(deg) parameters

$$\theta_z = 100.99 - 86.5(r_z - 2.215) \qquad (4)$$

On the other hand, since the r_z(P–Br) is estimated to be 2.2155 ± 0.004 Å from the electron diffraction $r_\alpha{}^0$ parameter given in Table III, the θ_z angle is calculated to be 100.95 ± 0.35°. Accordingly, θ_z (the angle defined with reference to the average nuclear positions *for the ground vibrational state*) is nearly equal to the θ_α (the angle defined with reference to the *temperature-averaged* nuclear positions) given in Table III (100.98 ± 0.4°). In other words, the θ_α angle appears to be almost temperature independent, in spite of the relatively low frequencies[19] of bending vibrations. A similar remark has previously been made by one of the authors.[5,23]

The observed bond angle is shown to be the largest among those in the phosphorus trihalides listed in Table V.

TABLE V

STRUCTURE OF PHOSPHORUS TRIHALIDES

	r_g(P–X), Å	θ_α(X–P–X), deg	Ref
PF_3	1.570 ± 0.0012	97.8 ± 0.2	5
PCl_3	2.040 ± 0.0014	100.27 ± 0.09	7
PBr_3	2.220 ± 0.003	101.0 ± 0.4	Present study

Acknowledgments.—The authors are indebted to Dr. T. Fukuyama for his technical assistance in the diffraction experiment and analysis. K. K. is also grateful to Professor R. A. Bonham and Dr. E. M. A. Peixoto of Indiana University and Dr. Y. Murata of Gakushuin University for their helpful discussions in the initial stage of the present study. The research was supported by grants from Takeda Science Foundation.

[23] K. Kuchitsu, *Bull. Chem. Soc. Jap.*, **44**, 96 (1971).

CONTRIBUTION FROM THE LAWRENCE BERKELEY LABORATORY AND THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720

The Crystal Structure of Cesium 3,3′-*commo*-Bis[nonahydro-1,2-dimethyl-1,2-dicarba-3-chroma-*closo*-dodecaborate] Hydrate, a Hydrate of a Chromium Metallocarborane Salt[1]

BY DAVID ST. CLAIR, ALLAN ZALKIN, AND DAVID H. TEMPLETON*

Received January 28, 1971

The crystal structure of the monohydrated cesium salt of $Cr[B_9C_2H_9(CH_3)_2]_2^-$, 3,3′-*commo*-bis[nonahydro-1,2-dimethyl-1,2-dicarba-3-chroma-*closo*-dodecaborate](1−), has been determined by X-ray diffraction. The crystals are tetragonal, space group $P4_12_12$ (or $P4_32_12$), with $a = 9.938 \pm 0.004$ Å and $c = 22.739 \pm 0.007$ Å. With four molecules of $CsCr[B_9C_2H_9(CH_3)_2]_2 \cdot H_2O$ in the unit cell the density is calculated to be 1.55 g/cm³. The model was refined by least squares to a conventional R of 0.047 for 1957 point group independent reflections, measured with a scintillation counter (θ–2θ scan). The metallocarborane anion consists of two icosahedra sharing a chromium atom as common vertex. Each icosahedron is composed of the chromium atom, nine boron atoms each bonded to a terminal hydrogen atom, and two carbon atoms each bonded to a methyl group. The carbon atoms in the cage are bonded to each other and to the chromium atom. The pair of methyl groups on one cage are rotated as far as possible from those on the other. The shape of the anion corresponds closely to symmetry $2/m$. Average bond distances are Cr–C = 2.27, Cr–B = 2.26, C–C(methyl) = 1.52, C–C(cage) = 1.64, C–B = 1.72, and B–B = 1.77 Å.

Introduction

Ruhle and Hawthorne have recently reported[2] the preparation of $Cr[B_9C_2H_9(CH_3)_2]_2^-$, another in the series of transition metal derivatives of the dicarbollide ion, $B_9C_2H_{11}{}^{2-}$. In this anion, 3,3′-*commo*-bis[nonahydro-1,2-dimethyl-1,2-dicarba-3-chroma-*closo*-dodecaborate](1−),[3] the chromium is in a formal 3+ valence state and is bonded to two icosahedral dicarbollide ions in which the hydrogen atoms on the carbons of $B_9C_2H_{11}{}^{2-}$ have been replaced by methyl groups. It was expected that the complex would have a sandwich-type structure in which the chromium would simultaneously occupy an apex in each of two icosahedra.

