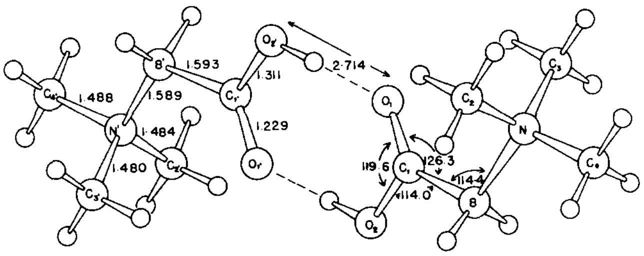


Figure 1. Conformation, interatomic distances (±0.017 Å), and valency angles (±1.0°), averaged according to C_i symmetry, in the asymmetric crystal unit of $Me_3NBH_2CO_2H$; valency angles around nitrogen do not deviate significantly from tetrahedral. Small circles denote calculated hydrogen atom positions.

CAD 3 automated diffractometer using Ni-filtered Cu K_α radiation (λ 1.5418 Å) and the θ-2θ scanning procedure as described previously.[11] The structure was solved by direct methods using the MULTAN program package.[12] Refinement of atomic positional and thermal parameters (anisotropic B, C, N, O; fixed H contributions) converged at $R = 0.109$ over 625 statistically significant $[I > 2.0\sigma(I)]$ reflections. The conformation and mean dimensions of the asymmetric crystal unit which comprises a hydrogen-bonded dimer with approximate C_{2h} symmetry are shown in Figure 1. Although the crystal structure of the corresponding carboxylic acid, 3,3-dimethylbutanoic acid, which lacks the $^-$B-N$^+$ dipole and consequently has a much lower melting point of 6–7 °C, has not been studied the dimensions of **4** may be compared with those of other carboxylic acids. The bond length and valency angle pattern at the carboxyl group in **4** are similar to that in simple carboxylic acids,[13] but the O-H···O hydrogen bonded distance at 2.714 Å in the dimer is slightly longer than the corresponding distance of ca. 2.64 Å in that same class of compounds. The remaining dimensions and molecular conformation reveal no unusual features.

Preliminary in vivo antitumor screens[14] in mice have demonstrated significant antitumor activity for **3** and **4** in the Ehrlich Ascites screen and for **3** in the P_{388} Lymphocytic Leukemia screen. In the Ehrlich screen, dosages of 33.3 mg/kg per day into CF_1 male mice resulted in inhibition of tumor growth[15] of 82.4% for **4** and 69.4% for **3**. In the P_{388} screen, using standard NCI protocols,[16] compound **3** at a dosage of 50 mg/kg per day into DBA/2 male mice exhibited a T/C of 132 compared to the control 5-fluorouracil of 126. Although no specific toxic dose studies have been completed, there have been no signs of toxicity exhibited in the tests at these dosage levels.

Betaine and choline have been implicated as cofactors in the liver for synthesis of cholesterol. Examinations of the serum blood cholesterol levels[14] of male mice after dosing with **4** for 1 week at 1 mg/day resulted in a lowering of serum cholesterol by 29%,[17] considered to be a significant reduction in the mouse.

The synthesis of other boron analogues of amino acids and biological activity studies are in progress.

Acknowledgment. This research was supported, in part, by the Army Research Office. One of us, B.F.S., wishes to thank the Army Research Office for a release time to carry out this research. We also wish to thank Dr. Charles Moreland, North Carolina State University, for obtaining the ^{11}B and ^{13}C data, and the helpful assistance of Dr. Raymond F. Bratton is appreciated.

References and Notes

(1) (a) B. F. Spielvogel, J. M. Purser, and C. G. Moreland, Abstracts Southeast Regional Meeting, American Chemical Society, Richmond, Va., Nov 1969; *Chem. Eng. News*, **33** (Nov. 10, 1969); (b) S. S. Uppal and H. C. Kelly, *Chem. Commun.*, 1619 (1970); (c) C. Weidig, S. S. Uppal, and H. C. Kelly, *Inorg. Chem.*, **13**, 1763 (1974); (d) B. F. Spielvogel, R. F. Bratton, and C. G. Moreland, *J. Am. Chem. Soc.*, **94**, 8597 (1972); (e) P. J. Bratt, M. P. Brown, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 2161 (1974).

