Two tridentate tri-1-pyrazolylborate ligands cap the two ends of the cluster, resulting in a confacial bioctahedral structure that is nearly congruent with the diiron(III) core geometries of azidomet forms of hemerythrin and myohemerythrin (Table I). The Fe–N and Fe–O(acetate) bond lengths are those typical of high-spin iron(III)[11] while the Fe–O(oxo) distances also agree well with literature values for antiferromagnetically coupled oxo-bridged high-spin diiron(III) compounds.[6] The two equivalent Fe–O(oxo) bond lengths and the significantly larger Fe–N bond distances trans to the bridging oxo ligand in the model compound compare well with results for the azidometmyohemerythrin structure (Table I). The latter feature reflects the greater structural trans influence[12] of oxo compared with carboxylato oxygen donor ligands.

Magnetic susceptibility data for solid **1**, obtained by the Faraday method in the range 4.2 K $\leq T \leq$ 296 K, were fit to the expression[6,13] for χ_M vs. T derived from the spin exchange Hamiltonian, $H' = -2JS_1S_2$, with $S_1 = S_2 = {}^5/_2$. Antiferromagnetic behavior was apparent from the calculated J value of -122 cm^{-1}, which compares favorably with $J = -134$ cm^{-1} reported for metaquohemerythrin.[14] The effective room-temperature moment of 1.67 μ_B per iron for solid **1** agrees with the value of $\mu_{\mathrm{eff}} = 1.71$ μ_B per iron measured by the Evan's method[15] at 294 K in 16 mM $CDCl_3$ solution. This result demonstrates that the bridged binuclear structure persists in solution. Especially noteworthy are the presence of 695 nm (ϵ 140 M^{-1} cm^{-1}) and $\sim$990 nm (ϵ 7 M^{-1} cm^{-1}) ligand field bands in the solution optical spectrum of **1**,[9] features characteristic of oxy and all methemerythrin derivatives.[3,16] The proton NMR spectrum of a 16.1 mM $CDCl_3$ solution of **1** exhibits two broad resonances[9] tentatively assigned to the pyrazole ring protons H(4) and H(5). Paramagnetically shifted histidine proton resonances have not yet been identified in the ^{1}H NMR spectra of hemerythrin derivatives.[17]

In summary, the (μ-oxo)bis(μ-carboxylato)diiron(III) core of met- and metmyohemerythrin has been assembled. Its structural and physical properties provide valuable bench marks against which the features of hemerythrin derivatives may be judged. Moreover, the present study provides a foundation for further synthetic chemistry required to mimic the reversible oxygen binding of hemerythrin and to help characterize the diiron centers in ribonucleotide reductase, the purple acid phosphatases, and related nonheme iron proteins.

Acknowledgment. This work was supported by National Institutes of Health Research Grant GM-32134 from the National Institute of General Medical Sciences. W.H.A. gratefully acknowledges support under NCI Training Grant CA-09112. We also thank S. Gorun and W. M. Davis for experimental advice and help, H. Lilienthal for assistance with the magnetic measurements, R. Stenkamp and W. Hendrickson for permission to quote their structural results prior to publication, B.-M. Sjöberg and R. Wilkins for preprints of their review articles on ribonucleotide reductase and hemerythrin, respectively, and R. H. Holm for stimulating discussions at the outset.

Registry No. **1**·4CH_3CN, 86177-71-1.

Supplementary Material Available: Table of atomic positional and thermal parameters for compound **1** (2 pages). Ordering information is given on any current masthead page.

---

(11) (a) Sinn, E.; Sim, G.; Dose, E. V.; Tweedle, M. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3375–3390. (b) Anderson, B. F.; Webb, J.; Buckingham, D. A.; Robertson, G. B. *J. Inorg. Biochem.* **1982**, *16*, 21–32.

(12) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335–422.

(13) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 204–283 and references cited therein.

