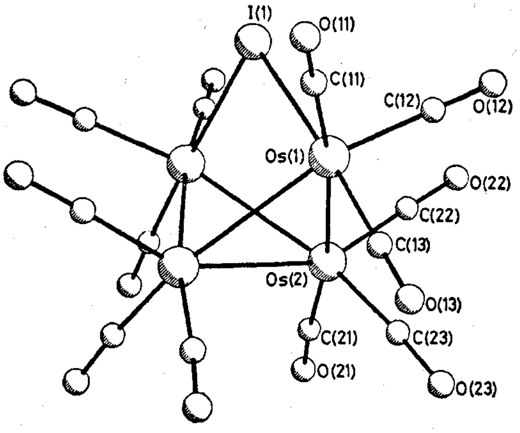
has 62 valence electrons, and thus the butterfly arrangement of the metal atoms is consistent with predictions from the various skeletal electron theories.[18,19]

An isoelectronic and structurally similar $H_3Os_4(CO)_{12}I$ cluster has been reported by Johnson, Lewis, and co-workers.[20] The structure of this compound is shown in **2** and has a crystallographically imposed twofold axis passing through the iodine atom and bisecting the Os(2)–Os(2′) hinge. The Os(1)–I–Os(1′) bridge angle (87.9°) in this cluster is similar to the Ru(3)–Cl–Ru(4) angle (88.3°) in $[ClRu_4(CO)_{13}]^-$, but the hinge angle was not given. A comparison of the drawings shown in **2** and Figure 1 reveals that the arrangements of the terminal carbonyl ligands in the two structures are remarkably similar with the slight differences apparently arising as a result of the influence of the different character and location of the bridging ligands. Although the hydrides were not located in $H_3Os_4(CO)_{12}I$, one was presumed to bridge the Os–Os hinge of the butterfly with the others bridging the long Os–Os bonds of the "wings" (Os(1)–Os(2′), Os(1′)–Os(2)).



2

The bridging chloride ligand in $[ClRu_4(CO)_{13}]^-$ would appear to offer a convenient means of functionalizing the cluster by abstracting it with Ag^+ or Tl^+ in the presence of a suitable substrate. A similar notion has been previously suggested for $Fe_2(CO)_6Cl(\mu\text{-}PPh_2)$ by Carty and co-workers.[21,22] Our preliminary experiments in this regard, summarized above, have been largely unsuccessful, but we are continuing to explore the possibility of reactions of this type.

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Registry No. [PPN]$[ClRu_4(CO)_{13}]$, 74231-12-2; $Ru_3(CO)_{12}$, 15243-33-1.

Supplementary Material Available: A listing of structure factor amplitudes (Table A, 26 pages). Ordering information is given on any current masthead.

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[17] Ru(1), Ru(2): 8(Ru) + 6{$(CO)_3$} + 3(Ru–Ru) + 1{CO_b} = 18. Ru(3), Ru(4): 8(Ru) + 6{$(CO)_3$} + 2(Ru–Ru) + 2(Cl) = 18.

[18] Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305.

[19] (a) Wade, K. *Chem. Br.* **1975**, *11*, 1977. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

[20] Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sheldrick, G. M.; Wong, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1978**, 673.

[21] Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1979**, *18*, 2926.

[22] Taylor, N. J.; Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1980**, *19*, 560.

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Low-Temperature Crystal and Molecular Structure of μ-Bromo-hexacarbonyl[octahydrotriborato(1−)]dimanganese, $(\mu\text{-}Br)(CO)_6(B_3H_8)Mn_2$

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The synthesis and characterization of $(\mu\text{-}X)(CO)_6(B_3H_8)Mn_2$, where X = Cl or Br, is reported. The $(\mu\text{-}Br)(CO)_6(B_3H_8)Mn_2$ forms crystals in the monoclinic space group $P2_1/c$ with $a = 10.921$ (8) Å, $b = 7.052$ (4) Å, $c = 18.982$ (12) Å, $\beta = 113.05$ (6)°, $V = 1345$ (2) Å^3, and $Z = 4$. The low-temperature X-ray structure, solved by MULTAN and Fourier methods and refined to $R_1 = 0.056$ and $R_2 = 0.059$, consists of two octahedral manganese atoms bridged by a simultaneously bidentate $B_3H_8^-$ anion and a bromine atom. The remaining octahedral coordination sites are occupied by carbon monoxide ligands. There is no apparent metal–metal bond. The simultaneously bidentate nature of the $B_3H_8^-$ moiety presents a heretofore unknown bonding mode for octahydrotriborate complexes.

Introduction

The inclusion of metal atoms along with boron atoms in boron hydride like clusters has become the subject of much attention in recent years and is now a rapidly expanding area within the field of inorganic chemistry.[1] The bonding observed in these metalloborane complexes can be divided into several broad categories: (1) complexes containing direct metal–boron bonding, as in $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}B_4H_8)$,[2] (2) metal hydroborates containing metal–hydrogen–boron bridge bonds, as in $Al(BH_4)_3$,[3] and (3) complexes containing both metal–boron and metal–hydrogen–boron bonding.

