300 *Inorg. Chem.* **1982,** *21,* 300-302

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Structure of a Novel Tetrahedral Boron Complex, Bis(acetato)(acetylacetonato)boron(III), $B(O_2CMe)_2(acac)$

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Received June 8, 1981

The structure of $B(O_2CMe)_2(acac)$ (**1**) is reported. The structure has been determined from single-crystal X-ray data collected by counter methods and solved by application of direct methods. Crystals of **1** are monoclinic with space group $P2_1/c$ with $Z = 4$ and cell dimensions of $a = 14.138$ (2) Å, $b = 7.440$ (1) Å, $c = 11.593$ (2) Å, $\beta = 107.60$ (1)°, and $V = 1162.3$ (6) Å^3. Full-matrix least-squares refinement gave final discrepancy factors of $R_1 = 0.035$ and $R_2 = 0.047$ for 919 data having $I > 3\sigma(I)$. The molecular structure consists of discrete $B(O_2CMe)_2[(MeCO)_2CH]$ units that have approximate C_{2v} symmetry.

Introduction

Boron is well-known to have a maximum coordination number of 4 with a tetrahedral arrangement of ligand atoms.[1] This type of coordination is commonly exhibited in anionic species such as the BX_4^- ($X = F, Cl, C_6H_5, H$) and various borates, rarely in cationic species such as the famous diammoniate of diborane, $[H_2B(NH_3)_2]^+[BH_4]^-$, and with some frequency in the neutral species that arise as adducts of BX_3 molecules with neutral donors, e.g., $BF_3(OEt_2)$ and BH_3PR_3.

We describe here the structural characterization of a type of neutral 4-coordinate boron complex for which we know of no well-defined precedent. This compound, $B(O_2CCH_3)_2(acac)$, where acac = $[(CH_3CO)_2CH]^-$, was discovered completely by accident while we were attempting the preparation of an entirely different substance. In the reaction we examined, no acac or Hacac was introduced as such and it is not clear to us how this ligand arose in the reaction mixture used. It seems likely that should a sample of this compound be required in the future it could be prepared rationally by a reaction employing the $CH_3CO_2^-$ and acac$^-$ ligands together with a simple boron compound. However, we have not undertaken any such designed synthesis because of the priority of other research goals.

Experimental Section

Preparation of $B(O_2CMe)_2(acac)$. The compound was isolated from the reaction between vanadium diboride and glacial acetic acid as described by Greenwood and co-workers.[2] The reaction was attempted in an effort to reproduce the reported preparation[2] of $V_2(O_2CCH_3)_6$. Although a green solution was obtained, as described in the report, we were unable to isolate any $V_2(O_2CCH_3)_6$ from the reaction mixture following the reported workup procedure. However, concentration of the reaction mixture did yield large white crystalline blocks of a compound, which, from the X-ray crystallographic analysis, was shown to be $B(O_2CCH_3)_2[(MeCO)_2CH]$.

X-ray Data Collection. A suitable crystal was secured to the end of a thin glass fiber with epoxy cement and mounted on a Syntex P$\bar{1}$ automatic diffractometer. Preliminary oscillation photographs indicated that the crystal belonged to the monoclinic crystal system, and examination of selected reflections showed that it was a single crystal of good quality. ω scans showed that several intense reflections had widths at half-height of less than 0.3°. Careful centering of 15 reflections in the range $22 < 2\theta < 28°$, selected to give varied crystal orientations, gave unit cell parameters listed in Table I. The procedures preliminary to data collection have been described previously.[3]

All data were collected by using Mo Kα ($\lambda = 0.71073$ Å) radiation monochromated in the incident beam with a graphite crystal. A total of 1227 independent reflections with $0 < 2\theta < 45°$ were collected at 22 °C with use of the θ–2θ scan technique. A variable scan rate from 4 to 24° min^{-1} was used with a scan to background time ratio of 2. The intensities of three standard reflections were measured after every 97 reflections and showed no significant variation during the period of data collection. Lorentz and polarization corrections were applied.[3] A summary of the important crystallographic parameters is presented in Table I.