(14) Dawson, J. W.; Gray, H. B.; Hoenig, H. E.; Rossman, G.; Schredder, J. M.; Wang, R.-H. *Biochemistry* **1972**, *11*, 461–465.

(15) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.

(16) Loehr, J. S.; Loehr, T. M.; Mauk, A. G.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 6992–6996.

(17) York, J. L.; Millett, F. S.; Minor, L. B. *Biochemistry* **1980**, *19*, 2583–2588.

Location of Internal Hydrogen Atoms in the Paradodecatungstate Polyanion by Neutron Diffraction

Howard T. Evans, Jr.*

U.S. Geological Survey
Reston, Virginia 22092

Edward Prince

National Bureau of Standards
Washington, D.C. 20234

Received April 25, 1983

The isopolyanion paradodecatungstate $[H_2W_{12}O_{42}]^{10-}$ has been studied by X-ray diffraction in six different compounds: (1) $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 10H_2O$ (orthorhombic),[1] (2) $(NH)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ (monoclinic),[2] (3) $Na_2(NH_4)_8[H_2W_{12}O_{42}]\cdot 12H_2O$ (orthorhombic),[3] (4) $(NH_4)_6H_4[H_2W_{12}O_{42}]\cdot 10H_2O$ (triclinic),[4] (5) $Mg_5[H_2W_{12}O_{42}]\cdot 38H_2O$ (triclinic),[5] (6) $Na_{10}[H_2W_{12}O_{42}]\cdot 20H_2O$ (triclinic).[6] The first full structure analysis by Allmann[1] firmly established the oxygen complement of the molecule ion as 42. The basicity of its salts commonly is 10 and has never been observed to exceed this value. It has long been suspected that the two nonreplaceable protons are located in some protected site within the molecule. Lunk et al.[7] have obtained direct evidence for the existence of these special protons from an NMR study of solid Na, K, and Li salts. They observed a line of medium breadth that does not shift but increases in intensity with dehydration and is distinct from the broad lines of intermolecular H_2O. From the line position, they calculate that the two protons within the molecule are separated by 2.22 (2) Å.

The Keggin-type, metadodecatungstic acid molecule $[H_2W_{12}O_{40}]^{6-}$ also contains two nonlabile H atoms, and these have been detected in similar fashion by Spicyn et al.[8] in solid Li, Na, and K salts. In solution, a sharp NMR signal for the nonlabile H atoms has been found in metadodecatungstic acid,[9,10] but no such signal can be detected for the paradodecatungstate[10] ion. These observations support the hypothesis that two H atoms are strongly bound internally in both the meta and para complexes but more strongly in the former than the latter.

The specific location of the H atoms in the paradodecatungstate molecule was first considered in detail by D'Amour and Allmann[2] in $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$. As with most X-ray structure determinations of such compounds, no direct evidence for the location of the two molecular H atoms could be obtained, but these authors inferred probable locations from an analysis of interatomic distances and bond-strength distributions in the molecule. Their argument leading to an association of H with an interior O atom triply shared with three W atoms is convincing, but their proposition that H lies nearly in line with another O atom to one side of the pseudomirror plane is more tenuous. Clearly, a neutron diffraction study is needed to settle the question of the H locations. We have carried out such a study, and report the results pertaining to this problem below. Full details of the structure analysis and

---

(1) Allmann, R. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1393–1404.

(2) D'Amour, H.; Allmann, R. *Z. Kristallogr.* **1972**, *136*, 23–47.

(3) D'Amour, H.; Allmann, R. *Z. Kristallogr.* **1973**, *138*, 5–18.

(4) Averbach-Pouchot, M. T.; Tordjman, I.; Durif, A.; Guitel, J. C. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1675–1677.

(5) Tsay, Y. H.; Silverton, J. V. *Z. Kristallogr.* **1973**, *137*, 256–279. In this paper, the coordinates for W(2) and W(3) are interchanged in Table 2; in this table also the z coordinate for O(82) should be 0.0318 (J. V. Silverton, private communication, 1983).