(2) Obtainable commercially from Aldrich Chemical Co., and Ventron Corporation.

(3) B. F. Spielvogel, M. K. Das, and R. F. Bratton, manuscript in preparation.

(4) In ppm from internal Me_4Si, positive sign indicates downfield from standard.

(5) (a) In ppm from external $BF_3 \cdot Et_2O$, positive sign indicates upfield from standard. (b) Analyses for indicated elements within ±0.3% were obtained.

(6) It is not necessary to vacuum distill **3** before proceeding with the hydrolysis if only **4** is desired.

(7) A saturated solution of **4** in water is ca. 0.67 M.

(8) After warming the solution for several days at 50–55 °C, eventually over 90% of the theoretical yield of H_2 was obtained.

(9) A decrease in the melting point (with decomposition) is noted after prolonged vacuum or desiccator drying but may be increased close to the original value by allowing the sample to stand in a H_2O saturated atmosphere. This process is currently under investigation. Essentially no change was observed in the elemental analysis of a sample stored in air in a stoppered flask after 4 months.

(10) (a) J. C. Carter and R. W. Parry, *J. Am. Chem. Soc.*, **87**, 2354 (1965); (b) L. J. Malone and R. W. Parry, *Inorg. Chem.*, **6**, 817 (1967).

(11) D. L. McFadden and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 363 (1971).

(12) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).

(13) I. Nahringbauer, *Acta Chem. Scand.*, **24**, 453 (1970); F. J. Strieter D. H. Templeton, R. F. Scheuerman, and R. L. Sass, *Acta Crystallogr.*, **15**, 1233 (1962); F. J. Strieter and D. H. Templeton, *ibid.*, **15**, 1240 (1962); R. F. Scheuerman and R. L. Sass, *ibid.*, **15**, 1244 (1962).

(14) Private communication, I. H. Hall, Department of Medicinal Chemistry, University of North Carolina, Chapel Hill, N.C.

(15) According to standard procedures; see C. Piantadosi, C. S. Kim, and J. L. Irwin, *J. Pharm. Sci.*, **58**, 821 (1969). The control in these screens, 6-mercaptopurine, showed 99.7% inhibition.

(16) R. I. Geran, N. H. Greenberg, M. M. Macdonald, A. M. Schumacher, and B. J. Abbott, *Cancer Chemother. Rep., Part 2*, **3**, 9 (1972).

(17) Hyperlipidemia is a problem in cancer patients.[18] Design of a drug which has both characteristics, i.e., antitumor and hypolipidemic activity is desirable.

(18) M. R. Grigor, M. L. Blank, and F. Snyder, *Cancer Res.*, **33**, 1870 (1973).

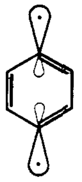
Bernard F. Spielvogel,* Leonard Wojnowich, Mrinal K. Das
Andrew T. McPhail,* Karl D. Hargrave
Paul M. Gross Chemical Laboratory, Duke University
Durham, North Carolina 27706

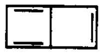
Received May 10, 1976

9,10-Dehydroanthracene. A Derivative of 1,4-Dehydrobenzene

Sir:

Dehydrobenzenes have fascinated chemists since the suggestion of 1,2-dehydrobenzene (benzyne) as a reaction intermediate.[1] Benzyne is now a well-characterized molecule[2,3] with a clearly defined triple bond[4] and a singlet ground state.[5] The isomeric 1,4-dehydrobenzene which has been reported as a transient in time-of-flight mass spectrometry[6] poses a particularly intriguing theoretical problem in that diradical (singlet or triplet) and bicyclic structures are possible.[7-13] It





has, in fact, been suggested that the diradical structure for 1,4-dehydrobenzene and the butalene structure may each represent minima on the C_6H_4 energy surface.[13] Chemical trapping evidence has been obtained for a 1,4-dehydrobenzene with a diradical structure (benzene-1,4-diyl)[14] and for a 1,4-dehydrobenzene with the butalene structure.[15,16] We wish to describe the synthesis, spectroscopic observation, and chemical characterization of 9,10-dehydroanthracene, a derivative of 1,4-dehydrobenzene.

