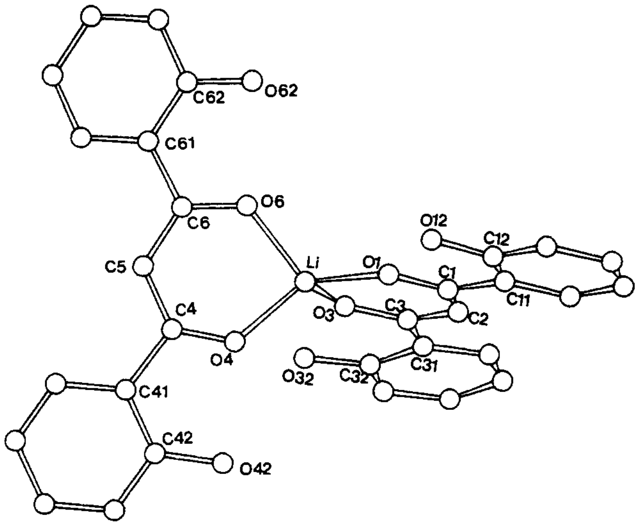

Figure 1. Perspective drawing of $[Li(bhppH_2)]^-$ showing the molecular structure and labeling scheme.

Positional parameters for the non-hydrogen atoms are given in Table I; selected bond distances and angles, in Table II; structure factors, positional parameters for hydrogen atoms, and anisotropic thermal parameters are available as supplementary material. The molecular geometry and labeling diagram are shown in Figure 1.

Results and Discussion

The interaction of $Zn(bhppH_2)_2 \cdot 2CH_3OH$ with 6 equiv of LiMeO in ethanol at 0 °C produces a yellowish homogeneous solution that, upon the addition of NEt_4Cl and a large excess of water, yields an amorphous solid. Purification of the solid was achieved by treatment with warm ethyl acetate. The insoluble residue was discarded. Cooling the warm solution to room temperature afforded yellow crystals that were suitable for X-ray diffraction studies. The compound is air stable.

Until recently, few well-characterized mononuclear lithium complexes where the only metal present is Li were known. Some of these complexes have at least one C–Li bond, examples are 2-lithio-2-phenyl-1,3-dithiane–tetrahydrofuran–tetramethylethylenediamine[10] and $Li[CH(SiMe_3)_2](pmdeta)$.[11] Others are not organometallic, but in them, lithium reaches tetrahedral coordination by means of different kind of ligands in a tridimensional arrangement. In most of them hydrogen bonds are involved. One example is lithium hydrogen acetylenedicarboxylate hydrate.[12] In this case the lithium is surrounded by four oxygen atoms from three anions and one water molecule. Another example is $(B15C5)Li(picrate) \cdot 2H_2O$[13] (B15C5 = benzo-15-crown-5). In it the cation is coordinated by two oxygen atoms from the chelating picrate anion and two water molecules. Surprisingly, the crown ether molecule is not bound to the Li ion but to water molecules through weak hydrogen bonds. To our knowledge there is no structural information about a discrete molecular complex as simple as the one presented in this paper, where the tetrahedral coordination around the Li ion is achieved by donor atoms from two identical bidentate $(bhppH_2)$ molecules. There was more information about these kind of compounds in solution where a few complexes of the type 1:2 Li:L (e.g., L = dipivaloylethane, diisobutyrylmethane)[14] had been described.

The structure of $NEt_4[Li(bhppH_2)_2]$ as revealed by X-ray crystallography shows a Li atom surrounded by four oxygen atoms in a distorted tetrahedral geometry where the 1,3-bis(2-hydroxyphenyl)-1,3-propanedionate ligand acts in a bidentate fashion. The Li–propanedionate rings adopt a half-chair form with Li deviating 0.10 (2) and 0.31 (2) Å from the mean plane defined by the propanedionate moiety. The most planar ring shows the shorter Li–O bond distances while the dihedral angle between the two ring planes is equal to 99 (1)°. The phenyl rings linked to C(1), C(3), C(4), and C(6) atoms are twisted by 10, 11, 12, and 13°, respectively with regard to the plane defined by the β-diketone moiety. These twistings and the $C(sp^2)$–C(phenyl) bond distances (e.g., C(1)–C(11)) indicate that the electron delocalization of the propanedionate ring does not extend to the phenyl rings. The hydroxy groups are hydrogen bonded to the adjacent metal-coordinated O atoms (O(1)···O(12), O(3)···O(32), O(4)···O(42), and O(6)···O(62) with distances equal to 2.47 (1), 2.47 (1), 2.44 (1), and 2.48 (1) Å, respectively). The Li–O bond distances are all different with values 1.85 (2), 1.90 (2), 1.89 (2), and 1.91 (2) Å (average value 1.885 (5) Å). This large Li–O bond distance is very similar to the value 1.99 (9) Å (average) found in LiSiONα[12] or 1.97 (5) Å found in 2-lithio-2-phenyl-1,3-dithiane–tetrahydrofuran–tetramethylethylene, precluding, consequently, the possibility of aromatic character in the six-membered β-diketonate chelate ring. On the other hand, the $C\overset{\cdots}{-}O$ distances of 1.29 (4) Å (average) found in this $NEt_4[Li(bhppH_2)_2]$ complex are similar to these observed in $Zn(bhppH_2) \cdot 2EtOH$ ($C\overset{\cdots}{-}O$ = 1.303 (13) Å). This close similarity is a clear indication of the lack of aromatic character in the Zn–β-diketone ring of $Zn(bhppH_2)_2 \cdot 2EtOH$.