The crystal structure determination of the monohydrate of the cesium salt of the metallocarborane anion, $CsCr[B_9C_2H_9(CH_3)_2]_2 \cdot H_2O$, is reported here. The sandwich nature of the anion structure, shown in Figure 1, is confirmed and it is shown that the cages are staggered across the chromium with the carbon atoms of one cage rotated as far as possible from those in the other.

Experimental Section

The dark red crystals of $CsCr[B_9C_2H_9(CH_3)_2]_2 \cdot H_2O$ were well-formed square prisms elongated along [001]. The largest faces were (110). The crystal used for the final intensity measurements was a prism 0.10 × 0.10 mm in cross section and was cut parallel to (001) to a thickness of 0.09 mm. It was glued to the tip of a glass fiber with [001] as the rotation axis.

After preliminary examination by photographic methods, the space group absences were checked and more accurate cell dimensions were obtained from measurements on the $h00$, $0k0$, and $00l$ reflections with a manually operated General Electric diffractometer using copper radiation (Cu Kα_1; λ 1.5405 Å). A card-controlled General Electric diffractometer equipped with a quarter-circle, Eulerian-cradle goniostat was used for collecting intensity data. Copper Kα radiation filtered with 0.003 in. of

---

[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] H. W. Ruhle and M. F. Hawthorne, *Inorg. Chem.*, **7**, 2279 (1968).

[3] This name comes from the American Chemical Society approved nomenclature rules: *ibid.*, **7**, 1945 (1968). The name given by Ruhle and Hawthorne in ref 2 is bis[π-(3)-1,2-dimethyl-1,2-dicarbollyl]chromium(III).

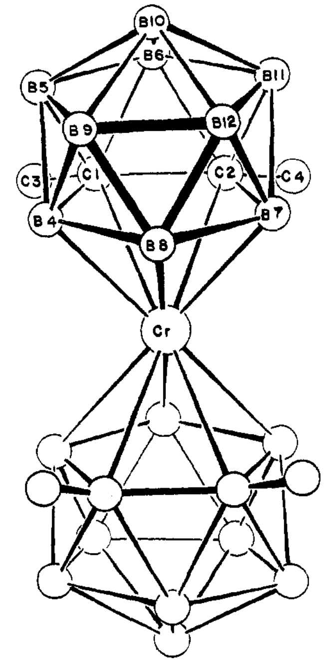


Figure 1.—Skeletal drawing of the $Cr[B_9C_2H_9(CH_3)_2]_2^-$ anion (hydrogen atoms not shown) and numbering system.

nickel was detected by a scintillation counter equipped with a pulse height discriminator. The integrated intensity of each reflection was measured by scanning in 2θ across the peak beginning 0.65° below the 2θ value for diffraction of $K\alpha_1$, scanning at a rate of 1°/min until 2θ reached 0.65° above the 2θ value at which the $K\alpha_2$ beam was diffracted. Ten-second background counts were taken with the apparatus stationary, 0.5° below and above the 2θ scan limits. The final ϕ value was approached in an increasing direction for all reflections to minimize the error due to backlash, which had become a problem. In order to check for possible systematic variations in the intensity data, four standard reflections were remeasured periodically. The maximum variations from the respective averages were 7, 9, 16, and 4%; however, no systematic trend in these variations was observed.

We used a CDC 6600 computer. The raw data were converted into intensities, I, and standard deviations, $\sigma(I)$, were derived according to the equations $I = C - (t_c/2t_b)(B_1 + B_2)$ and $\sigma^2(I) = C + (t_c^2/4t_b^2)(B_1 + B_2)$, where C is the total count accumulated in a scan of time t_c, and B_1 and B_2 are the background counts each obtained in time t_b. When a reflection was measured more than once, the intensities were averaged and the standard deviation was set equal to the greater of $(\Sigma\sigma_i^2)^{1/2}/n$ or $(\Sigma\Delta_i^2)^{1/2}/(n - 1)$, where σ_i and Δ_i are the standard deviation of the ith measurement and the deviation of the ith measurement from the average, respectively, and n is the number of measurements. To reduce the weight given to intense reflections, an additional term, $(0.08I)^2$, was included in the calculation of $\sigma^2(F^2)$: $\sigma^2(F^2) = [\sigma^2(I) + (0.08I)^2]/(Lp)^2$, where L and p are the Lorentz and polarization factors.