The series of metal–hydrogen–boron bond containing species has grown from the initial characterization of doubly bridged species such as $[(C_6H_5)_3P]_2CuBH_4$[4] to reports of single[5] and triple[6] M–H–B bridge bond containing species. In each of

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[1] Greenwood, N. N.; Ward, I. M. *Chem. Soc. Rev.* **1974**, *3*, 231–71.

[2] Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1973**, *95*, 5078–80.

[3] Almenningen, A.; Gunderson, G.; Haaland, A. *Acta Chem. Scand.* **1968**, *22*, 328–34.

[4] Lippard, S. J.; Melmed, K. M. *Inorg. Chem.* **1967**, *6*, 2223–28.

[5] (a) Bommer, J. C.; Morse, K. W. *J. Chem. Soc., Chem. Commun.* **1977**, 137–8. (b) Kutal, C.; Grutsch, P.; Atwood, J. L.; Rogers, R. D. *Inorg. Chem.* **1978**, *17*, 3558–62.

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these cases, the observed bonding mode has been one in which bridge bonding occurs from a boron hydride to a single metal center. With the exception of $HMn_3(CO)_{10}(BH_3)_2$,[7] in which there are six M–H–B bridge bonds from two boron atoms to three metal atom centers, there have been no previous reports of polymetallic M–H–B bonded metalloborane complexes.

We report here the synthesis and characterization of μ-bromo-hexacarbonyl[octahydrotriborato(1–)]dimanganese, μ-$Br(CO)_6(B_3H_8)Mn_2$, and the isostructural $(\mu$-$Cl)(CO)_6(B_3H_8)Mn_2$. The X-ray structural characterization of the former complex confirms the existence of a new class of metalloborane compounds which are characterized by the presence of an open-cage multidentate boron hydride ligand attached to separate metal atom centers soley through M–H–B bridge bonds. Furthermore, these complexes represent the first examples in which a $B_3H_8^-$ moiety is simultaneously bound to two metal centers through pairs of M–H–B bridge bonds.

Experimental Section

Synthesis of $(\mu$-$Br)(CO)_6(B_3H_8)Mn_2$. In a typical reaction, a dry 50-mL reaction vessel equipped with a 12-mm Teflon stopcock is charged with a small stirring bar and a catalytic amount of aluminum metal (foil). The reactor is evacuated on the vacuum line, and ca. 4 mmol of degassed bromine is distilled into the reactor at −196 °C. The reactor is then sealed and allowed to warm until reaction of the liquid bromine with the aluminum foil has occurred. The bromine/aluminum bromide mixture is then refrozen to −196 °C, and ca. 15 mL of dry CH_2Cl_2 (3-Å molecular sieve) and ca. 4 mmol of $(CO)_3MnB_3H_8$[8] are distilled into the reaction vessel. The vessel is then immersed in a −78 °C bath and allowed to warm to room temperature with stirring over a 5-h period. During this time, the initially opaque red-brown solution becomes clear reddish and deposits a yellow solid on the vessel walls. The reaction proceeds without the formation of noncondensable gases. Volatile side products obtained include trace amounts of HBr, B_2H_6, and B_4H_{10}.

The crude $(\mu$-$Br)(CO)_6(B_3H_8)Mn_2$ is a yellow solid which sublimes rapidly under vacuum conditions (10^{-4} torr) at 50 °C to a −78 °C probe. Crystalline samples suitable for single-crystal X-ray analysis may be obtained by employing a probe temperature of approximately 10 °C (cold water). The purified product is a red-brown crystalline solid or an orange-yellow powder and is obtained in yields of ~35% on the basis of manganese. It exhibits moderate air stability.

An alternative synthesis involves the solution-phase reaction of tetramethylammonium octahydrotriborate with $Mn_2(CO)_8Br_2$. In a typical reaction, a dry, 50-mL reaction vessel equipped with a Teflon O-ring stopcock is charged with 2 mmol of $Mn_2(CO)_8Br_2$, 1 mmol of $Me_4NB_3H_8$, a stirring bar, and approximately 20 glass beads. The reaction vessel is frozen to −196 °C, and ca. 20 mL of dry CH_2Cl_2 is added. The reactor is then warmed to ambient temperature and stirred for 36 h. At the end of this period the stirring is halted, revealing a red-orange solution over orange-brown solids. The reaction vessel is then frozen, and the small amount of carbon monoxide produced is removed. The volatile reaction products are separated on the vacuum line by trap-to-trap fractionation and identified as $Mn_2(CO)_{10}$ and $(CO)_4MnB_3H_8$ (0.3 mmol). Sublimation of the solids remaining in the reaction vessel at 50 °C and 10^{-3} torr to an 11 °C water-cooled probe gave 120 mg (0.3 mmol) of product, 15% yield on the basis of the $Mn_2(CO)_8Br_2$.