The interaction of $Zn(bhppH_2)_2 \cdot 2EtOH$ with 6 equiv of NaMeO, in conditions similar to these described to get $NEt_4[Li(bhppH_2)_2]$ yielded $Na(bhppH_2) \cdot H_2O$, as evidenced by analysis and ^1H NMR.

Following a similar procedure, reaction of $Zn(acac)_2 \cdot H_2O$ with 6 equiv of LiMeO did not yield $NEt_4[Li(acac)_2]$. No further attempts were made to identify the nature of the resulting compounds.

These results in the solid state and others previously reported in solution for dipivaloylethane and diisobutyrylmethane[14] as complexing β-diketones show the great affinity of chelating agents of the type R″COCH(R′)COR″, where R′, R″ are bulky terminal groups, for the lithium ion. The affinity for Na^+ had been proven to decrease in solution for large β-diketones; e.g., the chelating tendency of dipivaloylethane for lithium was 1000 times greater than that for sodium.[15] As indicated earlier these results are in agreement with ours where $[Li(bhppH_2)_2]^-$ has been obtained but not $[Na(bhppH_2)_2]^-$.

Registry No. $NEt_4[Li(bhppH_2)_2]$, 96212-06-5; $Zn(bhppH_2)_2$, 93401-40-2; $Na(bhppH_2)$, 96212-07-6; $Zn(acac)_2$, 14024-63-6; LiMeO, 865-34-9.

Supplementary Material Available: Tables of structure factors, positional parameters for hydrogen atoms, and anisotropic thermal parameters (12 pages). Ordering information is given on any current masthead page.

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Symmetry Lowering in B_3H_9 and B_4H_{12}

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The usual symmetry assignments are D_{3h} for B_3H_9 and D_{4h} for B_4H_{12}, both of which are ring structures in which BH_2 groups are

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Table I. Absolute Energies (–hartrees) and Zero-Point Energies (kcal/mol) for B_3H_9 and B_4H_{12} Optimized in Different Point Groups

	3-21G	6-31G	MP2/6-31G	MP3/6-31G	6-31G*	ZPE[a]
B_3H_9 (**1**), D_{3h}	78.71636	79.13092	79.33843	79.37471	79.17877	60.66 (3)
B_3H_9 (**2**), C_{3v}	78.71780	79.13240	79.34289	79.37971	79.18208	62.44 (0)
B_4H_{12} (**3**), D_{4h}	104.95111	105.49748	105.76428	105.81217	105.54898	79.18 (5)
B_4H_{12} (**4**), D_{2d}	104.95230	105.49879	105.76855	105.81653	105.55197	79.69 (4)
B_4H_{12} (**5**), C_{4v}	104.95336	105.49920	105.77033	105.81848	105.55627	82.31 (1)
B_4H_{12} (**5**), C_{2v}	104.95397	105.50053	105.77373	105.82192	105.55813	82.21 (0)

[a] Zero-point energy; the number in parentheses refers to the number of calculated negative (imaginary) frequencies.