The intensities were measured out to a limiting 2θ of 147° [$(\sin\theta)/\lambda = 0.622$] for all reflections in the octant with all-positive hkl. These reflections are independent in point group 422 but contain Friedel pairs hkl and khl which are equal except for anomalous dispersion effects. This gave a total of 2233 data, excluding the systematic space group absences, of which 274 had intensities less than the estimated standard deviation.

An absorption correction was attempted, but it failed to improve the agreement between observed and calculated structure factors. This failure is suspected to result from an error in the computer program, but the time available for this research did not permit this error to be identified. To avoid the risk of an invalid correction, we report the data uncorrected for absorption. The absorption coefficient for copper radiation is estimated as $\mu = 167$ cm^{-1}. We estimate an average error in F of the order of 5% because of absorption.

Refinements were done with our unpublished full-matrix least-squares program which minimizes $R_2^2 = \Sigma w(\Delta F)^2/\Sigma w|F_o|^2$, with weights $w = [\sigma(F)]^{-2}$. Temperature factors were of the form $\exp(-B(\sin\theta)^2/\lambda^2)$ for hydrogen atoms and $\exp(-\Sigma_i\Sigma_j B_{ij}h_i \cdot h_j b_i b_j/4)$ for other atoms, where b_i is the length of the ith reciprocal cell dimension. The neutral-atom scattering factors of Stewart, Davidson, and Simpson[4] were used for hydrogen and those of Cromer and Waber[5] for other atoms. Cromer's corrections[6] −1.40 and −0.13 for the real part and 7.75 and 2.59 for the imaginary part of the anomalous dispersion effect for cesium and chromium, respectively, were used. The stereoscopic drawings were made with Johnson's ORTEP program.[7]

Crystal Data

The unit cell is tetragonal with cell dimensions $a = 9.938 \pm 0.004$ Å and $c = 22.739 \pm 0.007$ Å. With four formula units, $CsCr[B_9C_2H_9(CH_3)_2]_2 \cdot H_2O$, in the unit cell, the density is calculated to be 1.55 g/cm^3. Reflections $00l$ are absent unless $l = 4n$, and reflections $h00$ are absent unless $h = 2n$. These rules are characteristic of two space groups $P4_12_12$ and $P4_32_12$ which are enantiomorphic and are equally likely for various specimens. They are equivalent in intensity calculations except for the effect of anomalous dispersion. For the crystal studied here the space group was $P4_12_12$, with equivalent positions: x, y, z; $-x, -y, {}^1/_2 + z$; ${}^1/_2 - y, {}^1/_2 + x, {}^1/_4 + z$; ${}^1/_2 + y, {}^1/_2 - x, {}^3/_4 + z$; $y, x, -z$; $-y, -x, {}^1/_2 - z$; ${}^1/_2 - x, {}^1/_2 + y, {}^1/_4 - z$; ${}^1/_2 + x, {}^1/_2 - y, {}^3/_4 - z$.

Determination of the Structure

At the start the space group was assumed to be $P4_12_12$. From a three-dimensional Patterson function it was easy to locate the cesium and chromium atoms in special positions 4e (site symmetry 2) and to determine their variable coordinates. Several cycles of least-squares refinement of these coordinates and isotropic thermal parameters gave $R = \Sigma|\Delta F|/\Sigma|F_o| = 0.24$. These atoms were used to phase a three-dimensional Fourier calculation on which appeared all the atoms except hydrogen, although the water molecule was not recognized until later. Atoms were designated as boron or carbon on the basis that the methyl groups were expected to be attached to carbon atoms in the cage. Several cycles of least-squares refinement (with isotropic thermal parameters) of these 15 atoms gave $R = 0.14$ for all 2233 data. A bond distance calculation indicated that the correct choice had been made for the positions of the carbon atoms in the cage. Giving the cesium and chromium atoms anisotropic thermal parameters and including the anomalous dispersion corrections, further least-squares refinement using only the data with $I \geqq \sigma(I)$ gave $R = 0.063$ for 1959 data.

To test the enantiomorphic structure in space group $P4_32_12$, the coordinates of all atoms were inverted through the origin. A refinement in $P4_32_12$ gave $R = 0.095$ compared to 0.063 in $P4_12_12$ under identical conditions. All further calculations were done in $P4_12_12$. This choice is confirmed by excellent agreement in magnitude and sign of observed and calculated values of $|F(hkl)| - |F(khl)|$ after the final refinement.