Synthesis of $(\mu$-$Cl)(CO)_6(B_3H_8)Mn_2$. $(\mu$-$Cl)(CO)_6(B_3H_8)Mn_2$ was formed in a reaction mixture containing $(CO)_3MnB_3H_8$, $AlCl_3$, ethylene, and anhydrous HCl.

Typically, 3 mmol of $(CO)_3MnB_3H_8$ were vacuum distilled into a 100-mL reaction vessel equipped with a 12-mm Teflon O-ring stopcock, a stirring bar, and an excess of freshly sublimed, anhydrous aluminum chloride. The reactor was then charged with 3.5 mmol of ethylene and a catalytic (<2 mol %) amount of anhydrous hydrogen chloride. The reactor was then warmed to ambient temperature and stirred for 115 h, after which the volatile contents of the reaction vessel were separated by high-vacuum trap-to-trap fractionation. The major volatile product of interest was $(CO)_4MnB_3H_8$. The large mass of orange solid material remaining in the reaction vessel was extracted 3 times with 20 mL (each) of dry (Na) toluene under nitrogen. The orange extracts were evaporated at 10^{-3} torr pressure, and the solid remaining was sublimed at 55 °C and 10^{-4} torr to a water cooled probe at ~11 °C. The resulting yellow-orange, microcrystalline $(\mu$-$Cl)(CO)_6(B_3H_8)Mn_2$ was obtained in 20% yield on the basis of manganese. It appeared to be indefinitely stable when stored in vacuo or under nitrogen and exhibited reasonable air stability, decomposing very slowly over a period of days.

Table I. ^1H and ^{11}B NMR Data for $(\mu$-$X)(CO)_6(B_3H_8)Mn_2$

	X	
assignment	Br	Cl
B(1,3)[a]	−38.3[b]	−37.1[b]
B(2)[a]	10.4	10.0
H(1,3,5,6)[c]	−8.3[d]	−8.5[d]
H(7,8)[c]	0.7[d]	−0.66[d]
H(2,4)[c]	3.3[c]	3.3[e]

[a] The 86-MHz ^{11}B spectra were measured relative to $BF_3 \cdot OEt_2$, with negative chemical shifts at higher field. [b] Complex multiplet. [c] The 270-MHz ^1H spectra were measured relative to $(CH_3)_4Si$. [d] Broad quartet. [e] Broad singlet.

Spectral Characterization

The ^1H and ^{11}B NMR spectra of $(\mu$-$X)(CO)_6(B_3H_8)Mn_2$ compounds are tabulated in Table I. The ^{11}B NMR spectra are similar to those obtained for bidentate $B_3H_8^-$ complexes.[8] The ^1H spectra are also similar to those for bidentate complexes except that the 3.3-ppm resonances are usually broad and ill resolved.

Infrared Spectra. The solution-phase (CH_2Cl_2) infrared spectrum of $(\mu$-$Br)(CO)_6(B_3H_8)Mn_2$ contains a broad CO stretching band which appears to consist of four overlapping peaks at 2010 (s, sh), 2000 (s, sh), 1990 (s), and 1965 cm^{-1} (s). The terminal B–H region shows two weak absorption bands at 2505 (w, br) and 2565 cm^{-1} (w, br). The spectrum of $(\mu$-$Cl)(CO)_6(B_3H_8)Mn_2$ contains an intense CO band which appears to be composed of three strong resonances, 2055 (s), 1990 (s), and 1970 cm^{-1} (s), and a very weak B–H stretching region with two resonances, 2525 (vw) and 2495 cm^{-1} (vw) for the BH_2 group.

Mass Spectra. The 30-eV mass spectrum of $(\mu$-$Br)(CO)_6(B_3H_8)Mn_2$ does not appear to exhibit a parent peak. However, the high-resolution peak match for the P − 2 mass gives a molecular weight of 397.8403 for $^{81}Br(^{12}C^{16}O)_6(^{11}B_3{}^1H_6)^{55}Mn_2^+$, calculated 397.8368. Recognizable mass envelopes corresponding to successive losses of carbon monoxide and B_3H_8 groups can be identified. The 30-eV mass spectrum of $(\mu$-$Cl)(CO)_6(B_3H_8)Mn_2$ shows a weak parent peak at *m/e* 353.9041 for $^{35}Cl(CO)_6(^{11}B_3H_8)Mn_2$, calculated 353.9050. Again, the main observed envelopes correspond to successive loss of the carbon monoxide ligands followed by the loss of B_3H_8.

Single-Crystal Data

Single crystals of $(\mu$-$Br)(CO)_6(B_3H_8)Mn_2$ were grown as red-brown rectangular blocks by slow sublimation as described previously. Several selected crystals were sealed into thin-walled Lindemann capillaries under an argon atmosphere. A suitable crystal was then aligned on a Syntex P$\bar{1}$ four-circle diffractometer controlled by a NOVA computer. With use of the associated Syntex LT-1 low-temperature accessory, the crystal was cooled to a regulated temperature of −160 °C (±2 °C). Test diffraction peaks remained single on cooling. Through the use of standard Syntex software routines,[9] the crystal was centered, indexed in *h*, *k*, and *l*, and lattice parameters were determined. A summary of the experimental conditions and final results from the data collection are presented in Table II.