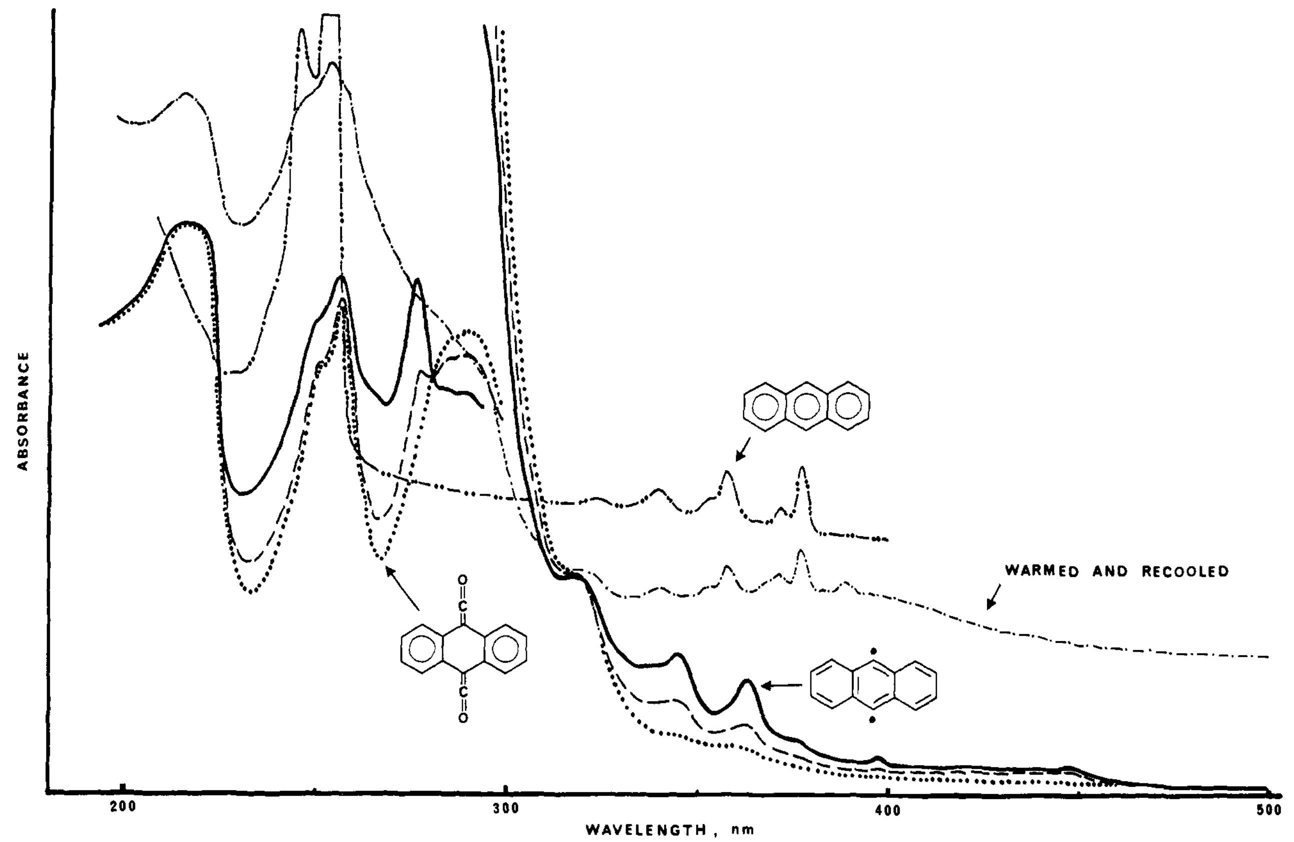
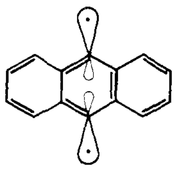
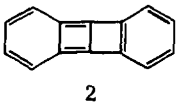


Figure 1. Ultraviolet spectra in a 3-methylpentane glass at 77 K of **5** (···), **5** after 60 min irradiation through quartz (- - -), **6** (—), **6** after warming (-·-·), and authentic anthracene (-·····-).