(6) Evans, H. T., Jr.; Rollins, O. W. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1565–1567.

(7) Lunk, H.-J.; Cuvaev, I. D.; Kolli, I. D.; Spicyn, V. I. *Dokl. Akad. Nauk SSSR* **1968**, *181*, 357–360.

(8) Spicyn, V. I.; Lunk, H.-J.; Cuvaev, V. F.; Kolli, I. D. *Z. Anorg. Allg. Chem.* **1969**, *370*, 191–201.

(9) Pope, M. T.; Varga, G. M. *Chem. Commun.* **1966**, 653.

(10) Launay, J. P.; Boyer, M.; Chauveau, F. *J. Inorg. Nucl. Chem.*, **1976**, *38*, 243–247.

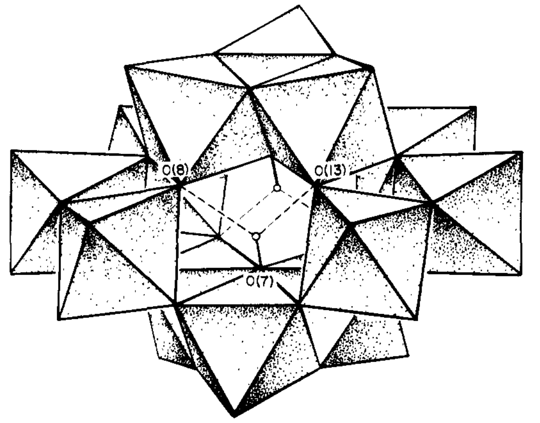


Figure 1. Pictorial view of the $[H_2W_{12}O_{42}]^{10-}$ molecule ion, showing location of the central H atoms.

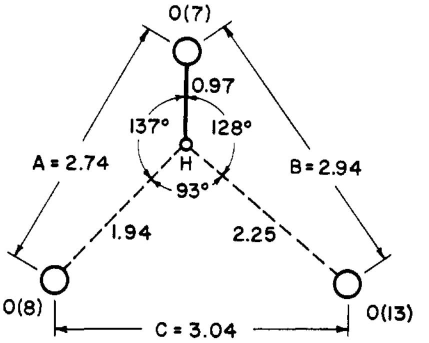


Figure 2. Projection of the four central atoms H, O(7), O(8), and O(13) onto the plane of the three oxygen atoms, showing interatomic distances in Å and angles at the H atom. Estimated errors of distances are ±0.03 Å for O-O, ±0.05 Å for O-H.

the overall structure will be published elsewhere.

We found that large crystals of $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ (no. 2 above) suitable for neutron diffraction study can be readily obtained by slow evaporation of a saturated solution of the salt at 85 °C. A stout prismatic crystal, 1.5 × 2 × 3 mm, was used for diffraction measurements. The unit cell is monoclinic, space group $P2_1/n$, with a = 15.079 (2) Å, b = 14.450 (2) Å, c = 10.968 (1) Å, β = 109.24 (1)°, and Z = 2 (dimensions obtained by least-squares refinement from X-ray powder data measured by the Guinier-Hägg method). Data were collected at the National Bureau of Standards research reactor with neutrons of wavelength 1.273 Å. Within the 2θ range of 15 to 118°, 1553 independent reflections were measured greater than $2\sigma(I)$, out of a possible 5256. Phases for the corresponding F values were calculated on the basis of the structure parameters obtained by D'Amour and Allmann.[2] The F Fourier synthesis calculated with this data set revealed the positions of all 25 H atoms in the asymmetric unit of the structure. In particular, the H atom within the molecule gave the sharpest and strongest image, at x, y, z = −0.023, 0.068, 0.014. Full anisotropic refinement of the structure (503 parameters) has converged at the conventional reliability indexes R = 0.151 and R_w = 0.123. The relatively high index values result from inadequate modeling of the NH_4 hydrogen atoms, which are subject to strong libration.