Solution and Refinement of the Structure

The solution of the structure was accomplished by using both MULTAN and Fourier[11] methods. An initial MULTAN solution revealed

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(6) (a) Bird, P. H.; Churchill, M. R. *J. Chem. Soc., Chem. Commun.* **1967**, 403. (b) Hildebrandt, S. J.; Gaines, D. F.; Calabrese, J. C. *Inorg. Chem.* **1978**, *17*, 790–94.

(7) Kaesz, H. D.; Fellmann, W.; Wilkes, G. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1965**, *87*, 2753–55.

(8) Gaines, D. F.; Hildebrandt, S. J. *Inorg. Chem.* **1978**, *17*, 794–806.

(9) Sparks, R. A. "P$\bar{1}$ Autodiffractometer Operations Manual"; Syntex Analytical Instruments Division: Cupertino, CA, 1970.

(10) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. B* **1970**, *B26*, 274–85.

Table II. Crystallographic Data for $(\mu\text{-Br})(CO)_6(B_3H_8)Mn_2$ at −160 °C

crystallizn method	sublimn at 50 °C, 10^{-4} torr
cryst shape, color	rectangular, red-brown
mol wt	398.84
data collecn temp, °C	−160 (±2)
radiation (graphite monochromator)	Mo Kα
scan speed, deg/min	2–24
range of 2θ, deg	3–45
total reflctns	1315
total independent reflctns	1261
total obsd reflctns	966
cryst system	monoclinic
systematic abs	*h0l* (*l* odd), 0*k*0 (*k* odd)
space group	$P2_1/c$ (No. 14, second setting)
equiv positions	$x, y, z; -x, {}^1/_2 + y, {}^1/_2 - z;$ $x, {}^1/_2 - y, {}^1/_2 + z; x, y, z$
no. of molecules/unit cell	4
D(calcd), g/cm³	1.97
D(found), g/cm³	1.94
lattice const (errors)	
a, Å	10.921 (8)
b, Å	7.052 (4)
c, Å	18.982 (12)
β, deg	113.05 (6)
V, Å³	1345 (2)
final discrepancy values	
data-to-parameter ratio	
anisotropic	5.9
rigid body	12.4
R_1	0.056
R_2	0.059

the positions for the three heavy atoms (two manganese, one bromine). Succeeding Fourier and least-squares refinement yielded positions for the remaining nonhydrogen atoms and five of eight hydrogen atoms. The remaining hydrogen atoms were assigned locations on the basis of the gross molecular C_{2v} symmetry. Due to the low data-to-parameter ratio (5.9:1), the final refinement sequence required the inclusion of carbon monoxide ligands as two-atom rigid groups. The final refinement, including anisotropic thermal factors for manganese, bromine, and boron, fixed hydrogen positions, and rigid-group carbonyl moieties converged at $R_1 = 0.056$[12] and $R_2 = 0.059$.[13] A final difference mapping indicated the presence of two one-electron peaks in the vicinity of the bromine atom. The final data-to-parameter ratio including the rigid bodies was 12.4:1. The scattering factors of Hanson et al.[14] were used for all atoms. All least-squares refinements were based on the minimization of $\sum w_i(|F_o| - |F_c|)^2$, with weights w_i set to $1/\sigma_{F_o}{}^2$. The estimated standard deviations given in all tables are calculated from the full variance–covariance matrix obtained from the last least-squares refinement cycle. Atomic coordinates and thermal parameters for the isotropic atoms are presented in Table III. Rigid-group coordinates are given in Table IV. Anisotropic temperature factors are listed in Table V. Interatomic distances and intramolecular angles are listed in Tables VI and VII, respectively.

Results and Discussion

The synthesis of $(\mu\text{-Br})(CO)_6(B_3H_8)Mn_2$ may be approached in several ways. Our first method (eq 1), which was

$$2(CO)_3MnB_3H_8 + Br_2 \xrightarrow[CH_2Cl_2]{AlBr_3} (\mu\text{-Br})(CO)_6(B_3H_8)Mn_2 + \ldots \quad (1)$$

initially intended to brominate the $B_3H_8^-$ ligand, proceeds in yields high enough (∼35%) to suggest that the reaction, though complex, is straightforward. The mechanism may involve Br^- displacement of a Mn–H–B bond to form a $[Br(CO)_3MnB_3H_8]^-$ intermediate which subsequently displaces $B_3H_8^-$ from a second $(CO)_3MnB_3H_8$. The same product may be obtained from $Mn_2(CO)_8Br_2$, according to eq 2, but the yield, 15%, is less.

$$Mn_2(CO)_8Br_2 + (CH_3)_4NB_3H_8 \rightarrow (\mu\text{-Br})(CO)_6(B_3H_8)Mn_2 + \ldots \quad (2)$$