Table I. Crystallographic Parameters

space group	$P2_1/c$	crystal size, mm	0.35 × 0.35 × 0.35
a, Å	14.138 (2)	μ(Mo Kα), cm^{-1}	1.161
b, Å	7.440 (1)	range 2θ, deg	0.01-45
c, Å	11.593 (2)	no. of unique data	1227
β, deg	107.60 (1)	no. of data, $F_o^2 > 3\sigma(F_o^2)$	919
V, Å^3	1162.3 (6)		
d_{calcd}, g/cm^3	1.303	no. of variables	197
Z	4	R_1	0.035
fw	228.01	R_2	0.047
		goodness of fit	1.057
		largest shift[a]	0.52

[a] Largest parameter shift in final refinement cycle.

Solution and Refinement. The structure was solved[4] in the monoclinic space group $P2_1/c$. The positions of nonhydrogen atoms were found by the application of direct methods using the program MULTAN. Full-matrix isotropic refinement of these positions gave discrepancy factors $R_1 = 0.098$ and $R_2 = 0.140$, where R_1 and R_2 are expressed as

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$$

The function $\sum w(|F_o| - |F_c|)^2$ was minimized with the weighting factor, w, equal to $4F_o^2/[\sigma(F_o^2)]^2$. Subsequent full-matrix anisotropic least-squares refinement gave discrepancy factors $R_1 = 0.067$ and $R_2 = 0.098$. Positions of the hydrogen atoms were then determined from a difference map. Full-matrix anisotropic least-squares refinement of all atoms yielded final discrepancy factors of $R_1 = 0.035$ and $R_2 = 0.047$ and a goodness of fit of 1.057. All structure factor calculations and least-squares refinements were executed by using only those 919 reflections for which $F_o^2 > 3[\sigma(F_o)]^2$. Atomic scattering factors were those of Cromer and Waber.[5] The observed and calculated structure factors are available as supplementary material.

Results

The structure of the compound is presented in Figure 1, which also defines the atomic numbering scheme. The atomic positional and thermal parameters are given in Table II. Bond distances and angles are presented in Tables III and IV, respectively.

The structure was solved in the monoclinic space group $P2_1/c$ with each molecule occupying a general position within

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $B(O_2CMe)_2[(MeCO)_2CH]$ (1)

