Molecular structures of 1,12-$B_{12}H_{10}(CO)_2$ and its dihydrate 1,12-$B_{12}H_{10}[C(OH)_2]_2$—a novel bis-carbene complex

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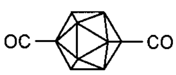
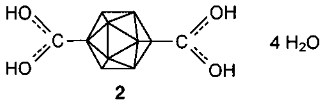
Crystal structures of the dicarbonyl 1,12-$B_{12}H_{10}(CO)_2$ and its hydrated form 1,12-$B_{12}H_{10}(CO_2H_2)_2\cdot 4H_2O$ show little π-bond character in their B–C bonds but contain significant distortions from the regular B_{12} icosahedron geometry; the hydrate, until now thought to be a hydroxonium salt, contains dihydroxycarbene ('protonated carboxylic acid') ligands $C(OH)_2$.

The three-dimensional aromaticity and π-acidity of polyhedral boranes[1] lends interest to their derivative chemistry when potentially π-bonding ligands are present.[2,3] The dianion $[B_{12}H_{12}]^{2-}$ has particular interest in this connection as it contains the electronically highly delocalized robust B_{12} icosahedron[4] present in tough ceramic materials like elemental boron, boron carbide and metal borides. The I_h symmetry of the dianion is expected to be lowered on attachment of ligands with π bonding potential. We here report structural studies on two neutral complexes 1,12-$B_{12}H_{10}L_2$ in which two opposed hydride ligands of $[B_{12}H_{12}]^{2-}$ are replaced by neutral potentially π-acidic ligands L of a type normally associated with transition metals, namely the carbonyl ligand L = CO or a Fischer carbene ligand L = $C(OH)_2$. The known dicarbonyl $B_{12}H_{10}(CO)_2$ **1**, synthesized from $[B_{12}H_{12}^{2-}]$ and CO under high pressure and temperature in low yield,[5,6] had been subjected to a recent photoelectron and theoretical study[7] which suggested it contained single B–C and triple C≡O bonds though this had not been structurally confirmed. The bis(dihydroxycarbene) complex $B_{12}H_{10}[C(OH)_2]_2$ **2**, prepared by us in a neutral hydrated form by hydration of **1**, had hitherto been regarded[5,6,8] as a hydroxonium salt $[H_3O^+]_2[B_{12}H_{10}(CO_2H)_2]^{2-}$ **3** with two carboxylic acid residues CO_2H replacing two hydrogen ligands of $B_{12}H_{12}^{2-}$. The hydrate **2** appears to be the first structurally characterized compound with two carbene diol groups. A preliminary potentiometric titration of **2** in water gave pK_a values of 4.2 and 9.0 for loss of the first and second protons respectively.



1



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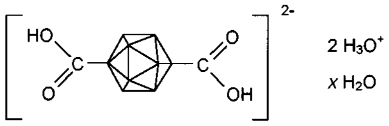

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Suitable crystals of $B_{12}H_{10}(CO)_2$ **1** for X-ray crystallography were formed by slow sublimation at 40–50 °C (0.005 mmHg) for 2–3 days. A crystal of the dicarbonyl **1**† was flash-cooled to 100 K and an X-ray diffraction study reveals a well ordered structure in the space group *Cmca*.‡ The molecule has 2/*m* site symmetry, which results in only nine atoms being crystallographically unique. The bond lengths of B–C and C–O and the nearly linear BCO angle in **1** are typical of BCO groups in neutral borane carbonyls.[9] The molecular structure with significant bond lengths and angles is shown in Fig. 1. A crystal of the hydrate $B_{12}H_{10}(CO_2H_2)_2\cdot 4H_2O$ **2**,§ formed by recrystallization with water, was also flash-cooled to 90 K and shows a well ordered structure in space group *C*2/*c* with two independent water molecules in the asymmetric unit.¶ The hydrate **2** has two carbene diol $C(OH)_2$ groups with identical C–O and O–H bond lengths within experimental error. Fig. 2 shows the molecular structure with significant bond lengths and angles. The supramolecular structure of **2** consists of sheets of cages mediated by water molecules on the (101) plane with hydrogen bond distances (O···H/Å) of 1.73(2) and 1.80(2) between the diol groups and the water molecules, and 1.92(2) and 1.97(2) between the water molecules.

