S_4,[11,12] and Fe_4S_4[12,13] have been found.

All the experiments were carried out under a dinitrogen atmosphere. An iron wire (3 g) was introduced to a conical flask containing the aqua ion I (0.05 M, 25 mL) in 2 M HCl. The color of the solution turned from green to red-purple in a few hours. After the remaining iron was removed, the resultant solution was purified by the use of the ion exchange technique. The solution was absorbed on a Dowex 50W-X2 cation exchanger. Ferrous ion was eluted with 0.5 M HCl and red-purple eluent was obtained by the use of 1 M HCl.[14] This was analyzed to give Mo/Fe = 2.93 ± 0.15 (three determinations). An HPTS (*p*-toluenesulfonic acid) solution of the ion was obtained by the absorption of the ion on the cation exchanger from the HCl solution followed by the elution of it with 2 M HPTS. The analytical result of Mo/Fe $\approx$ 3 and the behavior of the aqua ion on the cation exchanger are indicative of the presence of heterometal $Mo_3FeS_4^{4+}$ aqua ion (II). This is in remarkable contrast to the case[15] of reaction of the $Mo_3O_4^{4+}$ aqua ion (III) with iron, the reaction product being simply the reduced form[16] of III with no addition of an iron atom. Exposure of II to the air gives the starting material, i.e., I together with ferrous ion.

Preparation of $[Mo_3FeS_4(NH_3)_9(H_2O)]Cl_4$ (IV) is as follows. The red-purple solution obtained from the mixture of I and an iron wire was introduced into an ice-cold flask containing concentrated aqueous ammonia. Black-purple crystals deposited in a few days.[17]

X-ray crystal structural analysis[18] revealed the existence of a heterometal cubane-type $Mo_3FeS_4^{4+}$ core in IV. The unit cell has two independent chemical units, but no significant structural difference can be seen between the two units. One of the cluster cation is shown in the Figure 1 together with selected bond distances and angles.[19]

There is no clear structural evidence for localized bonding in the $Mo_3FeS_4^{4+}$ core. Therefore if the oxidation state of iron is assumed to be 2+, a mean $Mo^{3.33+}$ state or a formal oxidation state of Mo(IV) + 2Mo(III) is assigned. Each molybdenum is approximately octahedrally coordinated (three μ_3-S and three ammonia molecules, the Mo–Mo and Mo–Fe bonds being ignored), while the iron is tetrahedrally coordinated (three μ_3-S and one water molecule). Electronic spectrum of II, which is shown in Figure 2, together with those of I and IV has peaks at 955 (ϵ 130 (M^{-1} cm^{-1})/mol), 602 (ϵ 454), 505 (ϵ 726), and 470 nm, sh (ϵ 669). The spectrum of II is similar to that of IV. This similarity and the X-ray structure analysis support the presence of heterometal cubane-type $Mo_3FeS_4^{4+}$ aqua ion (probably $[Mo_3FeS_4(H_2O)_{10}]^{4+}$) in solution.

The reaction of I with other metals (e.g., Cu or Hg) is under investigation.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances and angles, and the perspective view of the other $[Mo_3FeS_4(NH_3)_9(H_2O)]^{4+}$ cation (3 pages). Ordering information is given on any current masthead page.

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(11) Palermo, R. E.; Singh, R.; Bashkin, J. K.; Holm, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2600 and references therein.

(12) (a) Averil, B. A. In "Structure and Bonding"; Springer-Verlag: Berlin, 1983; Vol. 53, pp 59–103. (b) Cramer, S. P. In "Advances in Inorganic and Bioinorganic Mechanisms"; Sykes, A. G., Ed.; Academic Press: London, 1983; Vol. 2, pp 259–316.

(13) O'Sullivan, T.; Millar, M. M. *J. Am. Chem. Soc.* **1985**, *107*, 4096 and references therein.

(14) The green band of the unreacted ion I followed the red-purple band.

(15) Shibahara, T.; Akashi, H.; Kuroya, H., unpublished result.

(16) Richens, D. T.; Sykes, A. G. *Inorg. Chim. Acta* **1981**, *54*, L3.