Table III. Final Atomic Positional Parameters and Isotropic Thermal Parameters[a] (Å²) for $(\mu\text{-Br})(CO)_6(B_5H_8)Mn_2$

atom	10^4x	10^4y	10^4z	10^3B
Br	1355 (1)	4427 (2)	7961 (1)	
Mn(1)	2459 (2)	6572 (2)	7336 (1)	
Mn(2)	2040 (2)	6606 (2)	9096 (1)	
B(1)	3651 (16)	7465 (20)	8616 (7)	
B(2)	3765 (18)	10087 (18)	8662 (8)	
B(3)	2203 (17)	8713 (17)	8211 (7)	
C(11)	3160	4545	7051	27 (3)[b]
O(11)	3584	3227	6876	35 (2)
C(12)	3271	8105	6915	25 (3)
O(12)	3831	9037	6621	39 (2)
C(13)	1025	6481	6436	35 (3)
O(13)	133	6427	5861	42 (2)
C(21)	2575	4606	9743	27 (3)
O(21)	2926	3366	10163	42 (2)
C(22)	2506	8208	9875	33 (3)
O(22)	2826	9236	10404	37 (8)
C(23)	389	6477	9101	39 (4)
O(23)	−652	6369	9107	63 (3)
H(1)	3494	6590	9084	510
H(2)	4234	11484	9313	510
H(3)	1485	8331	8498	510
H(4)	4212	10826	8205	510
H(5)	3457	6344	8145	510
H(6)	1937	8553	7709	510
H(7)	4541	8418	8876	510
H(8)	2298	10361	8222	510

[a] The standard deviations of the least significant digits are given in parentheses except for the coordinates of the rigid-group carbon monoxide ligands and the arbitrarily fixed hydrogen atoms in this and all following tables. [b] Breakdown of rigid-group thermal parameters (see Table IV).

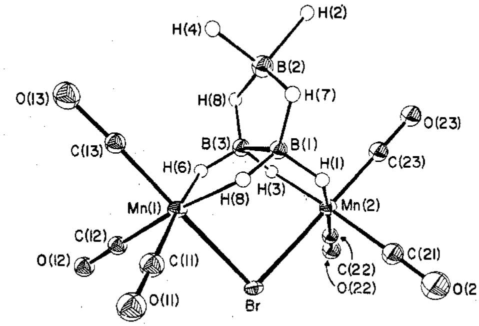

Figure 1. Static molecular structure of $(\mu\text{-Br})(CO)_6(B_3H_8)Mn_2$ showing the atomic numbering system used in this work. In this ORTEP representation, the atomic thermal ellipsoids are plotted at the 30% probability contour. The hydrogen atoms are shown as hard spheres of 0.12-Å radius.

The static molecular structure of $(\mu\text{-Br})(CO)_6(B_3H_8)Mn_2$ and the numbering system employed in this study are shown in Figure 1. The molecular structure consists of two manganese atoms, each surrounded by a pseudooctahedral arrangement of three carbonyl groups arranged in a *fac* configuration, a bromine atom, and a bidentate $B_3H_8^-$ group. The octahedral environment of each manganese atom is represented by the carbon atoms in the carbon monoxide groups, the bromine, and the M–H–B bridge hydrogen atoms from the $B_3H_8^-$ ligand. The manganese atoms are separated by a

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(11) Programs used in the structural analysis included MAP, written by J. C. Calabrese and adapted by L. G. Hoard for Fourier calculations, ORFLS and ORFFE, the W. P. Busing, K. O. Martin, and H. A. Levy least-squares and error analysis programs, and ORTEP II, the C. K. Johnson thermal ellipsoid plotting program.

(12) $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$.

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

(14) Hanson, H. P.; Herman, F.; Lea, J. D.; Skillman, S. *Acta Crystallogr.* **1964**, *17*, 1040–44.

Table IV. Rigid-Group[a] Parameters for the Carbon Monoxide Ligands in $(\mu\text{-Br})(\mathrm{CO})_6(\mathrm{B_3H_8})\mathrm{Mn_2}$

group	10^4x	10^4y	10^4z	ϕ	θ	ρ
CO(11)	3372 (8)	3886 (11)	6964 (3)	−65.79 (109)	−152.41	162.46 (75)
CO(13)	579 (9)	6454 (10)	6148 (4)	−178.48 (161)	−178.66	118.59 (89)
CO(21)	2751 (8)	3986 (10)	9953 (4)	−114.80 (137)	149.56	−131.90 (89)
CO(23)	−132 (16)	6423 (10)	9104 (4)	−176.17 (88)	180.00	−179.52 (81)
CO(12)	3551 (8)	8571 (10)	6768 (3)	79.23 (84)	126.61	132.88 (75)
CO(22)	2666 (9)	8722 (10)	10140 (4)	135.17 (190)	−152.42	−117.48 (103)

[a] Further clarification of group refinement techniques can be found: Doedens, R. J. In "Crystallographic Computing"; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970; pp 198–200.