Table II. Energies (kcal/mol) Relative to either B_3H_9 or B_4H_{12} at Difference Levels of Theory[a]

	3-21G	6-31G	MP2/ 6-31G	MP3/ 6-31G	6-31G*	[MP3/ 6-31G*]	[MP3/6-31G*] + ZPC
B_3H_9 (**1**), D_{3h}	0	0	0	0	0	0	0
B_3H_9 (**2**), C_{3v}	-0.9	-0.9	-2.8	-2.8	-2.1	-4.0	-2.2
B_4H_{12} (**3**), D_{4h}	0	0	0	0	0	0	0
B_4H_{12} (**4**), D_{2d}	-0.7	-0.8	-2.7	-2.7	-1.9	-3.8	-3.3
B_4H_{12} (**5**), C_{4v}	-1.4	-1.1	-4.0	-4.6	-4.2	-7.7	-4.6
B_4H_{12} (**5**), C_{2v}	-1.8	-1.9	-5.8	-6.0	-5.7	-9.8	-6.8

[a] The last two entries are computed by using the approximation of additivity.

bridged by the remaining hydrogen atoms. These probable or possible transient intermediates have been assigned these symmetries in theoretical studies.[1] However, a tendency for low-coordinated boron to acquire additional interactions has previously been observed in theoretical studies in which electron correlation has been included[2] in a few other boranes. For that reason we have reexamined the stable geometries of B_3H_9 and B_4H_{12} and show below that their most stable symmetries are C_{3v} and C_{2v}, respectively.

Optimized geometries were obtained by using stated symmetry constraints at the 3-21G level from the GAUSSIAN 82 program.[3] The same program was used for calculation of vibrational frequencies by the CPHF method[3] in a 3-21G basis. "Single-point" assumed geometries were used for subsequent calculations at the (Hartree–Fock) 6-31G level augmented by correlation at the MP2 and MP3 (Møller–Plesset) levels and polarization at the 6-31G* level (d orbitals on B). Relative energies $\Delta E = E_b - E_a$ for the distorted structure b as compared with those for the most symmetrical structure a were estimated by using the approximation[4]

$$\Delta E(\mathrm{MP2/6\text{-}31G^*}) \approx \Delta E(\mathrm{MP2/6\text{-}31G}) + \Delta E(\mathrm{HF/6\text{-}31G^*}) - \Delta E(\mathrm{HF/6\text{-}31G})$$

The approximation that the correlation and polarization corrections are additive has been found to reproduce relative energies of these basis sets to within a few kcal/mol for isomerizations and several kcal/mol for more complex reactions.[4]

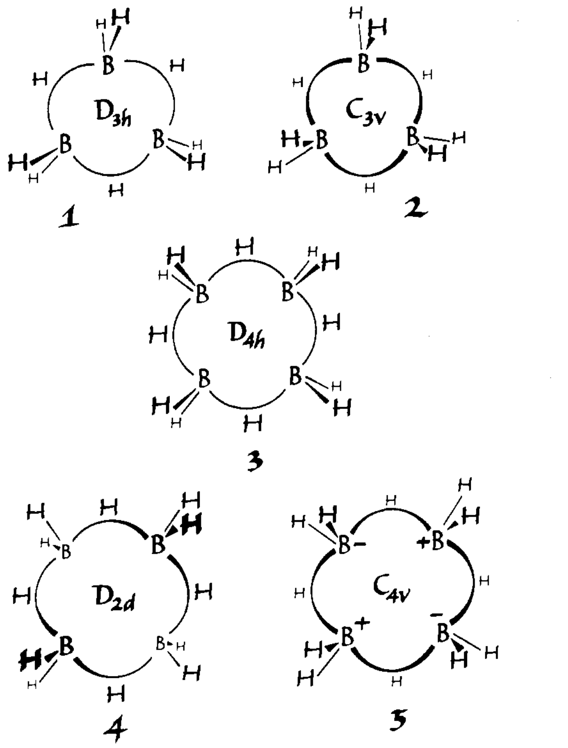

Figure 1. Structures for B_3H_9 and B_4H_{12}. In **5**, + and – indicate displacements of 0.26 Å closer to or further from the plane containing the four bridges, as the symmetry lowers to C_{2v}.

Table III. Geometric Differences for B_3H_9 and B_4H_{12} Optimized by Using the 3-21G Basis in Different Point Groups

	B–B, Å	B–H_b, Å	B–H_b–B, deg	B–B(trans), Å	vert dist,[a] Å
1 (D_{3h})	2.351	1.305	128.5		0.0
2 (C_{3v})	2.256	1.310	118.9		0.31
3 (D_{4h})	2.606	1.306	172.8	3.686	0.0
4 (D_{2d})	2.574	1.304	161.4	3.410	0.45[b]
5 (C_{4v})	2.485	1.312	142.6	3.514	0.40
5 (C_{2v})	2.471	1.310/1.310	141.3	3.235/3.593	0.12/0.64[b]

[a] Distance between the plane containing the boron atoms and the plane containing the bridge hydrogens. [b] Vertical distance of boron atoms from the plane containing the bridge hydrogens.