Bond order calculations carried out on the molecular geometries of **1** and **2** using the AM1 program[2] show little π bonding between the borane cluster and the carbonyl groups in **1** and negligible between the cluster and the carbene diol groups

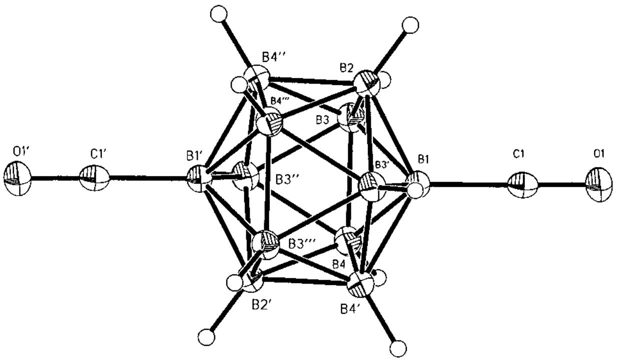

Fig. 1 Molecular structure of **1** (50% ellipsoids). Important interatomic distances (Å) are: O(1)–C(1) 1.119(2), C(1)–B(1) 1.543(2), average B–B distances; polar–tropical 1.768, tropical–tropical 1.824, tropical–tropical′ 1.779. Selected angles (°) O(1)–C(1)–B(1) 179.18(12), C(1)–B(1)–B(2) 117.28(9), C(1)–B(1)–B(3) 118.26(5), C(1)–B(1)–B(4) 119.66(8).

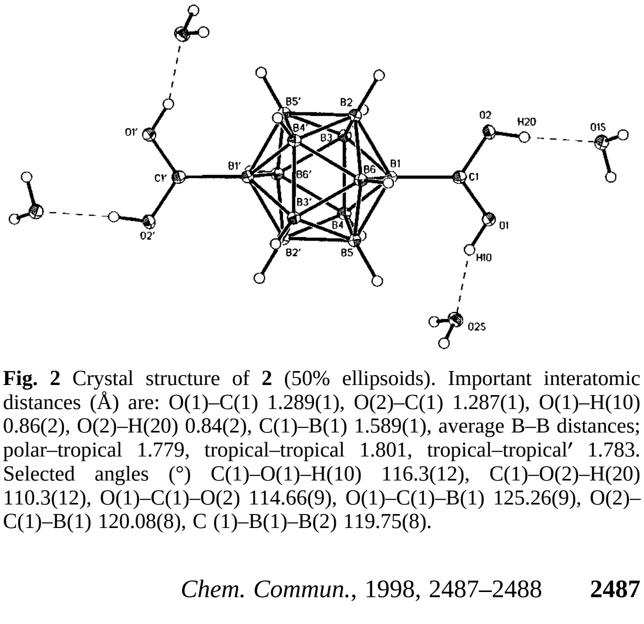

Fig. 2 Crystal structure of **2** (50% ellipsoids). Important interatomic distances (Å) are: O(1)–C(1) 1.289(1), O(2)–C(1) 1.287(1), O(1)–H(10) 0.86(2), O(2)–H(20) 0.84(2), C(1)–B(1) 1.589(1), average B–B distances; polar–tropical 1.779, tropical–tropical 1.801, tropical–tropical′ 1.783. Selected angles (°) C(1)–O(1)–H(10) 116.3(12), C(1)–O(2)–H(20) 110.3(12), O(1)–C(1)–O(2) 114.66(9), O(1)–C(1)–B(1) 125.26(9), O(2)–C(1)–B(1) 120.08(8), C (1)–B(1)–B(2) 119.75(8).

Table 1 Bond lengths and bond orders for B–C and C–O bonds in **1** and **2**

	Bond length (Å)		Total bond order		π-Bond order	
	B–C	C–O	B–C	C–O	B–C	C–O
1	1.543(2)	1.119(2)	0.843	2.422	0.114	1.464
2	1.589(1)	1.287(1)	0.828	1.328	0.064	0.407
		1.289(1)		1.274		0.369

in **2** (Table 1). There is π electron delocalization in all C–O bonds, the carbonyl group bond order is roughly 2.5 in **1** whereas the carbenediol group in **2** has two C–O bond orders of around 1.5 (like those found in symmetrical chelating carboxylates). AM1 calculated Mulliken charges give an overall charge of +0.4 for the carbonyl group in **1** and +0.5 for the diol group in **2**. The molecular structures of **1** and **2** remain largely unchanged in solution as experimental ^{11}B NMR data are in accord with calculated GIAO/NMR data|| (using the GAUSSIAN94 program) generated from their X-ray geometries.