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	0.6659 (1)	0.5326 (3)	0.3457 (1)	4.36 (8)	4.28 (9)	4.06 (8)	0.27 (8)	1.34 (6)	0.54 (7)
O(2)	0.5730 (1)	0.7028 (3)	0.1966 (2)	5.32 (9)	7.1 (1)	5.89 (9)	1.5 (1)	1.83 (7)	1.9 (1)
O(3)	0.8192 (1)	0.4073 (3)	0.3782 (2)	4.34 (8)	4.8 (1)	4.71 (9)	0.72 (8)	0.86 (7)	1.08 (8)
O(4)	0.9255 (1)	0.4048 (3)	0.2704 (2)	4.96 (9)	7.5 (1)	7.3 (1)	1.1 (1)	2.18 (8)	0.9 (1)
O(5)	0.7110 (1)	0.4257 (2)	0.1746 (2)	4.35 (8)	3.77 (9)	4.11 (8)	−0.15 (7)	1.12 (6)	−0.30 (7)
O(6)	0.7870 (1)	0.6963 (3)	0.2828 (1)	4.48 (8)	3.76 (9)	3.83 (8)	−0.34 (7)	1.14 (6)	−0.14 (7)
C(1)	0.5855 (2)	0.6302 (4)	0.2929 (3)	4.4 (1)	4.0 (1)	4.7 (1)	−0.3 (1)	1.3 (1)	0.2 (1)
C(2)	0.5148 (2)	0.6389 (5)	0.3645 (3)	5.0 (1)	7.1 (2)	6.9 (2)	0.1 (1)	2.9 (1)	−0.2 (2)
C(3)	0.9038 (2)	0.3600 (4)	0.3578 (3)	4.5 (1)	4.2 (1)	5.6 (1)	0.1 (1)	0.7 (1)	−0.0 (1)
C(4)	0.9668 (3)	0.2469 (5)	0.4583 (4)	6.1 (2)	6.5 (2)	9.3 (2)	1.9 (2)	−0.4 (2)	1.7 (2)
C(5)	0.7161 (2)	0.4993 (4)	0.0756 (2)	3.7 (1)	5.3 (2)	3.8 (1)	1.1 (1)	1.16 (8)	−0.2 (1)
C(6)	0.7563 (2)	0.6661 (5)	0.0752 (2)	5.0 (1)	5.3 (2)	3.6 (1)	0.3 (1)	1.51 (9)	0.7 (1)
C(7)	0.7886 (2)	0.7620 (4)	0.1796 (2)	3.7 (1)	4.0 (1)	4.8 (1)	0.2 (1)	1.44 (9)	0.7 (1)
C(8)	0.8266 (3)	0.9492 (5)	0.1857 (3)	7.0 (2)	4.5 (2)	8.5 (2)	−0.9 (1)	3.3 (1)	0.8 (2)
C(9)	0.6730 (3)	0.3931 (5)	−0.0350 (3)	6.7 (2)	8.0 (2)	4.8 (1)	0.1 (2)	1.2 (1)	−1.8 (2)
B(1)	0.7463 (2)	0.5165 (5)	0.2924 (3)	4.0 (1)	4.0 (2)	3.4 (1)	0.0 (1)	1.0 (1)	0.2 (1)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
H(21)	0.458 (2)	0.704 (5)	0.326 (3)	8.3 (9)	H(81)	0.831 (3)	0.985 (6)	0.111 (3)	10.4 (11)
H(22)	0.483 (3)	0.525 (6)	0.363 (3)	10.1 (10)	H(82)	0.895 (3)	0.952 (5)	0.220 (3)	10.0 (11)
H(23)	0.544 (3)	0.675 (5)	0.437 (3)	10.1 (10)	H(83)	0.793 (3)	0.018 (6)	0.220 (3)	11.1 (12)
H(41)	1.011 (3)	0.189 (6)	0.428 (3)	11.4 (12)	H(91)	0.609 (2)	0.367 (4)	−0.045 (3)	7.9 (9)
H(42)	0.933 (3)	0.143 (5)	0.463 (3)	10.8 (11)	H(92)	0.682 (2)	0.436 (5)	−0.105 (3)	9.5 (10)
H(43)	0.986 (4)	0.308 (8)	0.523 (5)	17.9 (18)	H(93)	0.703 (3)	0.292 (6)	−0.028 (3)	11.4 (12)
H(61)	0.759 (2)	0.709 (4)	0.000 (2)	5.1 (6)					

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Bond Distances (Å) for $B(O_2CMe)_2[(MeCO)_2CH]$

O(1)–C(1)	1.332 (4)	C(7)–C(8)	1.487 (5)
–B(1)	1.455 (4)	C(2)–H(2)	0.93 (5)
O(2)–C(1)	1.204 (4)	–H(22)	0.96 (6)
O(3)–C(3)	1.335 (4)	–H(23)	0.86 (5)
–B(1)	1.446 (4)	C(4)–H(41)	0.91 (6)
O(4)–C(3)	1.191 (4)	–H(42)	0.92 (6)
O(5)–C(5)	1.293 (4)	–H(43)	0.85 (9)
–B(1)	1.469 (4)	C(6)–H(61)	0.94 (3)
O(6)–C(7)	1.298 (4)	C(8)–H(81)	0.92 (5)
–B(1)	1.473 (4)	–H(82)	0.92 (5)
C(1)–C(2)	1.481 (5)	–H(83)	0.87 (6)
C(3)–C(4)	1.494 (6)	C(9)–H(91)	0.89 (4)
C(5)–C(6)	1.365 (5)	–H(92)	0.92 (5)
–C(9)	1.473 (5)	–H(93)	0.85 (6)
C(6)–C(7)	1.359 (5)		