For B_3H_9 the D_{3h} and C_{3v} structures, **1** and **2**, respectively, in Figure 1, were optimized. The total energies (Table I) and relative energies (Table II) show that the C_{3v} structure is more stable at all levels of calculation. The difference is small, 2.2 kcal/mol at [MP3/6-31G*][4] + ZPC (zero-point vibrational corrections) and 4.4 kcal/mol if the ZPC corrections are omitted. This C_{3v}

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Table IV. Calculated Vibrational Frequencies (cm^{-1}) from 3-21G Optimized Geometries

1 (D_{3h})	**2** (C_{3v})	**3** (D_{4h})	**4** (D_{2d})	**5** (C_{4v})	**5** (C_{2v})
165*i* e''	218 e	44*i* b_{1u}	92*i* b_2	34*i* b_2	93 a_1
214*i* a_2''	274 a_1	108*i* b_{2u}	143*i* e	220 a_1	160 b_1
430 a_1'	491 a_1	160*i* e''	146*i* a_2	242 e	208 a_1/237 b_2
491 e'	551 e	164*i* a_{2u}	72 a_1	268 b_1	239 a_2
715 a_2'	734 a_2	278 b_{1g}	212 b_1	354 b_1	309 a_2
870 e''	862 e	361 b_{2g}	459 b_2	396 b_2	391 a_1
970 a_1''	966 e	501 e'	508 a_1	576 e	586 b_2/592 b_1
990 e'	1009 a_2	504 a_{1g}	531 e	577 a_1	604 a_1
1059 a_2''	1165 a_1	521 b_{1g}	566 b_1	617 a_2	628 a_2
1189 e'	1200 e	563 a_{2g}	594 a_2	634 b_1	649 a_2
1197 e''	1216 e	852 b_{1u}	754 e	868 b_2	808 b_2
1224 a_1'	1242 a_1	879 e''	818 a_1	886 e	816 b_1/839 a_1
1487 e'	1656 e	898 e'	972 b_1	930 e	976 b_1/985 b_2
1592 a_1'	1674 a_1	902 a_{1u}	992 e	987 a_2	996 a_2
2293 a_2'	2228 a_2	1120 e'	1132 e	1156 e	1143 b_1/1153 b_2
2402 e'	2278 e	1147 a_{2u}	1146 b_2	1171 a_1	1178 a_1
2752 e'	2764 e	1167 a_{1g}	1180 a_2	1212 b_2	1208 a_1
2762 a_1'	2776 a_1	1179 e''	1186 e	1243 b_1	1230 a_1
2872 e''	2885 e	1183 b_{2g}	1194 b_2	1258 e	1241 b_2/1252 b_1
2880 a_2''	2896 a_1	1189 b_{2u}	1208 a_1	1265 a_1	1259 a_1
		1243 b_{1g}	1258 a_1	1382 a_1	1389 a_1
		1246 e'	1264 e	1391 e	1400 b_2/1404 a_2
		1248 a_{1g}	1272 b_1	1393 b_1	1410 b_1
		2183 a_{2g}	2240 a_2	2110 a_2	2143 a_2
		2599 e'	2574 e	2457 e	2442 b_2/2474 b_1
		2655 b_{2g}	2636 b_2	2509 b_2	2508 a_1
		2762 e'	2761 e	2755 b_2	2752 a_1
		2763 a_{1g}	2762 a_1	2760 e	2753 b_2/2762 b_1
		2765 b_{2g}	2762 b_2	2767 a_1	2766 a_1
		2868 b_{1u}	2871 a_1	2873 b_2	2871 a_1
		2874 e''	2872 e	2883 e	2873 b_2/2883 b_1
		2882 a_{2u}	2880 b_2	2894 a_1	2893 a_1

structure is more compact than the D_{3h} structure: the B–B distance is contracted from 2.351 to 2.256 Å, and the angle at the bridge hydrogen is reduced from 128.5 to 118.9° (Table III).

Vibrational frequencies (Table IV) for B_3H_9 indicate that the C_{3v} structure is at a minimum, since all are positive and real. The three negative frequencies for the D_{3h} structure indicate that it is not a candidate for the transition state between interconverting C_{3v} structures. Although the negative frequency of 214*i* cm^{-1} of the imaginary mode having a_2'' symmetry could interconvert C_{3v} structures, the 65*i* cm^{-1} frequency belongs to an imaginary mode in which two bridge hydrogens move in one direction and the third moves in the other direction out of the major plane of the molecule. Thus, the correct transition state is probably one in which one bridge "flips" first, followed by the other bridge hydrogens.