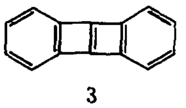
Several structures can be considered for 9,10-dehydroanthracene (**1–4**). Singlet and triplet diradicals (**1**), dibenzobutalenes (**2**, **3**), and a *quintet* state (**4**) are possible. It is an open question whether structures **2** and **3** represent resonance forms of the same structure or tautomeric structures with different equilibrium geometries. We wish to describe the synthesis of 9,10-dehydroanthracene, under conditions which permit spectroscopic observation and chemical characterization.



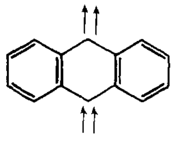
1



2

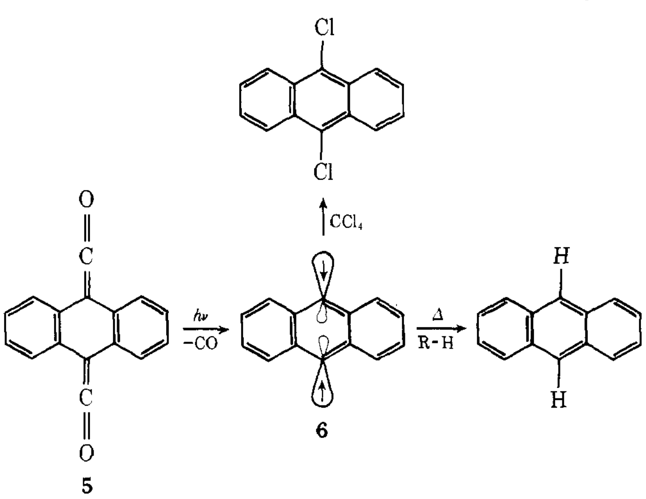


3



4

The bisketene (**5**) prepared by Blomquist and Meinwald[17] was irradiated (λ >200 nm) in a 3-methylpentane glass at 77 K. The progress of the reaction was monitored by ultraviolet spectroscopy (Figure 1). A new species was produced which gave anthracene on warming.[18] Similar photolysis in a 3-methylpentane glass containing 5% carbon tetrachloride gave the same reactive intermediate which on warming gave anthracene and 9,10-dichloroanthracene (identified by ultraviolet spectrum and thin layer chromatographic behavior).[19] Irradiation (λ >200 nm) of **5** matrix-isolated in argon at 8 K gave carbon monoxide (2139 cm^{-1}) and a new species with intense bands at 710, 760 cm^{-1}. When this matrix was warmed to room temperature, the product isolated from the cesium iodide window was anthracene (identified by comparison of the ultraviolet spectrum, mass spectrum, and thin layer chromatographic behavior) and an intractable polymer. These experiments are sensibly interpreted in terms of 9,10-dehydroanthracene as the intermediate. The structure of 9,10-dehydroanthracene is of considerable interest. We have been unable to observe a triplet ESR signal from 9,10-dehydroanthracene (matrix isolated in argon at 10 K)[20] and tentatively conclude that it has a singlet ground state. The choice is then between a singlet diradical structure (**6**) and a dibenzobutalene structure (**2**, **3**). The radical-like abstraction reactions of 9,10-dehydroanthracene suggest that it reacts as the diradical.[21] This could, however, be due to ring opening of a dibenzobutalene structure during the warming process. The general similarity of the ultraviolet spectrum of 9,10-dehydroanthracene ($\lambda_{max}^{3\text{-MeC}_5\text{H}_{11}}$ 256, 276, 320, 345, 363, 378, 397, and 449 nm) to that of anthracene strongly suggests that the singlet



diradical **6** is, in fact, the species we have observed. It remains an open question whether or not dibenzobutalene also represents a potential minimum on this energy surface. The characterization of **6** strongly supports Bergman's evidence[14] on the existence of 1,4-dehydrobenzene. The chemistry of 9,10-dehydroanthracene suggests that it may be an intermediate in the conversion of 1,5-didehydro-3,4-benz[10]annulene to anthracene.[22]

A final point of interest deserves comment. The isosbestic points (280, 320 nm) observed in the ultraviolet spectra during photolysis of **5** and the absence of carbene intermediates (which should have been detected in the ultraviolet and ESR experiments)[23] suggests either that the loss of both molecules of carbon monoxide is operationally concerted or that the intermediate ketene-carbene is destroyed photochemically at a much faster rate than the bisketene.

