheon, *J. Am. Chem. Soc.*, **75**, 2493 (1953).

(10) M. J. Buerger, "The Precession Method," John Wiley and Sons, Inc., New York, N. Y., 1964, p 71.

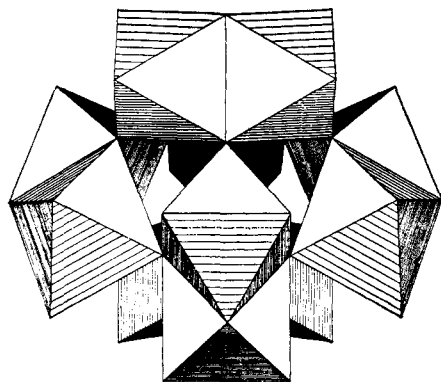


Figure 1. Idealized sketch of the  $[\text{CeMo}_{12}\text{O}_{42}]^{3-}$  ion showing the linkage of the  $\text{MoO}_6$  octahedra.

deviations from centrosymmetry, no indication of such deviations was seen, and space group  $R\bar{3}$  was assumed and molybdenum positions were deduced from the map on that basis. (The cerium atom is at the unit cell origin.) After refinement of the molybdenum coordinates, a difference map gave the positions of the light atoms. The structure has now been refined by block-diagonal least squares, using isotropic thermal parameters, to a conventional  $R$  factor of 0.09. (The refinement is being continued using anisotropic thermal parameters.) The successful refinement appears to confirm the choice of space group. Programs used were those written for the IBM 360 system by Ahmed, *et al.*<sup>11</sup>

The anion consists of six  $\text{Mo}_2\text{O}_9$  units formed by two octahedra sharing a face. The  $\text{Mo}_2\text{O}_9$  units share corners with each of four adjacent  $\text{Mo}_2\text{O}_9$  units to build up the anion (see Figure 1). Two corners are on the shared face and the other two are the innermost ones opposite the shared face. Mo–O distances presently have estimated standard deviations of 0.01 Å and vary from 1.68 to 2.28 Å. The Mo–O bond lengths fall into three classes, 1.68 Å (unshared oxygen atoms), 2.28 Å (shared-face oxygen atoms involved in corner-sharing), 1.98 Å (the oxygen atom in the shared face, not involved in corner sharing and the inner oxygen atoms involved in corner sharing). The lengths can be correlated with the number of heavy atoms with which an oxygen atom is associated, the shortest lengths being those corresponding to oxygen atoms associated with only one molybdenum atom. This variation of length with the number of heavy atoms with which an oxygen atom is associated, and resultant displacement of the molybdenum atoms toward the outside of the anion, was first noted by Keggin<sup>2</sup> and again by Yannoni<sup>6</sup> and Evans<sup>7</sup> and was confirmed by Perloff<sup>3</sup> in a more accurate study. The 12 molybdenum atoms form a slightly distorted icosahedron around the central cerium atom.

The cerium atom is 12-coordinate and the coordination polyhedron is an icosahedron formed by two shared-face oxygen atoms from each of the six  $\text{Mo}_2\text{O}_9$  units. The two independent Ce–O distances are both 2.50 Å with an estimated standard deviation of 0.01 Å. This distance may be compared with the average Ce–O distance of 2.51 Å in the icosahedrally coordinated cerium atom

(11) F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Saunderson, Division of Pure Physics and Pure Chemistry, National Research Council of Canada, Ottawa, Canada.

in ceric ammonium nitrate as reported by Beineke and Del Gaudio.<sup>12</sup> The cerium coordination polyhedron, in the present work, is not a completely regular icosahedron (only 3 symmetry is required by the space group), but deviations from regularity are fairly small. The angles in the triangular faces, for example, vary from 57.2 to 61.7° with estimated standard deviations of 0.3°.

The water molecules and ammonium ions appear to fill the space between the anions and to connect the structure in a hydrogen-bonded network.

**Acknowledgment.** This investigation was supported by PHS Training Grant No. DE159 of the National Institute of Dental Research.

(12) T. A. Beineke and S. Del Gaudio, Paper M11, presented before the American Crystallographic Association Meeting, Minneapolis, Minn., 1967.

(13) Author to whom all communications should be addressed.

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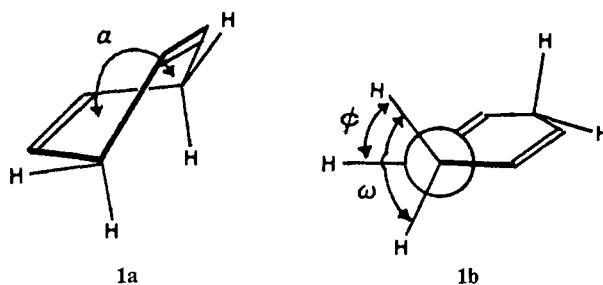
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### The Conformation of 1,4-Cyclohexadiene from Stereoisomeric Allylic–Allylic Proton Couplings

Sir:

It has been nearly 20 years since Gerding and Haak<sup>1</sup> deduced from vibrational spectral analyses that 1,4-cyclohexadiene (**1**) is planar ( $D_{2h}$ ) or nearly so. Yet, unexplainably, **1** is regarded generally to occupy the boat ( $C_{2v}$ ) conformation.<sup>2</sup> Recent analyses of the vibrational<sup>3a</sup> and rotational<sup>3b</sup> spectra of **1** confirm the original conclusions of Gerding and Haak, and Hendrickson-type calculations give a shallow potential minimum for the  $D_{2h}$  conformation.<sup>4</sup> We present here additional evidence for the near-planar conformation of **1**.



Should the five-bond allylic–allylic proton couplings in **1** be dominated by  $\sigma$ – $\pi$  interaction contributions, then the present theory for such interactions<sup>5</sup> leads to eq 1,

$$J_c/J_t = \{(\sin^2 \phi)^2 + [\sin^2(\omega - \phi)]^2\} / 2(\sin^2 \phi) \times [\sin^2(\omega - \phi)] \quad (1)$$

(1) H. Gerding and F. A. Haak, *Rec. Trav. Chim.*, **68**, 293 (1949).

(2) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 125.

(3) (a) H. D. Stidham, *Spectrochim. Acta*, **21**, 23 (1965); (b) B. J. Monostori and A. Weber, *J. Mol. Spectry.*, **12**, 129 (1964).

(4) The calculations were performed using normal bond lengths, the torsional potential function of propene, a C–C–C bending force constant of 17.5 cal mol<sup>-1</sup> deg<sup>-2</sup>, and 122 and 112° for the normal equilibrium bond angles for the C=C–C and C–C–C fragments, respectively. The assistance of Carol M. Sprecher in carrying out these calculations is gratefully acknowledged.

(5) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).