Further refinement was done with anisotropic temperature factors for all atoms. In a three-dimensional difference Fourier function the largest peak (magnitude 4 e$^-$/Å^3) was identified as a water of crystallization. Nine of the twelve next largest peaks corresponded to hydrogen atoms attached to the boron atoms. Indications for the presence of the methyl hydrogen atoms were found but were less clear than the peaks for hydrogen on boron. The hydrogen atoms of the water molecule were not found in this map.

Hydrogen atoms were assigned isotropic temperature factors with the constraints that the parameter had the same value for all hydrogen atoms on boron and a different common value for methyl hydrogen atoms. Oxygen was given an anisotropic temperature factor. Refinement gave $R = 0.052$ for 1959 data. It was noticed that the strongest reflections were observed weaker than calculated, as results from the extinction effect or from exceeding the capacity of the scintillation counter. Zero weight was assigned to the two strongest reflections. The discrepancies of the other structure factors did not correlate well enough with intensity to justify an extinction correction and

---

[4] R. G. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175, Table II (1965).

[5] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[6] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[7] C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

none was made. It is estimated that the correction (of the structure factor) would be of the order of 10% for the third strongest reflection and less than 5% for all others.

Further refinement gave $R = 0.047$ for 1957 data and $R = 0.062$ for all 2233 data. The weighted R value, $R_2 = [\Sigma w \cdot (\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$, was 0.058. The standard deviation of an observation of unit weight is calculated to be 1.08. Root-mean-square averages of $w^{1/2}|\Delta F|$ taken over small intensity intervals approximated 1.1 over the entire intensity range. On the final cycle of refinement no coordinate shifted by more than 0.1σ and no thermal parameter by more than 0.2σ.

Final atomic coordinates and thermal parameters are given in Tables I–III. Bond distances are given in Table IV. Average values for various types of bond angles are listed in Table V. In Table VI are listed the distances from cesium and oxygen to their neighbors.[8]

TABLE I

COORDINATES FOR ATOMS EXCEPT HYDROGEN[a]

Atom	x	y	z
Cs	0.13791 (5)	x	0
Cr	0.52992 (9)	x	0
C(1)	0.3266 (6)	0.6165 (6)	−0.0239 (2)
C(2)	0.4413 (7)	0.7344 (7)	−0.0222 (3)
C(3)	0.2776 (8)	0.5576 (9)	−0.0819 (3)
C(4)	0.5068 (10)	0.7858 (8)	−0.0783 (3)
B(4)	0.3231 (7)	0.5302 (8)	0.0410 (3)
B(5)	0.1987 (8)	0.6531 (8)	0.0254 (3)
B(6)	0.2740 (8)	0.7802 (8)	−0.0158 (3)
B(7)	0.5222 (7)	0.7339 (7)	0.0430 (3)
B(8)	0.4453 (8)	0.6056 (8)	0.0864 (3)
B(9)	0.2741 (7)	0.6477 (8)	0.0954 (3)
B(10)	0.2457 (8)	0.8050 (8)	0.0595 (3)
B(11)	0.3990 (8)	0.8567 (9)	0.0282 (3)
B(12)	0.3989 (7)	0.7762 (8)	0.0968 (3)
O(1)	0.9064 (13)	x	0

[a] The numbering system is shown in Figure 1. Standard deviations of the least significant digits estimated by least squares are given in parentheses.