Table IV. Bond Angles (Deg) for $B(O_2CMe)_2[(MeCO)_2CH]$

C(1)–O(1)–B(1)	121.2 (2)	C(1)–C(2)–H(21)	113 (2)
C(3)–O(3)–B(1)	121.0 (3)	–H(22)	110 (2)
C(5)–O(5)–B(1)	122.4 (3)	–H(23)	111 (3)
C(7)–O(6)–B(1)	121.8 (3)	H(21)–C(2)–H(22)	97 (4)
O(1)–C(1)–O(2)	122.4 (3)	–H(23)	113 (4)
–C(2)	113.1 (4)	H(22)–C(2)–H(23)	112 (4)
O(2)–C(1)–C(2)	124.4 (4)	C(3)–C(4)–H(41)	106 (4)
O(3)–C(3)–O(4)	123.5 (3)	–H(42)	109 (4)
–C(4)	111.4 (5)	–H(43)	110 (6)
O(4)–C(3)–C(4)	125.1 (5)	H(41)–C(4)–H(42)	93 (5)
O(4)–C(5)–C(6)	121.5 (3)	–H(43)	120 (7)
–C(9)	115.2 (4)	H(42)–C(4)–H(43)	116 (6)
C(6)–C(5)–C(9)	123.2 (4)	C(5)–C(6)–H(61)	117 (2)
C(5)–C(6)–C(7)	120.1 (3)	C(7)–C(6)–H(6)	123 (2)
O(6)–C(7)–C(6)	121.9 (3)	C(7)–C(8)–H(81)	111 (3)
–C(8)	114.6 (4)	–H(82)	111 (3)
C(6)–C(7)–C(8)	123.6 (4)	–H(83)	110 (4)
O(1)–B(1)–O(3)	103.8 (2)	H(81)–C(8)–H(82)	93 (4)
–O(5)	110.1 (2)	–H(83)	117 (5)
–O(6)	109.3 (3)	H(82)–C(8)–H(83)	115 (5)
O(3)–B(1)–O(5)	110.6 (3)	C(5)–C(9)–H(91)	111 (3)
–O(6)	110.5 (2)	–H(92)	117 (3)
O(5)–B(1)–O(6)	112.2 (3)	–H(93)	109 (4)
		H(91)–C(9)–H(92)	111 (4)
		–H(93)	106 (5)
		H(92)–C(9)–H(93)	101 (5)

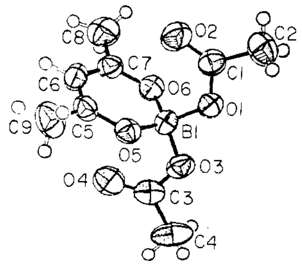


Figure 1. Molecular structure of $B(O_2CMe)_2[(MeCO)_2CH]$ as drawn by the ORTEP program. Atoms are represented by their ellipsoids of thermal vibration drawn to enclose 40% of the electron density. The atom-labeling scheme is defined.

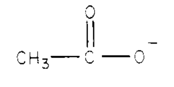
Table V. Selected Planes and Dihedral Angles for $B(O_2CMe)_2[(MeCO)_2CH]^a$

atoms	dev from plane, Å	atoms	dev from plane, Å
	In Plane 1		
B(1)	−0.003	C(5)	0.006
O(5)	0.002	C(6)	−0.014
O(6)	−0.005	C(7)	0.014
	Out of Plane 1		
O(1)	1.153	O(3)	−1.130
O(2)	2.622	O(4)	−2.659
C(1)	2.392	C(3)	−2.383
C(2)	3.430	C(4)	−3.373
	In Plane 2		
O(1)	0.035	O(3)	−0.003
O(2)	0.007	O(4)	−0.016
C(1)	0.005	C(3)	−0.002
C(2)	−0.030	C(4)	0.005
B(1)	−0.003		
	dihedral angle: plane 1/plane 2 = 88.7°		

[a] Planes are defined by the equation $Ax + By + Cz = D$, where the coefficients have the following values: plane 1, $A = -0.9048$, $B = 0.3982$, $C = -0.1508$, $D = -7.5727$; plane 2, $A = -0.3117$, $B = -0.8265$, $C = -0.4688$, $D = 7.6577$.