For B_4H_{12}, we find that the D_{2d}, C_{4v}, and C_{2v} structures are all more stable than the D_{4h} structure at all levels of computation (Table III). The C_{2v} structure is more stable than the D_{4h} structure by 6.8 kcal/mol at the [MP3/6-31G*] + ZPC level and is only 2.2 kcal/mol (3.5 kcal/mol) more stable than the C_{4v} (D_{2d}) structure at this level (Table II). If ZPC corrections are omitted, the C_{2v} structure is 9.8 kcal/mol more stable than the D_{4h} structure and is 3.5 kcal/mol more stable than the D_{2d} structure at the [MP3/6-31G*] level. Both of these lower symmetry structures are slightly more compact than the D_{4h} structure, as indicated by the shortening of B–B distances and decrease in the bond angle about the bridge hydrogens (Table III).

The vibrational frequencies (Table IV) reveal five imaginary modes for the D_{4h} structure, four imaginary modes for the D_{2d} structure, one imaginary mode for the C_{4v} structure, and no imaginary modes for the C_{2v} structure. Distortion of the C_{4v} structure to C_{2v} is indicated in **5**, where diagonal borons are displaced 0.26 Å closer to (+) or further (−) form the plane containing the four bridge hydrogens while the average displacement is nearly identical with that found in the C_{4v} structure. Because of its negative eigenvalues, the D_{4h} structure cannot be the transition state for interconversion of C_{2v} structures, and we suggest that some sequence of consecutive or nonsimultaneous flips occurs during the interconversion such that the barrier remains below 6.8 kcal/mol. Both B_3H_9 and B_4H_{12} are therefore double-minimum vibrational problems and should show the expected splitting of rotational lines.

Reduced symmetry[2] appears in BH_5, $B_2H_7^-$, B_4H_8, and B_5H_{11} and, here, in B_3H_9 and B_4H_{12}. There are two main effects. The first is a tendency for low-coordinated boron to raise its coordination number, particularly if underuse of boron orbitals by bridge hydrogens occurs. The second is the conversion of terminal hydrogens to bridge hydrogens as long as strain is not excessive. This latter effect is primarily due to correlation: the pair of electrons in a bridge bond are separated by a nucleus, while these electrons show comparatively greater repulsion effects if they are in a single terminal bond.

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Vibrational Study of Ionic Association in Aprotic Solvents. 8. Copper(I) Thiocyanate in Soft Donor Solvents

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Copper(I) thiocyanate is insoluble in water and in most usual solvents, but it is readily soluble in *N,N*-dimethylthioformamide (DMTF), which is highly polar, donating through the soft S atom. This salt is also slightly soluble ((~1–4) × 10^{-2} M) in tetrahydrothiophene (THT), dimethyl sulfoxide (Me_2SO), and hexamethylphosphoric triamide (HMPT). The existing species and the bonding mode of SCN can be identified by infrared spectroscopy.

Experimental Section

THT was distilled on a 20-plate column, and DMTF was distilled under reduced pressure. Other solvents were of the best commercial grade. All solvents were stored on 4-Å molecular sieves. Solutions were prepared in a drybox. IR spectra were recorded on an interferometric Bruker IFS 45 spectrometer and Raman spectra on a Coderg T 800 spectrometer.

Results and Discussion

The CuSCN solutions in pure DMTF were first investigated in the ν(CN) and ν(CS) regions of SCN. In both regions two absorption bands were observed at 2055 and 2076 cm^{-1} (Figure 1b) and at 737 and 780 cm^{-1}. The bands at 2055 and 737 cm^{-1} are characteristic of the SCN^- ion. They appeared at the same frequency in spectra of NBu_4SCN solutions (Figure 1a). This assignment was confirmed by dilution effects on the relative intensities in the ν(CN) region. The other two bands were assigned to the isothiocyanate ion pair CuNCS because the frequency shift of ν(CS) relative to SCN^- is positive while it is negative for thiocyanate complexes such as AgSCN.[1,2] The frequency shifts (27 and 43 cm^{-1}) of ν(CN) and ν(CS) are in the same ratio as for LiNCS (14 and 30 cm^{-1}) and somewhat larger, which indicates that the structures of both ion pairs are similar. The isothiocyanate structure of CuNCS was also proved by the variation in integrated intensity between SCN^- and CuNCS. This variation was more easily measured in THT where the integrated intensity of ν(CN) rises from 17 100 in NBu_4SCN to 20 700 mol^{-1} L cm^{-2} in CuNCS.

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