TABLE II

THERMAL PARAMETERS FOR ATOMS EXCEPT HYDROGEN

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cs	4.14 (2)	B_{11}	2.11 (2)	0.70 (2)	−0.16 (2)	$-B_{13}$
Cr	2.17 (3)	B_{11}	1.69 (5)	0.01 (4)	0.18 (3)	$-B_{13}$
C(1)	2.6 (3)	2.6 (3)	1.5 (2)	0.6 (2)	0.0 (2)	−0.3 (2)
C(2)	3.3 (3)	2.1 (3)	2.0 (2)	−0.2 (2)	0.4 (2)	0.2 (2)
C(3)	3.5 (4)	4.2 (4)	2.6 (3)	0.7 (3)	−0.9 (2)	−0.9 (2)
C(4)	4.8 (4)	3.2 (3)	2.7 (3)	0.7 (3)	1.0 (3)	0.7 (2)
B(4)	2.1 (3)	2.4 (3)	1.9 (3)	0.1 (2)	0.5 (2)	0.0 (2)
B(5)	2.2 (3)	2.9 (3)	2.3 (3)	−0.1 (3)	0.0 (2)	−0.1 (3)
B(6)	3.1 (3)	2.2 (3)	2.5 (3)	0.8 (2)	0.4 (2)	0.2 (2)
B(7)	2.0 (3)	2.0 (3)	2.2 (3)	−0.5 (2)	0.3 (2)	−0.6 (2)
B(8)	2.7 (3)	3.5 (4)	1.4 (2)	0.7 (2)	0.2 (2)	0.0 (2)
B(9)	2.2 (3)	2.2 (3)	2.4 (3)	0.2 (2)	0.2 (2)	0.2 (2)
B(10)	3.0 (3)	2.3 (3)	2.1 (3)	0.4 (3)	0.3 (2)	−0.4 (2)
B(11)	3.0 (3)	2.6 (3)	2.5 (3)	−0.1 (3)	0.6 (2)	0.0 (3)
B(12)	2.3 (3)	2.8 (3)	2.3 (3)	0.0 (2)	0.2 (2)	−1.0 (2)
O(1)	12.5 (8)	B_{11}	15.8 (15)	−2.2 (11)	−0.7 (9)	$-B_{13}$

TABLE III

PARAMETERS FOR HYDROGEN ATOMS[a]

Atom	x	y	z
H(4)	0.283 (7)	0.419 (7)	0.038 (3)
H(5)	0.095 (7)	0.615 (7)	0.012 (3)
H(6)	0.239 (7)	0.835 (7)	−0.056 (3)
H(7)	0.641 (7)	0.763 (6)	0.047 (3)
H(8)	0.497 (7)	0.547 (7)	0.127 (3)
H(9)	0.222 (7)	0.619 (7)	0.139 (3)
H(10)	0.173 (6)	0.871 (7)	0.078 (3)
H(11)	0.428 (7)	0.969 (7)	0.015 (3)
H(12)	0.427 (7)	0.838 (7)	0.136 (3)
H(31)	0.32 (1)	0.60 (1)	−0.112 (6)
H(32)	0.31 (1)	0.46 (1)	−0.089 (5)
H(33)	0.17 (1)	0.55 (1)	−0.085 (5)
H(41)	0.60 (1)	0.81 (1)	−0.064 (5)
H(42)	0.44 (1)	0.81 (1)	−0.103 (6)
H(43)	0.55 (1)	0.72 (1)	−0.095 (6)

[a] Atoms H(4)–H(12) are numbered according to the boron to which each is bonded. The refined common thermal parameter for these atoms is $B = 2.2 \pm 0.6$ Å². Atoms H(31)–H(33) and H(41)–H(43) are bonded to the methyl carbons C(3) and C(4), respectively. The refined common thermal parameter for these is $B = 8 \pm 1$ Å².

TABLE IV

BOND DISTANCES (Å)[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Cr	C(1)	2.262	B(8)	B(12)	1.77
Cr	C(2)	2.272	B(9)	B(12)	1.78
Cr	B(4)	2.257	B(10)	B(5)	1.76
Cr	B(7)	2.251	B(10)	B(6)	1.75
Cr	B(8)	2.266	B(10)	B(9)	1.79
C(1)	C(3)	1.52	B(10)	B(11)	1.76
C(1)	C(2)	1.64	B(10)	B(12)	1.77
C(1)	B(4)	1.71	B(11)	B(12)	1.76
C(1)	B(5)	1.73	B(4)	H(4)	1.18
C(1)	B(6)	1.72	B(5)	H(5)	1.14
C(2)	C(4)	1.52	B(6)	H(6)	1.12
C(2)	B(6)	1.73	B(7)	H(7)	1.22
C(2)	B(7)	1.69	B(8)	H(8)	1.21
C(2)	B(11)	1.72	B(9)	H(9)	1.15
B(4)	B(5)	1.77	B(10)	H(10)	1.06
B(4)	B(8)	1.76	B(11)	H(11)	1.19
B(4)	B(9)	1.77	B(12)	H(12)	1.11
B(5)	B(6)	1.74	C(3)	H(31)	0.9
B(5)	B(9)	1.76	C(3)	H(32)	1.1
B(6)	B(11)	1.77	C(3)	H(33)	1.1
B(7)	B(8)	1.79	C(4)	H(41)	1.0
B(7)	B(11)	1.76	C(4)	H(42)	0.9
B(7)	B(12)	1.78	C(4)	H(43)	0.9
B(8)	B(9)	1.76			

[a] Standard deviations estimated by least squares: Cr–B and Cr–C, 0.007 Å; C–C, C–B, and B–B, 0.01 Å; B–H, 0.07 Å; C–H, 0.1 Å.