A pictorial view of the molecule, including the molecular H atoms as found in this study, is shown in Figure 1. The H atom is bonded to the central O(7) atom as predicted by D'Amour and Allmann.[2] Their suggestion that the OH bond is directed primarily toward O(8) is also generally confirmed. The H atom lies near to the plane defined by O(7), O(8), and O(13) at a distance of 0.10 Å (toward the molecular center), and the dimensions of the atomic arrangement projected onto this plane are shown in Figure 2. Although the hydrogen bond is most strongly directed toward O(8), it is clearly bifurcated and is also substantially involved with O(13). The distance between the two H atoms in the molecule is 2.14 (5) Å, in good agreement with the value of 2.22 (2) Å found from NMR measurements by Lunk et al.[7]

Table I

compd	A	B	C	esd (O-O)	ref
1 1	2.86	2.86	3.11	0.035	1
2	2.83	3.04	3.16	0.05	2
	2.74	2.94	3.04	0.03	this work
3	2.89	2.96	3.17	0.05	3
4	{2.85	3.08	3.20}	0.04	4
	{2.81	3.03	3.16}		
5	2.80	2.83	3.03	0.07	5
6	2.80	2.90	3.03	0.06	6
	av 2.822	2.968	3.112		

The disposition of the molecular H atoms also bears on the question as to whether the free molecule has $2/m$ or only $\bar{1}$ symmetry. Evans[6] concluded from a comparison of W-W distances in five published structures that departures from $2/m$ symmetry do not appear to be systematic and could result from the surrounding asymmetry of cations and water molecules in the crystal structure. If the molecular H atoms are assumed to be essentially unaffected by the external environment of the molecule, there is now reason to postulate that its symmetry is inherently $\bar{1}$. Presumably the distortion is rooted in the disposition of the central H atoms, and so the dimensions of the oxygen triangle may be examined for a systematic triclinicity in other structures. These dimensions (in Å) for the measured molecules are set forth in Table I, referring to the compounds listed above, and in Figure 2. From these data, we may definitely conclude that the paradodecatungstate molecule has $\bar{1}$ (C_i) symmetry, at least in the crystal. However, the displacement of the nonlabile H atom from the pseudomirror plane is only ~0.1 Å, so that the atom can be expected to be easily shifted from one side to the other by modest external forces. Therefore, the free molecule in solution probably oscillates in this way, and would most likely have time-averaged symmetry of $2/m$ (C_{2h}).

Registry No. $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$, 11113-17-0.

Formation of Ozonides: A Kinetic Secondary Isotope Effect for the Carbonyl Oxide

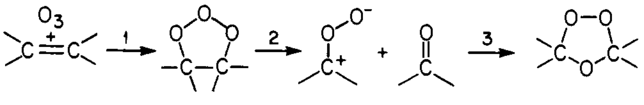
Jong-In Choe and Robert L. Kuczkowski*

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

Received March 30, 1983

The ozonolysis of alkenes is usually described by the Criegee mechanism (Scheme I).[1] In recent stereochemical studies it was postulated that the reaction steps are concerted cycloadditions or cycloreversions.[2-4] Considerable data support this conclusion for step 1.[5,6] However, the evidence that steps 2 and 3 are

Scheme I



---

(1) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745.

(2) Lattimer, R. P.; Kuczkowski, R. L.; Gillies, C. W. *J. Am. Chem. Soc.* **1974**, *96*, 348.

(3) Bailey, P. S.; Ferrell, T. M. *J. Am. Chem. Soc.* **1978**, *100*, 899.

(4) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199; **1981**, *103*, 3619, 3627, 3633.

(5) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1.

(6) Kuczkowski, R. L. *Acc. Chem. Res.* **1983**, *16*, 42.

0002-7863/83/1505-4839$01.50/0