(17) Anal. Found (Calcd): NH_3, 19.49 (19.54)%; H, 3.96 (3.73)%; Cl, 17.76 (18.06)%.

(18) Crystal data: monoclinic system, space group $P2_1$, a = 18.662 (3) Å, b = 14.959 (3) Å, c = 9.208 (2) Å, β = 119.54 (1)°, V = 2236.7 (7) $Å^3$, Z = 4. The structure was solved by direct method (MULTAN) and refined by least squares to a current R value of 0.078 for 3913 reflections ($F_o \geq 2\sigma(F_o)$).

(19) The X-ray structural analysis could not discriminate unequivocally oxygen from nitrogen, a water molecule is tentatively coordinated to the iron atom, and all the coordination sites of the three molybdenum atoms were occupied by ammonia molecules.

X-ray Structure Analysis of the Pentagonal Dodecahedrane Hydrocarbon $(CH)_{20}$

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It has been stated that "the dodecahedrane geometry is exquisite in its perfection".[1] A significant part of the fascination surrounding this almost spherical $(CH)_{20}$ hydrocarbon arises from its exceptional I_h symmetry,[2] regular polyhedral nature, and aesthetically appealing topology. These features, in combination with occlusion by the structural cage of a cavity incapable of solvation, have fostered many innovative theoretical treatments of dodecahedrane's molecular properties. These include assessments of its vibrational frequencies,[3] ordering of orbital energies,[4,5] ionization potential,[6] formation of inclusion compounds,[5,7,8] NMR spin–spin coupling constants,[7a,9] and heat of formation.[10] Following the successful synthetic elaboration of dodecahedrane (**1**) by Paquette and co-workers,[11] some of the unusual physical characteristics of the hydrocarbon were elucidated experimentally.

A matter of continuing interest has been definition of the three-dimensional structure of dodecahedrane by X-ray crystal structure analysis. Precise measurement of bond lengths and bond angles, together with detailed knowledge of the dimensions of the cavity, would provide, inter alia, a reliable foundation for future theoretical work.[12] As a direct result of dodecahedrane's unique shape, however, it has been widely anticipated that the molecule would not crystallize in any preferred orientation. We find instead that the molecule not only adopts a preferred orientation, but takes advantage of the highest crystallographic symmetry available to it.

The X-ray structure determination was achieved with data from a clear, colorless, twinned crystal grown from benzene solution.

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(1) Laszlo, P. *Nouv. J. Chim.* **1983**, *7*, 69.

(2) Gruber, B., Millman, R. S., Eds. "Symmetries in Sciences"; Plenum Press: New York, 1980.

(3) Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 411.

(4) Schulman, J. M.; Venanzi, T.; Disch, R. L. *J. Am. Chem. Soc.* **1975**, *97*, 5335.

(5) Dixon, D. A.; Deerfield, D.; Graham, G. D. *Chem. Phys. Lett.* **1981**, *78*, 161.

(6) Scamehorn, C. A.; Hermiller, S. M.; Pitzer, R. M. *J. Chem. Phys.*, in press.

(7) (a) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 5677. (b) Disch, R. L.; Schulman, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 3297.

(8) Allinger, N. L., private communication (April 21, 1975).

(9) Mislow, K., private communication. For discussion of the method used, see: Baum, M. W.; Guenzi, A.; Johnson, C. A.; Mislow, K. *Tetrahedron Lett.* **1982**, *31*.

(10) (a) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (b) Clark, T.; Knox, T. M.; Mackle, H.; McKervey, M. A. *J. Chem. Soc., Chem. Commun.* **1975**, 666. (c) Clark, T.; Knox, T. M.; McKervey, M. A.; Mackle, H.; Rooney, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 2404. (d) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 1202.

(11) (a) Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503. (b) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *J. Am. Chem. Soc.* **1983**, *105*, 5446. (c) Paquette, L. A.; Miyahara, Y.; Doecke, C. W., *J. Am. Chem. Soc.*, submitted for publication.