Acknowledgments. This research was supported by Grant MPS75-10939 from the National Science Foundation.

References and Notes

(1) J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsman, and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953).

(2) R. S. Berry, G. N. Spokes, and M. Stiles, *J. Am. Chem. Soc.*, **82**, 5240 (1960); **84**, 3570 (1962).

(3) O. L. Chapman, K. C. Mattes, C. L. McIntosh, J. Pacansky, G. V. Calder, and G. Orr, *J. Am. Chem. Soc.*, **95**, 6134 (1973).

(4) O. L. Chapman, C.-C. Chang, J. Kolc, N. R. Rosenquist, and H. Tomioka, *J. Am. Chem. Soc.*, **97**, 6586 (1975).

(5) R. W. Murray, cited in R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, N.Y., 1967, p 274.

(6) R. S. Berry, J. C. Clardy, and M. E. Schafer, *Tetrahedron Lett.*, 1003 (1965).

(7) J. D. Roberts, *J. Am. Chem. Soc.*, 74, 4579 (1952).

(8) M. J. S. Dewar and G. J. G. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

(9) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Am. Chem. Soc.*, **87**, 1499 (1967).

(10) M. D. Gheorghiu and R. Hoffmann, *Rev. Roum. Chim.*, **14**, 947 (1969).

(11) J. F. Olsen, *J. Mol. Struct.*, **8**, 307 (1971).

(12) D. L. Wilhite and J. L. Whitten, *J. Am. Chem. Soc.*, **93**, 2858 (1971).

(13) M. J. S. Dewar and W.-K. Li, *J. Am. Chem. Soc.*, **96**, 5569 (1974).

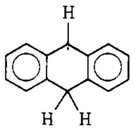
(14) R. R. Jones and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 661 (1972).

(15) R. Breslow, J. Napierski, and T. C. Clarke, *J. Am. Chem. Soc.*, **97**,6275 (1975).

(16) For general accounts of work on 1,4-dehydrobenzenes see R. G. Bergman, *Acc. Chem. Res.*, **6**, 25 (1973), and R. Breslow, *Pure Appl. Chem.*, **28**, 111 (1971).

(17) A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **79**, 2021 (1957).

(18) A referee has raised the question whether the species observed in the ultraviolet spectroscopic experiments might be the radical i. In an effort



i

to exclude i on a rigorous basis, we have irradiated (λ >200 nm) 9,10-dihydroanthracene in 3-methylpentane at 77 K to generate i (see E. Migirdicyan and J. Bandet, *J. Am. Chem. Soc.*, **97**, 7400 (1975), for the technique). In this experiment anthracene and a reactive species believed to be the radical i are generated. The reactive species is converted to anthracene on warming to room temperature. The reactive intermediate has a sharp ultraviolet maximum at 352 nm (which corresponds to a minimum in the ultraviolet spectrum of 9,10-dehydroanthracene). The position of this band is in the wavelength range expected for the radical i. Diphenylmethyl radical, for example, is reported to have λ_{max} 338 nm (H. T. J. Chilton and G. Porter, *Spectrochim. Acta*, **16**, 390 (1960)) and λ_{max} 335 nm (G. Porter and M. W. Windsor, *Nature (London)*, **180**, 187 (1957)). Irradiation of diphenylmethane in our apparatus under the same conditions used for 9,10-dihydroanthracene gave diphenylmethyl radical (λ_{max} 335 nm). The ESR spectrum of the radical i has been observed in the γ-irradiation of solid anthracene (L. A. Harrah and R. C. Hughes, *Mol. Cryst.*, **5**, 141 (1968); H. Blum, D. L. Mattern, and R. A. Arndt, *ibid.*, **3**, 269 (1967).

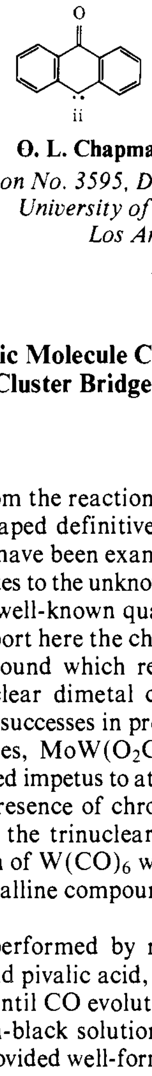
(19) Significantly higher concentrations of carbon tetrachloride in the 3-methylpentane gave problems in generation of the intermediate..