Table V. Anisotropic Thermal Parameters[a] for $(\mu\text{-Br})(\mathrm{CO})_6(\mathrm{B_3H_8})\mathrm{Mn_2}$

atom	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
Br	193 (16)	241 (7)	321 (6)	−44 (7)	69 (6)	−24 (6)
Mn(1)	144 (22)	211 (10)	241 (9)	9 (10)	28 (9)	−3 (8)
Mn(2)	187 (21)	236 (10)	270 (9)	7 (11)	68 (10)	7 (8)
B(1)	168 (162)	270 (79)	234 (70)	41 (86)	−83 (74)	−56 (61)
B(2)	246 (172)	196 (81)	491 (90)	−57 (82)	215 (91)	14 (64)
B(3)	65 (155)	155 (68)	358 (72)	−16 (78)	138 (75)	−16 (61)

[a] Anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}kb^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

Table VI. Selected Interatomic Distances (Å) for $(\mu\text{-Br})(\mathrm{CO})_6(\mathrm{B_3H_8})\mathrm{Mn_2}$

Br···Mn(1)	2.505 (3)	B(2)···H(2)	1.504
Br···Mn(2)	2.509 (2)	B(2)···H(4)	1.263
Mn(1)···C(11)	1.801 (11)	B(2)···H(7)	1.414
Mn(1)···C(12)	1.774 (10)	B(2)···H(8)	1.501
Mn(1)···C(13)	1.810 (8)	B(3)···H(3)	1.148
Mn(1)···H(5)	1.504	B(3)···H(6)	0.889
Mn(1)···H(6)	1.759	B(3)···H(8)	1.166
Mn(2)···C(21)	1.810 (8)	Br···B(1)	3.16 (2)
Mn(2)···C(22)	1.770 (9)	Br···B(3)	3.14 (1)
Mn(2)···C(23)	1.809 (18)	Br···H(1)	2.90
Mn(2)···H(1)	1.597	Br···H(3)	2.92
Mn(2)···H(3)	1.611	Br···H(5)	2.57
C(11)···O(11)	1.144	Br···H(6)	3.06
C(12)···O(12)	1.177	Mn(1)···Mn(2)	3.55 (0)
C(13)···O(13)	1.144	Mn(1)···B(1)	2.35 (1)
C(21)···O(21)	1.144	Mn(1)···B(2)	3.42 (1)
C(22)···O(22)	1.177	Mn(1)···B(3)	2.34 (2)
C(23)···O(23)	1.144	Mn(2)···B(1)	2.36 (2)
B(1)···B(3)	1.707 (21)	Mn(2)···B(2)	3.39 (2)
B(1)···H(1)	1.148	Mn(2)···B(3)	2.30 (2)
B(1)···H(5)	1.149	B(1)···B(2)	1.85 (2)
B(1)···H(7)	1.125	B(2)···B(3)	1.85 (2)

distance of 3.55 Å and are bound together through halogen bridge and the boron–hydrogen bridge bonds. The octahydrotriborate moiety functions as a simultaneously bidentate ligand, bound to each manganese atom through two metal–hydrogen–boron bridge bonds. The bonding of a $\mathrm{B_3H_8}^-$ ligand to two metals in the manner found in this investigation is unprecedented in metalloborane chemistry. Its discovery, however, supports the earlier preliminary report of the structure of $\mathrm{HMn_3(CO)_{10}(BH_3)_2}$[10] and leads us to suspect that a potentially large class of cluster molecules will be found in which several metals are bound via MHB bonds to multidentate borane ligands.

Although the X-ray-determined molecular structure of $(\mu\text{-Br})(\mathrm{CO})_6(\mathrm{B_3H_8})\mathrm{Mn_2}$ possesses actual C_1 symmetry, Figure 1 shows that it closely approaches a C_{2v} molecular configuration. The distortion from exact C_{2v} molecular symmetry is a result of a minor twist in the $\mathrm{B_3H_8}^-$ ligand, allowing the $\mathrm{B_3}$ triangle to bend slightly towards Mn(2). The nonideality of the molecular configuration is accentuated by the asymmetry in the $\mathrm{BH_2}$ group.

The crystal packing appears normal, and the closest intermolecular distances are 2.87 Å for hydrogen–heteroatom contact between C(21) and H(2) and 2.96 Å for nonhydrogen contact between O(21) and O(22).