The distortion of the B_{12} cage geometry in **1** from regular I_h is interesting. If one regards the B_{12} icosahedron as globular, with the substituted boron atoms occupying polar sites, the remainder occupying tropical sites, the dicarbonyl **1** show lengthening of the boron–boron bonds within the tropics, shortening of the bonds linking tropical to polar boron atoms, but little change in the distances linking northern to southern tropical boron atoms (average bond distances shown in the figure captions) compared to $B_{12}H_{12}^{2-}$ (average B–B distance 1.784 Å). The icosahedron is thus squashed from pseudospherical to oblate spheroidal along the polar axis (distances: polar–polar 3.19 Å and tropical–tropical′ 3.45 in **1**, *cf.* 3.39 in $B_{12}H_{12}^{2-}$). Compound **2** and the only other known 1,12-$B_{12}H_{10}L_2$ derivative structurally characterized[10] (L = SMe_2) show similar distortions but these are not as extreme as in **1**.

The remarkably close structural relationship of the substituents in boranes **1** and **2** and in carbocations[11] $MeCO^+$ (C–O 1.110 Å) and $MeC(OH)_2^+$ (C–O 1.273 Å) respectively implies that compounds **1** and **2** can be viewed as neutral main group analogues of bis-carbocations. Further evidence of the close relationship is shown in the ^{13}C NMR peak seen at 200.2 ppm in **2** like those carbene carbons in the carbocations $RC(OH)_2^+$ whose peaks are observed in the 215–190 ppm region.[12] There are parallels of the boranes **1** and **2** with transition metal carbonyl and dioxycarbene $C(OR)_2$ complexes,[13] in which the metal–carbon bonds are always shorter to the carbonyl group than to the dioxycarbene group.

Our findings have implications for other supposed carboxylic acid derivatives of other borane anions. Hydration of the borane dicarbonyls, 1,10-$B_{10}H_8(CO)_2$ and 1,7-$B_{12}H_{10}(CO)_2$, have been reported[5,6] to give carboxylic acids, $[H_3O^+]_2$[1,10-$B_{10}H_8(CO_2H)_2^{2-}$] and $[H_3O^+]_2$[1,7-$B_{12}H_{10}(CO_2H)_2^{2-}$], respectively whereas the related mono-anions, 2-$B_{10}H_9(CO)^-$ and $B_{12}H_{11}(CO)^-$, were reported[14] to produce $[H_3O^+]_2$[2-$B_{10}H_9(CO_2H)^{2-}$] and $[H_3O^+]_2[B_{12}H_{11}(CO_2H)^{2-}]$. Carbenediol groups are probably present in these hydrates. The dicarboxylic acid dianion in **3** is likely to exist in metal salts[6] generated from **2**.

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Notes and references

† *Spectroscopic data* for **1**: ν_{max}/cm^{-1} 2557s (BH); 2209s (CO). δ_C (solvent CD_3CN), 163 (br); δ_B (standard $BF_3\cdot Et_2O$), −11.4 (1B, s), −22.4 [5B, d, *J*(BH) 141 Hz], δ_H 1.92 (s, BH).

‡ *Crystal data* for **1**: $C_2H_{10}B_{12}O_2$, *M* = 195.82, orthorhombic, space group *Cmca* (no. 64), *a* = 9.2538(3), *b* = 10.6482(3), *c* = 10.9415(2) Å, *U* = 1078.14(5) Å^3, *Z* = 4, D_c = 1.206 g cm^{-3}, *μ* = 0.064 mm^{-1}, *F*(000) = 392, *T* = 100(2) K, 653 unique reflections, R_1 = 0.0323 [606 data $I > 2\sigma(I)$], wR_2 = 0.0951 (all data), GOF = 1.101. Hydrogen atoms were refined freely. CCDC 182/1046.

§ *Spectroscopic data* for **2**: ν_{max}/cm^{-1} 3441br s (OH); 2501s (BH); 1651s (CO). δ_C (solvent CD_3CN), 200.2 [1:1:1:1 q, *J*(BC) 87 Hz], δ_B (standard $BF_3\cdot Et_2O$), −12.3 (1B, s), −14.4 [5B, d, *J*(BH) = 133 Hz], δ_H 6.19 (12H, brs, 4 H_2O, 4 OH), 1.63 (10H, s, BH).

¶ *Crystal data* for **2**: $C_2H_{22}B_{12}O_8$, *M* = 303.92, monoclinic, space group *C*2/*c* (no. 15), *a* = 13.6298(7), *b* = 7.3018(4), *c* = 15.9244(10) Å, *β* = 105.720(2)°, *U* = 1525.6(2) Å^3, *Z* = 4, D_c = 1.323 g cm^{-3}, *μ* = 0.099 mm^{-1}, *F*(000) = 632, *T* = 90(2) *K*, 1749 unique reflections, R_1 = 0.0286 [1591 data $I > 2\sigma(I)$], wR_2 = 0.0814 (all data), GOF = 1.132. Hydrogen atoms were refined freely. CCDC 182/1046.

|| Calculated GIAO (HF/6-31G*) ^{11}B NMR data for **1**: δ −11.8 (5B), −21.7 (1B); **2**: δ −11.4 (1B), −13.7 (5B).