(20) A weak $g = 2$ (radical) signal is observed. It is much narrower than the signal reported for i (see footnote 18). It is, in fact, not reasonable that i should be formed since no hydrogen donor is available in the argon matrix.

(21) Compare this result with the earlier observations of Jones and Bergman[14] and Breslow, Napierski, and Clarke.[15]

(22) N. Darby, C. V. Kim, J. A. Salaün, K. W. Shelton, S. Takada, and S. Masamune, *Chem. Commun.*, 1516 (1971).

(23) We have, for example, observed 9-oxo-10-anthracenylidene (ii).



ii

O. L. Chapman,* C.-C. Chang, J. Kolc
Contribution No. 3595, Department of Chemistry
University of California, Los Angeles
Los Angeles, California 90024
Received March 1, 1976

A Novel Heterometallic Molecule Consisting of a New Triangular Tungsten Cluster Bridged by Oxochromium and Alkoxy Ligands

Sir:

Species resulting from the reactions of $W(CO)_6$ with carboxylic acids have escaped definitive characterization even though such reactions have been examined in several laboratories[1-3] as possible routes to the unknown dimers $W_2(O_2CR)_4$, isostructural with the well-known quadruply bonded dimers $Mo_2(O_2CR)_4$.[4] We report here the characterization of a new tungsten cluster compound which resulted from efforts to prepare the heteronuclear dimetal carboxylate derivatives $WCr(O_2CR)_4$. Recent successes in preparation of the related heteronuclear analogues, $MoW(O_2CC(CH_3)_3)_4$[5] and $MoCr(O_2CCH_3)_4$,[6] provided impetus to attain this goal. However, as shown below, the presence of chromium in the reactions instead served to trap the trinuclear tungsten carboxylate, resulting from reaction of $W(CO)_6$ with carboxylic acids, in a readily isolated crystalline compound of fascinating architecture.

The reaction was performed by refluxing a solution of $W(CO)_6$, $Cr(CO)_6$, and pivalic acid, in the mole ratio 1:1:2, in *o*-dichlorobenzene until CO evolution ceased. Removal of solvent from the green-black solution by very slow vacuum distillation at 25 °C provided well-formed crystals of the dark green product. The mass spectrum showed a set of lines for the molecular ion centered around 2055 amu, having relative intensities in good agreement with those calculated for the composition $W_3Cr_3O_{28}C_{65}H_{119}$. Subsequent x-ray diffraction structure determination[7] showed the compound is best formulated as $W_3(OCH_2C(CH_3)_3)O_3Cr_3(O_2CC(CH_3)_3)_{12}\cdot 2C_6H_4Cl_2$. Both the analytical data and structure determination indicated, however, that full occupancy of the two sites for the solvent molecules is not achieved, resulting in the inclusion of about 1.5 mol of solvent per mole of compound.[8] The molecular structure of $W_3(OCH_2C(CH_3)_3)O_3Cr_3(O_2CC(CH_3)_3)_{12}$ is depicted in Figure 1. At the center of this beautifully interwoven, multiply connected molecule is the important new triangular tungsten cluster with bridging "oxo" oxygen atoms over the edges and the "alkoxo" oxygen of $OCH_2C(CH_3)_3$ triply bridging over the opposite face as shown in Figure 2. In addition to the bridging oxo and alkoxo O atoms each tungsten is bound to three carboxylate O atoms, one from each of three different carboxylate groups. As shown in Figure 2, the Cr atoms are bound to the bridging oxo O atoms to form W_2CrO triangular arrays reminiscent of the Cr_3O units found previously in $Cr_3O(O_2CCH_3)_6(H_2O)_3{}^+$.[9]

The coordination sphere about both W and Cr includes six O atoms in deformed octahedral arrangement. Each W atom also is bonded to the two adjacent W atoms to form the equilateral triangle, d(W-W) = 2.608 (1), 2.608 (1), 2.614 (1) Å. The nearest neighbor W-Cr distances, average 3.528 (4) Å, attest to the absence of W-Cr bonding. There are no important differences in the bonding about the individual metal atoms