The bonding in the title compound is readily described via use of the effective atomic number (EAN) rule. With use of this convention, either two Mn^0 atoms are present, to which halogen, $\mathrm{B_3H_8}^0$ and CO are attached, or two Mn^+ atoms are present, to which are complexed CO, halide ion, and $\mathrm{B_3H_8}^-$. The latter concept, being somewhat conventional, allows the inert-gas configuration to be obtained for each metal atom

Table VII. Selected Intramolecular Angles (Deg) for $(\mu\text{-Br})(\mathrm{CO})_6(\mathrm{B_3H_8})\mathrm{Mn_2}$

Mn(1)--Br--Mn(2)	90.02 (9)	C(22)--Mn(2)--H(1)	93.09	H(4)--B(2)--H(8)	100.36
Br--Mn(1)--C(11)	90.19 (37)	C(22)--Mn(2)--H(3)	90.72	H(7)--H(2)--H(8)	131.02
Br--Mn(1)--C(12)	178.55 (22)	C(23)--Mn(2)--H(1)	176.70	H(3)--B(3)--H(6)	118.83
Br--Mn(1)--C(13)	91.56 (38)	C(23)--Mn(2)--H(3)	86.63	H(3)--B(3)--H(8)	107.35
Br--Mn(1)--H(5)	75.06	H(1)--Mn(2)--H(3)	95.57	Mn(2)--H(1)--B(1)	117.02
Br--Mn(1)--H(6)	89.83	Mn(1)--C(11)--O(11)	178.2 (11)	Mn(2)--H(3)--B(3)	111.89
C(11)--Mn(1)--C(12)	90.17 (49)	Mn(1)--C(12)--O(12)	176.38 (88)	Mn(1)--H(5)--B(1)	124.05
C(11)--Mn(1)--C(13)	90.08 (44)	Mn(1)--C(13)--O(13)	178.9 (12)	Mn(1)--H(6)--B(3)	120.80
C(12)--Mn(1)--C(13)	89.86 (43)	Mn(2)--C(21)--O(21)	178.68 (77)	B(1)--H(7)--B(2)	93.04
C(11)--Mn(1)--H(5)	89.90	Mn(2)--C(22)--O(22)	178.39 (79)	B(3)--H(8)--B(2)	87.10
C(11)--Mn(1)--H(6)	173.54	Mn(2)--C(23)--O(23)	179.0 (11)	Mn(1)--B(1)--B(2)	108.46 (69)
C(12)--Mn(1)--H(5)	103.54	H(1)--B(1)--B(3)	103.46	Mn(1)--B(1)--B(3)	68.44 (59)
C(12)--Mn(1)--H(6)	89.68	H(1)--B(1)--H(5)	101.21	Mn(2)--B(1)--B(2)	106.5 (10)
H(5)--Mn(1)--H(6)	83.86	H(1)--B(1)--H(7)	110.23	Mn(2)--B(1)--B(3)	66.80 (85)
Br--Mn(2)--C(21)	90.79 (28)	H(1)--B(1)--B(3)	103.46	B(2)--B(1)--B(3)	62.61 (84)
Br--Mn(2)--C(22)	178.10 (29)	H(5)--B(1)--B(3)	98.57	Mn(1)--B(3)--B(1)	68.90 (70)
Br--Mn(2)--C(23)	90.65 (36)	B(1)--B(2)--B(3)	54.84 (75)	Mn(1)--B(3)--B(2)	108.7 (10)
Br--Mn(2)--H(1)	87.00	H(2)--B(2)--H(4)	101.20	Mn(2)--B(3)--B(1)	70.22 (71)
Br--Mn(2)--H(3)	87.39	H(2)--B(2)--H(7)	109.65	Mn(2)--B(3)--B(2)	108.7 (7)
C(21)--Mn(2)--H(1)	86.88	H(2)--B(2)--H(8)	108.60	B(2)--B(3)--B(1)	62.56 (84)
C(21)--Mn(2)--H(3)	176.87	H(4)--B(2)--H(7)	101.04		

center as follows: Mn^+ contributes 24 electrons, three carbonyl ligands donate 6 electrons, two metal-hydrogen-boron bonds contribute 4 electrons, and the halogen contributes the final 2 electrons for a total of 36.

Similar bonding schemes will undoubtedly be found in other metal-borane cluster systems. The presence of multidentate M-H-B bonding to several metal centers may have important implications vis-à-vis our future understanding of the mechanisms of metal cluster growth processes.

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Supplementary Material Available: A listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Metal-Mercaptide Chemistry. Synthesis and Structural Characterization of the $[Cu(SC_6H_5)_3]^{2-}$ Anion. A Rational Synthesis and the Structure of the $[Cu_4(SC_6H_5)_6]^{2-}$ Cluster