the unit cell. Each boron atom is coordinated to two acetate ligands and one acac ligand. The acetate ligands are bent back toward the acac ligand and occupy a plane perpendicular to the plane of the acac ligand. Each molecule, therefore, possesses approximate C_{2v} symmetry as is evident from Table V. The central boron atom is bonded to four oxygen atoms, one from each acetate ion and two from the acac ligand with average B–O distances of 1.450 (4) Å and 1.471 (4) Å, respectively; the difference, 0.021 (6) Å, is barely significant. These four oxygen atoms adopt an almost perfect tetrahedral arrangement about the boron with only a slight expansion (i.e., O(5)–B(1)–O(6) = 112.2(3)°) of the angle subtended by the acac oxygen atoms and a small compression (O(1)–B(1)–O(3) = 103.8 (2)°) of the angle between the acetate ligands. In addition to the four oxygen atoms that are directly bonded to the boron atom, there are two additional oxygen atoms, one from each acetate ion, at 2.741 (4) and 2.750 (4) Å from the boron atom. These distances can clearly be interpreted as nonbonded contact distances. If, in describing the geometry about the boron, we include these oxygen atoms as part of the coordination sphere, the geometry about the boron would be described as that of a bicapped tetrahedron.

The acetate ligands show two distinctly different C–O bond lengths with average distances of 1.198 (4) and 1.334 (4) Å, respectively. These distances are consistent with the predominance of contribution A rather than B to the bonding description of the acetate ligands. The average C–O and central HC–C distances of the acac ligand are 1.296 (4) and 1.362 (4) Å, respectively, and are consistent with the fully delocalized description of the acac ligand.



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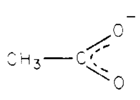

B

Acknowledgment. We are grateful to the Robert A. Welch Foundation for support under Grant No. A-494.

Registry No. 1, 51455-04-0.

Supplementary Material Available: A listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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Survey of the Bonding in Several Structural Types of Trinuclear Molybdenum and Tungsten Cluster Compounds

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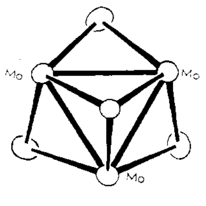
Received June 8, 1981

The bonding within equilateral triangular clusters of molybdenum and tungsten and the bonding of μ_3-O, μ-O, and μ-Cl to them have been examined by using nonempirical Fenske–Hall calculations. Calculations on the bipyramidal and trigonal-prismatic metal–oxygen "core" species $[Mo_3(\mu_3\text{-}O)_2]^{8+}$ and $[Mo_3(\mu\text{-}O)_6]$ indicate that both capping and edge bridging cause the movement of charge out of the main metal–metal bonding orbitals, resulting in the occupation of higher lying nonbonding and antibonding metal–metal orbitals. The electronic structure of the pyramidal fragment $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3]^{4+}$ is shown to be dominated by the influence of the three edge-bridging μ-O groups. The ability of the trinuclear framework to accommodate a variable number of electrons has been investigated by comparative calculations on $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3]^{4+}$ and $[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3]^{5+}$, as representatives of the pyramidal type, with six and eight electrons, respectively. The results presented are consistent with the generally longer M–M bonds in systems containing the $M_3(\mu_3\text{-}O)_2$ core relative to those containing the $M_3(\mu_3\text{-}O)(\mu\text{-}O)_3$.

Introduction

Within the past few years a number of studies have shown the discrete equilateral triangle with M–M bonds to be a favored structural element for molybdenum and tungsten in higher oxidation states.[2-8] A comprehensive review with complete references has recently appeared.[9] Since the appearance of that review, several further discoveries that show even more forcefully the importance of such compounds have been reported.[10,11] In this report we shall deal with two structural types, which, apart from some variability in the nature and arrangement of the peripheral ligands, may be classified as follows. In the first type there is a triply bridging, or capping, ligand above the plane of the metal atoms and three edge-briding ligands below it (**1**). In the second type there are capping ligands on both sides of the metal atom triangle (**2**). We shall refer to these structural types as pyramidal (pyr) and trigonal bipyramidal (tbp), respectively. Both the pyr and the tbp structural types are stable for more than one



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