(12) The X-ray crystal structure analysis of the D_{3d}-symmetric 1,16-dimethyldodecahedrane has been reported: Christoph, G. G.; Engel, P.; Usha, R.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 784.

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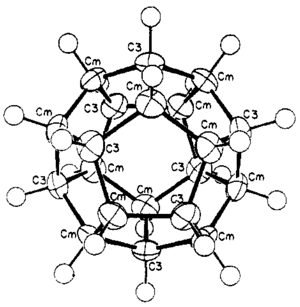
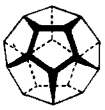
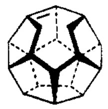


Figure 1. Carbon atoms are drawn at the 50% probability level and hydrogen atoms are drawn on an arbitrary scale. C(3) designates the atom on the threefold axis and C(m) is the atom on the mirror plane.

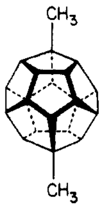
The diffraction pattern was interpreted in terms of a crystal composed of two twins distributed unequally. The unit cell is face-centered cubic with *m*3 Laue symmetry and the systematic absences restrict the space group possibilities to *F*23 or *Fm*3. At room temperature, the cell constant is $a = 10.610$ (3) Å with $Z = 4$ and $\rho_{calcd} = 1.448$ g/cm^3. This structure is therefore isomorphous with that earlier reported for disordered secododecahedrene **2**.[13] Noteworthily, the calculated density of **1** is higher than that of **3** (1.412 g/cm^3).[12]



1



2



3

The twinning was recognized as a result of collecting data in the triply primitive hexagonal cell representation.[14] The not uncommon mode of twinning is such that the h,k,l and k,h,l reflections are interchanged in position.[15] Exact superposition occurs when $l = 3n$, and no overlap occurs otherwise. The intensities were corrected for twinning by using the following relationships:[16]

$$I(hkl) = (1 - \alpha)J(hkl) + \alpha J(khl)$$

$$I(khl) = (1 - \alpha)J(khl) + \alpha J(hkl)$$

A comparison of the intensities of the nonoverlapping reflections resulted in a value for the twin fraction, α, of 0.246. So approximately 25% of the crystal used for data collection is in twin orientation. The standard deviations in the intensities were also corrected for twinning.[16b]

The structure was solved and successfully refined in the centrosymmetric space group *Fm*3. The final *R* value (on *F*) was 0.049 based on 118 intensities with $F_o^2 > 3\sigma F_o^2$. T_h symmetry is crystallographically imposed on the molecule, with the asymmetric unit containing two carbon atoms and two hydrogen atoms.[17] This result conforms to the prediction that gaseous dodecahedrane will have I_h symmetry since T_h is the subgroup of I_h with the highest possible crystallographically allowed symmetry.

The geometry of the molecule obtained here does not deviate significantly from I_h symmetry as can be seen in Figure 1. The framework bonds, at C(3)–C(m) = 1.541 (2) Å and C(m)–C(m) = 1.535 (5) Å, are somewhat shorter than the 1.546-Å value determined for cyclopentane.[18] The exterior C–C–C bond angles [C(m)–C(3)–C(m) = 108.1 (1)°; C(3)–C(m)–C(3) = 107.7 (2)°; C(3)–C(m)–C(m) = 107.9 (4)°] conform nicely to the value expected for perfect dodecahedral symmetry (108°).

Intracavity distances across the center of the molecule are 4.310 (3) Å for C(3)---C(3) and 4.317 (5) Å for C(m)---C(m). Taking account of the generally accepted number for the van der Waals radius of carbon,[19] the transcavity diameter is only 0.91–0.93 Å, too small for encapsulation of any but the smallest ions. Since the structure is face-centered cubic and the centers of the dodecahedrane molecules occupy the corners and the centers of the faces of the unit cell, the packing is cubic closest packing. The shortest intermolecular contacts are 3.98 Å for C---C and 2.33 Å for H---H.

Now that the three-dimensional structure of **1** has become known, the effect of substitution on dodecahedral distortion can now begin to be assessed. We hope to report on these matters at a later date.

Acknowledgment. We gratefully acknowledge the National Institutes of Health for their financial support via Grant AI-11490.