TABLE V

AVERAGE BOND ANGLES IN THE CAGE[a]

Angles around triangular faces			Angles around pentagonal rings		
Atoms	N	Angle, deg	Atoms	N	Angle, deg
CCrC	1	42.3 (2)	CCrB	4	75.1 (3)
CCrB	2	44.1 (4)	BCrB	1	77.8 (3)
BCrB	2	46.2 (4)	CrCB	4	126.1 (8)
CrCC	2	68.9 (5)	CrBB	6	122.9 (4)
CrBC	2	68.4 (6)	CCB	4	110.5 (2)
CrCB	2	67.6 (2)	BCB	2	112.5 (4)
CrBB	4	66.9 (3)	CBB	12	105.9 (2)
CCB	2	61.7 (4)	BBB	23	107.8 (2)
BCB	4	61.6 (4)			
CBB	8	59.2 (3)			
BBB	30	60.0[b]			

[a] In parentheses are the standard deviations of the last digits, estimated from the least-squares results or the scatter of the N values included in the average, whichever gives the larger result.
[b] Cannot be otherwise for a triangle.

Discussion

This study confirms the expected identity and structure of this substance with the exception that the water of crystallization was not known to be present. Its topology as a sandwich compound permits various conformations which differ in the rotation of one cage with respect to the other and in the angular positions of the methyl hydrogen atoms. The structure found for the anion skeleton is shown in Figure 1, and stereoscopic drawings of the complete anion are in Figure 2. The

---

[8] A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

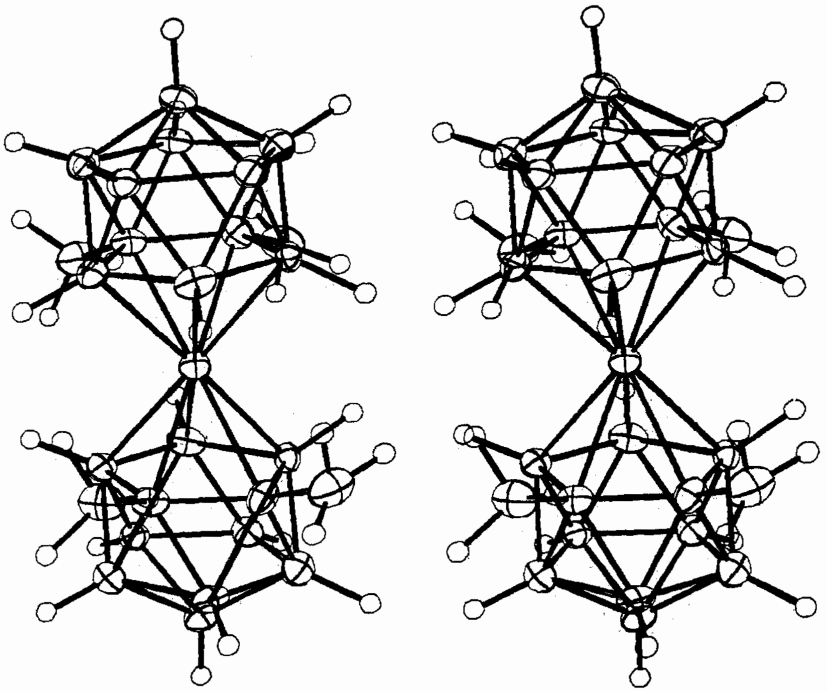


Figure 2.—Stereoscopic pair drawing of the anion.