1 G. A. Olah, G. K. S. Prakash, R. E. Williams, L. E. Field and K. Wade, *Hypercarbon Chemistry*, Wiley, New York, 1987; V. I. Bregadze, *Chem. Rev.*, 1992, **92**, 177; B. J. Gimarc and M. Zhao, *Inorg. Chem.*, 1996, **35**, 825.

2 For examples see: D. A. Brown, W. Clegg, H. M. Colquhoun, J. A. Daniels, I. R. Stephenson and K. Wade, *J. Chem. Soc., Chem. Commun*, 1987, 889; W. Clegg, R. Coult, M. A. Fox, W. R. Gill and K. Wade, *Polyhedron*, 1992, **11**, 2717; R. C. B. Copley, M. A. Fox, W. R. Gill, J. A. K. Howard, J. A. H. MacBride, R. J. Peace, G. P. Rivers and K. Wade, *Chem. Commun.*, 1996, 2033; M. A. Fox, J. A. H. MacBride, R. J. Peace and K. Wade, *J. Chem. Soc., Dalton Trans.*, 1998, 401.

3 R. Kivekas, R. Sillanpaa, F. Teixidor, C. Vinas and R. Nunez, *Acta Crystallogr., Sect. C*, 1994, **50**, 2027; D. M. Murphy, D. M. P. Mingos and J. M. Forward, *J. Mater. Chem.*, 1993, **3**, 67.

4 P.v.R. Schleyer, G. Subramanian, H. Jiao, K. Najafian and M. Hofmann, *Advances in Boron Chemistry*, ed. W. Siebert, The Royal Society of Chemistry, Cambridge 1997, p. 3.

5 W. H. Knoth, J. C. Sauer, H. C. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, 1964, **86**, 115.

6 W. H. Knoth, J. C. Sauer, J.H. Balthis, H. C. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, 1967, **89**, 4842.

7 P. Brint, B. Sangchakr, M. McGrath, T. R. Spalding and R. J. Suffolk, *Inorg. Chem.*, 1990, **29**, 47.

8 L. D. Hansen, J. A. Partridge, R. M. Izatt and J. J. Christensen, *Inorg. Chem.*,1966, **5**, 569; L. Barton, T. Onak, R. J. Remmel and S. G. Shore, in *Gmelin Handbuch der Anorganischen Chemie*, Borverbindungen 20, Springer-Verlag, Germany, 1979, p. 238; E.L. Muetterties and W. H. Knoth, *Polyhedral Boranes*, Arnold, London, 1968, p. 117; C. E. Housecroft, *Boranes and Metalloboranes*, Wiley, New York, 1990, p.146.

9 S. H. Bauer, *J. Am. Chem. Soc.*, 1937, **59**, 1804; W. Gordy, H. Ring and A. B. Burg, *Phys. Rev.*, 1950, **78**, 512; J. Rathke and R. Schaeffer, *Inorg. Chem.*, 1974, **13**, 760; J. D. Glore, J. W. Rathke and R. Schaeffer, *Inorg. Chem.*, 1973, **12**, 2175; S. J. Cranson, P. M. Davies, R. Greatrex, D. W. H. Rankin and H. E. Robertson, *J. Chem. Soc., Dalton Trans.*, 1990, 101.

10 E. J. M. Hamilton, G. T. Jordan IV, E. A. Meyers and S. G. Shore, *Inorg. Chem.*, 1996, **35**, 5335.

11 G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, 1967, **89**, 3591; J. M. Le Carpentier and R. Weiss, *Acta Crystallogr., Sect. B.*, 1972, **28**, 1421; K. Bartmann and D. Mootz, *Z. Anorg. Allg. Chem.*, 1991, **601**, 31.

12 R. Minkwitz, S. Schneider, M. Seifert and H. Hartl, *Z. Anorg. Allg. Chem.*, 1996, **622**, 1404.

13 See for example; M. M. Singh and R. J. Angelici, *Angew. Chem. Int. Ed. Engl.*, 1983, **22**, 163; G. L. Miessler, S. Kim, R. A. Jacobson and R. J. Angelici, *Inorg. Chem.*, 1987, **26**, 1690; G. Bondietti, R. Ros, R. Roulet, F. Musso and G. Gervasio, *Inorg. Chim. Acta*, 1993, **213**, 301.

14 K. Shelly, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, 1992, **31**, 2889; I. B. Sivaev, V. I. Bregadze and S. Sjoberg, *Russ. Chem. Bull.* (Engl. Transl.), 1998, **47**, 193.

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