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The reaction of the $[Cu(S_2C_4O_2)_2]^{2-}$ complex anion with KSC_6H_5 in acetonitrile results in the formation of the orange-red, monomeric $[Cu(SC_6H_5)_3]^{2-}$ dianion (I). This complex readily dissociates in solution to form the white monoanion $[Cu(SC_6H_5)_2]^-$. The reaction of I with Cu(I) ions in acetonitrile in a 1:1 molar ratio affords the $[Cu_4(SC_6H_5)_6]^{2-}$ cluster (II). The same cluster also is obtained by a metathesis reaction in which the SC_6H_5 ligand displaces the dithiosquarate ligands in the $Cu_8(S_2C_4O_2)_6{}^{4-}$ cubane. Bis(tetraphenylphosphonium) tris(thiophenolato)cuprate(I) crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The cell dimensions are $a = 22.300$ (7) Å, $b = 13.717$ (5) Å, $c = 17.686$ (6) Å, and $\beta = 94.59$ (1)°. Bis(tetraphenylphosphonium) hexakis(thiophenolato)tetracuprate(I) crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The cell dimensions are $a = 26.93$ (5) Å, $b = 14.121$ (7) Å, $c = 23.57$ (5) Å, and $\beta = 119.41$ (2)°. Intensity data for both I and II were collected with a four-circle computer-controlled diffractometer using the θ-2θ scan technique. In both I and II the copper, sulfur, and phosphorus atoms were refined with anisotropic thermal parameters while the remaining nonhydrogen atoms were refined with isotropic thermal parameters. Refinement by full-matrix least squares of 319 parameters on 1806 data for I and 349 parameters on 1744 data for II gave final R values of 0.064 for I and 0.099 for II. The coordination of the Cu(I) ion in I is trigonal and nearly planar with two "small" S-Cu-S angles of 112.95 (19) and 111.65 (18)° and a larger S-Cu-S angle of 135.37 (20)°. The Cu-S bond length opposite to the large S-Cu-S angle, at 2.335 (4) Å, is significantly larger than the other two at 2.274 (4) and 2.276 (4) Å. The mean value of the C-S bond lengths is 1.749 (14) Å. The overall description of the Cu_4S_6 core in II can be considered as a tetrahedron of copper atoms inscribed in a distorted octahedron of sulfur atoms. Each sulfur atom is coordinated to two copper atoms across an edge of the Cu_4 tetrahedron, and each copper is trigonally coordinated by three sulfur atoms of three different ligands. Average values of selected structural parameters in II and the standard deviations of the mean are as follows: Cu-Cu, 2.76 (2) Å; S-S, 3.94 (20) Å; Cu-S, 2.29 (3) Å; Cu-S-Cu, 73.8 (10)°; S-Cu-S, 120 (10)°. An analysis of the data and a comparison to the structures of the $Cu_8L_6{}^{4-}$ cubanes lead to the suggestion that the Cu_4S_6 core which is obtained with monodentate thiolate ligands cannot be obtained with 1,1-dithiolate ligands because of the short intraligand S-S distance of ~3.00 Å. In the Cu_4S_6 core structure the $\overline{S-S}$ distance is 3.94 (20) Å.

Introduction

An interesting aspect in the studies of copper-sulfur coordination chemistry is the apparent tendency of Cu(I) ions to form various clusters with sulfur ligands. A remarkable variety in composition and structures is observed in these clusters where the molecular architecture is based on the existence of cores such as Cu_4S_8,[1] Cu_5S_7,[2] Cu_5S_6,[3] Cu_4S_6,[4,5] and Cu_8S_{12}.[6]

The Cu_8S_{12} core is a common feature in what appears to be a general class of clusters obtained by the reaction of cuprous ions and bidentate sulfur chelates. An outstanding feature in the structures of the $[Cu_8(i\text{-MNT})_6]^{4-}$,[6b] $[Cu_8(DED)_6]^{4-}$,[6a] and $[Cu_8(DTS)_6]^{4-}$ [6a] clusters is the similarity of the three, nearly perfect Cu_8 cubes. An analysis of the structural features of these clusters has led us to suggest[6a] that the constancy of the Cu-Cu distances in the three Cu_8 cubes at ~2.82 Å indicates weak, attractive Cu-Cu interactions.

Mehrotra and Hoffmann[7] have analyzed the bonding relationships in d^{10}-d^{10} systems for Cu(I) cluster compounds.[7] They found the expected closed-shell repulsions only when the d orbitals of the metal were considered. When an admixture of the metal d orbitals with higher s and p functions were allowed, the metal-metal interactions were found to be slightly attractive in nature. These attractive interactions were found to persist even after the stereochemical requirements of the bridging ligands had been taken into account.

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(1) R. Hesse, *Ark. Kemi*, **20**, 481 (1962).
(2) I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 103 (1976).
(3) I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 68 (1976).
(4) (a) D. Coucouvanis, C. N. Murphy, and S. K. Kanodia, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976; (b) I. G. Dance and J. C. Calabrese, *Inorg. Chim. Acta*, **19**, L41 (1976).
(5) E. H. Griffith, G. W. Hunt, and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 432 (1976).
(6) (a) F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc.*, **99**, 6268 (1977). (b) L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *ibid.*, **90**, 7357 (1968). Abbreviations used in text: *i*-MNT = 1,1-dicyano-2,2-ethylenedithiolate, $[(CN)_2C{=}CS_2]^{2-}$; DED = 1,1-dicarboethoxy-2,2-ethylenedithiolate, $[(COOC_2H_5)_2C{=}CS_2]^{2-}$; DTS = dithiosquarate dianion, $[S_2C_4O_2]^{2-}$.
(7) P. K. Mehrotra and R. Hoffmann, *Inorg. Chem.*, **17**, 2187 (1978).

0020-1669/80/1319-2993$01.00/0