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(13) Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 251.

(14) The triply primitive hexagonal cell is related to the face-centered cubic cell like so: $a_{hexagonal} = 2^{1/2}/2(a_{cubic})$ and $c_{hexagonal} = 3^{1/2}(a_{cubic})$. In the obverse setting for the triply primitive hexagonal cell, the extinction condition is $-h+k+l = 3n$. In this case many reflections satisfying $h-k+l = 3n$ were also observed and were such that the ratios $I(hkl\colon\ h-k+l = 3n)/I(khl)$ were constant for $l \neq 3n$. An awareness of this phenomenon for several crystals along with other observations led to the deduction of the twinning problem. A full description of the structure and the twinning analysis will be forthcoming.

(15) This mode of twinning can be described in real space in the hexagonal system by either a rotation about the *c* axis or by reflection across the (100) plane. Other examples of this type of twinning have been reported by: Jameson, G. B.; Schneider, R.; Dubler, E.; Oswald, H. R. *Acta Crystallogr., Sect. B* **1982**, *B38*, 3016. Zalkin, A.; Forrester, J. D.; Templeton, D. H. *Acta Crystallogr.* **1964**, *17*, 1408.

(16) *I* is the observed intensity, *J* is the corrected intensity based on an untwinned crystal of the same total volume, and α is the twin fraction as defined in: (a) Britton, D. *Acta Crystallogr., Sect. A* **1972**, *A28*, 296. (b) Grainger, C. T. *Acta Crystallogr., Sect. A* **1969**, *A25*, 427.

(17) Prior to recognition of the twinning problem, the structure could be solved in *Fm*3 but could not be successfully refined to a reasonable *R* index in either *Fm*3 or *F*23. The final results after correction for twinning and expressed in the cubic unit cell: Mo Kα radiation, $2\theta_{max} = 55°$, $R_w = 0.051$, weight = $1/\sigma^2(F_o)$, carbon atoms refined anisotropically, hydrogen atoms isotropically. One C–H unit lies on a threefold axis and the other C–H unit lies on a mirror plane: C(3)$x = y = z = 0.1173$ (2), $U_{11} = U_{22} = U_{33} = 0.037$ (1), $U_{12} = U_{13} = U_{23} = -0.009$ (1), and C(m), $x = 0$, $y = 0.1902$ (2), $z = 0.0723$ (2), $U_{11} = 0.045$ (2), $U_{22} = 0.023$ (1), $U_{33} = 0.043$ (2), $U_{12} = U_{13} = 0$, and $U_{23} = -0.008$ (1).

(18) Adams, W. J.; Geise, H. J.; Bartell, L. S. *J. Am. Chem. Soc.* **1970**, *92*, 5013.

(19) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Highly Reduced Organometallics. 18.[1] Tetracarbonylcyclopentadienylmetalates(1–) of Titanium and Zirconium. Structural Characterization of [$(C_6H_5)_4As$][$C_5H_5Ti(CO)_4$]

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Anionic metal carbonyls are important materials in many areas of chemistry, particularly as reagents in chemical synthesis, and have been reported for all d-block transition elements except those of the group 3, 4, and 11 triads.[2] Our recent development of a facile, atmospheric pressure synthesis of the hexacarbonylmetalates(1–) of niobium and tantalum[3] prompted attempts to prepare carbonyl anions of titanium, zirconium, and hafnium by this method. We now report on the synthesis, characterization, and some reactions of the anionic carbonyls of titanium and zirconium, $C_5H_5M(CO)_4^-$. These substances are the first cyclopentadienyl derivatives of the hypothetical heptacarbonyls, $M(CO)_7$, and are the most thermally stable zero-valent carbonyls now known for Ti and Zr.[4] The only previously reported com-

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(1) Part 17: Warnock, G. F. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5016.

(2) (a) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221. (b) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1. (c) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417. (d) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

(3) Dewey, C. G.; Ellis, J. E.; Fjare, K. L.; Pfahl, K. M.; Warnock, G. F. P. *Organometallics* **1983**, *2*, 388.