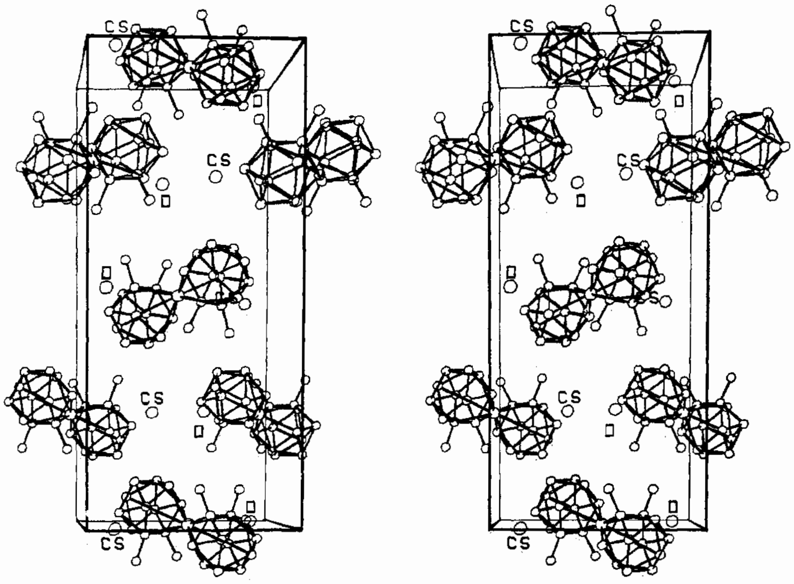


Figure 3.—Stereoscopic pair drawing of the unit cell (hydrogen atoms not shown) looking down the *b* axis. The *a* axis is horizontal and the *c* axis is vertical. The anions centered at $z = {}^1/_4$ and ${}^3/_4$ should be duplicated at the rear of the cell, but these repetitions have been omitted for clarity.

Table VI

Nearest Neighbors of Oxygen and Cesium

Oxygen neighbors		Cesium neighbors	
Atoms	Distance, Å	Atoms	Distance, Å
2 H (7)	3.18 (7)	2 H(9)	2.90 (7)
2 H(10)	3.21 (7)	2 H(10)	3.20 (7)
2 H(31)	3.24 (14)	2 H(8)	3.23 (7)
Cs	3.25 (2)	O(1)	3.25 (2)
2 H(8)	3.26 (7)	2 H(4)	3.26 (7)

space group symmetry includes a twofold axis which relates one cage to the other, but no restriction is imposed by this symmetry on the relative rotation of the cages or of the methyl groups in the same cage. If one disregards hydrogen atoms, the anion is nearly centric and can be brought into exact conformity with symmetry C_{2h} if atoms are shifted by 0.08 Å or less. On steric grounds one expects the cages to be in a staggered rather than an eclipsed relation to each other. Of the three such conformations which are distinct, the observed one is the only one which does not have methyl groups on the two cages in close proximity to each other. On the other hand, the conformation of the methyl hydrogen atoms is not at all centric, a structure which would place hydrogen atoms in opposition to each other. The methyl groups are rotated so that atom H(31) is approximately equidistant (2.5 ± 0.2 Å) from H(42) and H(43).

The bond distances and angles listed in Tables IV and V reveal no surprises when compared with other polyhedral carborane structures.[9] The Cr atom is situated very nearly exactly over the center of the pentagonal face of each carbollide ion, with the differences in Cr–B and Cr–C bond distances hardly exceeding the standard deviations.

The molecular packing, shown in Figure 3, is dominated by the bulky anions which are close to a body-centered-cubic packing. The cesium ions and water molecules fit into the structure without any strong interactions with neighbors. The water molecule has no neighbors suitable for hydrogen bonding, and therefore it is not surprising that it is observed to have large amplitudes of thermal motion nor that we failed to detect its hydrogen atoms. We cannot exclude the possibility that the large thermal parameters in part reflect incomplete occupancy of the water sites. The thermal parameters listed in Table II correspond to rms displacements along the principal axes: 0.16, 0.21, and 0.25 Å for Cs; 0.36, 0.42, and 0.46 Å for oxygen.

Acknowledgment.—We thank Professor M. Frederick Hawthorne for providing the crystals used in this work.

[9] D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **8**, 2080 (1969); P. T. Greene and R. F. Bryan, *ibid.*, **9**, 1464 (1970); R. W. Rudolph, J. L. Pflug, C. M. Bock, and M. Hodgson, *ibid.*, **9**, 2274 (1970); T. F. Koetzle and W. N. Lipscomb, *ibid.*, **9**, 2279 (1970); D. St. Clair, A. Zalkin, and D. H. Templeton, *J. Amer. Chem. Soc.*, **92**, 1173 (1970); M. R. Churchill and K. Gold, *ibid.*, **92**, 1180 (1970); R. M. Wing, *ibid.*, **92**, 1187 (1970), and references to earlier work found therein.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF ARKANSAS, FAYETTEVILLE, ARKANSAS 72701,
AND CALVIN COLLEGE, GRAND RAPIDS, MICHIGAN 49506

The Crystal and Molecular Structure of Tris(1,2-dimethylhydrazino)diphosphine, $P_2(NCH_3)_6$, a Phosphorus–Nitrogen Cage Molecule

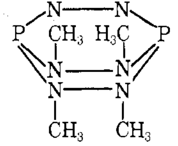
BY WILLIAM VANDOORNE, GARY W. HUNT, RICHARD W. PERRY, AND A. W. CORDES*

Received March 2, 1971

The crystal and molecular structure of the bicyclic tris(1,2-dimethylhydrazino)diphosphine, $P_2(NCH_3)_6$, has been determined by single-crystal X-ray diffraction methods. The unit cell is monoclinic, with $a = 7.312$ (4) Å, $b = 13.361$ (7) Å, $c = 7.133$ (4) Å, $\beta = 116.24$ (1)°, and $d_{\text{calcd}} = 1.256$ g/cm^3. The space group is $P2_1/c$ (C_{2h}^5: no. 14), and there are two molecules per unit cell. Diffractometer methods (Mo radiation, λ 0.71069 Å) were used to obtain 261 observed reflections at 23°. Refinement of the structure by full-matrix least-squares methods with isotropic thermal parameters for all atoms gave a final R index of 0.087. The molecule, which consists of three 1,2-dimethylhydrazino groups linking two phosphorus atoms, has nearly threefold symmetry. The crystal is disordered: two enantiomorphs related by an inversion center at the center of the molecule share the same lattice sites. The average P–N, N–N, and N–C bond distances and their rms deviations are 1.68 (3), 1.44 (2), and 1.49 (5) Å, respectively. The NPN, PNN, PNC, and NNC bond angles average 100 (3), 117 (4), 118 (4), and 110 (5)°, respectively. The sum of the angles about the N atoms is 345 (2)°. The P–N–N–P linkages are planar within 0.06 (2) Å, and the carbon atoms are 1.1 (1) Å from these planes. These structural parameters suggest little or no p → d P–N π bonding.

Introduction

Tris(1,2-dimethylhydrazino)diphosphine was first prepared by Payne, Nöth, and Henniger,[1] who proposed a bicyclic structure for this molecule



One feature of interest in this molecule is the extent of π bonding which might prevail in the P–N framework. The general topic of a (p → d)π interaction in P–N bonds of aminophosphines has received considerable attention.[2] The P–N bond distance and the stereochemistry at the nitrogen atoms of $P_2(NCH_3)_6$ provide a good opportunity for obtaining information on the extent of the π bonding in a P–N cage molecule of this type. Completely planar PN(C)N(C)P linkages (sp^2 N) with P–N distances of 1.59–1.62 Å could be used as evidence for extensive P–N π bonding and would allow only one conformation for this molecule, while nonplanar PN(C)N(C)P units (tetrahedral N) with P–N distances of about 1.77 Å would be expected for a σ-bonded system and would allow the possible existence of a number of isomers differing in the orientations of the methyl groups with respect to the P–N cage.

Collection and Treatment of Data

The sample of $P_2(NCH_3)_6$ was prepared by the method of Payne, Nöth, and Henniger,[1] and crystals were grown by vacuum sublimation. A nearly spherical crystal of radius 0.14 (1) mm was sealed in a Lindemann capillary with a parallel to the ϕ axis. All handling of the crystal was done under an atmosphere of dry nitrogen. Preliminary Weissenberg photographs showed Laue symmetry and systematic absences which uniquely indicated space group $P2_1/c$. The diffractometer data were obtained with a GE XRD-5 manually operated unit using Mo Kα (λ 0.71069 Å) radiation filtered with 1-mil zirconium foil, a scintillation counter, and a pulse height analyzer set for a 90% window. Least-squares refinement[3] of the setting angles of 13 carefully centered reflections gave the following cell parameters at

---

[1] D. S. Payne, H. Nöth, and G. Henniger, *Chem. Commun.*, 327 (1965).

[2] *Cf.* A. B. Burg, *Accounts Chem. Res.*, **2**, 353 (1969); A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 5206 (1970); J. E. Smith, R. Steen, and K. Cohn, *ibid.*, **92**, 6359 (1970), and references therein.

[3] A. Foust, Program ANGSET, University of Wisconsin, 1968.