analogous linkage isomers of the type M–SeCN and M–NCSe and possibly M–NCO and M–OCN.

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Registry No. $K_2[Fe(NCS)_4]$, 88295-75-4; $(Me_4N)_2[Fe(NCS)_4]$, 13978-34-2; $(Et_4N)_2[Fe(NCS)_4]$, 14127-42-5; $K_2[^{57}Co(NCS)_4]$, 88295-76-5; $(Et_4N)_2(FeCl_4)$, 15050-84-7; $(Et_4N)_2(^{57}CoCl_4)$, 88295-80-1; ^{57}Co, 13981-50-5.

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An ab Initio Study of the $B_2H_7^-$ Anion

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Shore et al.[1] have reported an X-ray diffraction study on the $B_2H_7^-$ anion as a part of the $[(Ph_3P)_2N]^+[B_2H_7]^-\cdot CH_2Cl_2$ compound. In disagreement with previous ab initio calculations carried out in the gas phase[2] on $B_2H_7^-$, Shore et al. found the ion to exhibit a bent B–H–B central linkae as well as to feature a certain asymmetry in the lengths of the boron distances from the bridging hydrogen. They report an overall C_s symmetry for the anion, with two hydrogens set trans to each other (one on each boron) and set in the same plane as the two borons and the central hydrogen.

A similar compound, $[Me_3Al(\mu\text{-}H)AlMe_3]^-$, as reported by Atwood et al.,[3] also through X-ray diffraction data and confirmed by our ab initio calculations[4] using a 3-21G basis set, reveals a linear Al–H–Al bond.

In this work, the $B_2H_7^-$ anion is subjected to an investigation by ab initio (Hartree–Fock) methods, in order to elucidate its geometry and to report eventual differences in the compound description introduced by the use of Gaussian basis sets with and without polarization functions. For comparison purposes, calculations are also carried out on the $B_2H_6F^-$ anion.

Method

The $B_2H_7^-$ ion is subjected to total geometry optimization using a split-valence 6-31G[5a] and a 6-31G**[5b] basis set, as implemented by the GAUSSIAN-80 computer program.[6c] The 6-31G** basis set adds d orbitals on the boron and p orbitals on the hydrogen. The optimization technique used is the Berny optimization technique,[5c] which determines singular points by minimizing the energy with all the parameters to be optimized simultaneously.

The initial value assigned to the B–H–B angle for the 6-31G minimization procedure was 150°.

In the 6-31G** calculations, two initial values were used: 136° (the experimental value reported by Shore et al.[1]) for one optimization and 180° for the second. The purpose of this procedure was to avoid local minima that could be misleading. An almost identical procedure is applied to the $B_2H_6F^-$ anion, again performing two sets f optimizations, one starting with a B–F–B angle of 136° and the other setting the B–F–B angle at 180° and optimizing the other paramters. Since the studies of the $B_2H_6F^-$ anion need further refinement, only the general conclusions are reported here.

Table I displays the energies corresponding to the optimum geometries, together with the geometrial parameters.

In Table II, the net atomic charges are displayed, as obtained for the lowest energy states. Figure 1a, b shows the bent and linear structures of the B_2H_7 anion. Figure 2 shows the $B_2H_6F^-$ anion.

Table I. Energies (au) and Geometrical Parameters[a]

	6-31G $E = -53.37002$	6-31G** $E = -53.40258$
Distances		
B_1H_1	1.33	1.34
B_2H_1	1.33	1.32
B_1H_2	1.21	1.21
$B_1H_3 = B_1H_4$	1.21	1.21
$B_1\text{-}B_2$	2.57	
B_2H_5	1.21	1.21
$B_2H_6 = B_2H_7$	1.21	1.22
Angles		
$B_1H_1B_2$	179.9	149.9
$H_2B_1H_1$	104.2	101.3
$H_3B_1H_1 = H_4B_1H_1$	104.2	104.3
$H_5B_2H_1$	104.2	106.9
$H_6B_2H_1 = H_7B_2H_1$	104.2	104.3
$H_3B_1H_2 = H_4B_1H_2$	114.2	114.0
$-H_6B_2H_5 = H_7B_2H_5$		
Dihedral Angles		
$H_2B_1H_1$ with $B_1H_1B_2$	180.0[b]	180.0
$H_5B_2H_1$ with $B_1H_1B_2$	0.0[b]	0.0

[a] Bond lengths in angstroms; bond angles in degrees. [b] Set values.

Table II. Net Atomic Charges (eu) As Obtained by 6-31G** Calculations for the Optimum Geometry

B_1	0.211	H_4	−0.189
B_2	0.206	H_5	−0.187
H_1	−0.226	H_6	−0.208
H_2	−0.209	H_7	−0.208
H_3	−0.189		

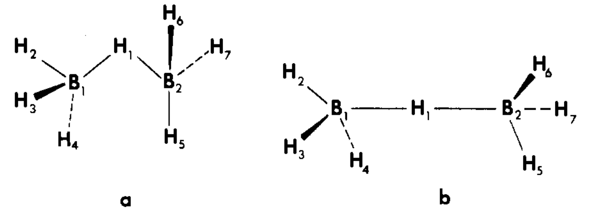

Figure 1. (a) Bent structure of $B_2H_7^-$. (b) Linear structure of $B_2H_7^-$.

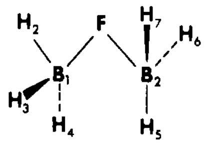

Figure 2. Structure of $B_2H_6F^-$.

Discussion of the Results

The 6-31G calculations predict a linear B–H–B bond. However, in disagreement with previous ab initio calculations, including those carried out with a large basis set with polar-

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ization functions,[2] it is evident that the calculations at the 6-31G** level predict a bent structure for the B–H–B bond.[7] This discrepancy with former results could be attributed to the different optimization techniques used.

As seen from Table I, the 6-31** basis set calculations assign a 149.9° value to the B_1–H_1–B_2 angle and show a slight asymmetry for the B_1–H_1 and B_2–H_1 bond, which feature a 0.02-Å difference in bond length. The B–H bonds where the hydrogen atom is *not* the bridge do not feature significant differences; however, they are all smaller than the central B–H bond. The same effect was found and discussed for the aluminum compound.[4]

The asymmetry mentioned above can be attributed, by using a resonance approach, to the contribution of the structure featuring the BH_4^- anion as a whole donating some of its charge to the electron-deficient BH_3, yielding the $BH_4^-\cdot BH_3$ entity.

As seen from Table I and Figure 1a, the anion features C_s symmetry, with the H_3 and H_5 atoms set in the plane of the B1,H1,B2 atoms. The optimized C_{2v} structure is found by us to feature a slightly higher energy than the C_s structure (0.3 kcal/mol). The preference for a bent structure of some bridged metallic compounds has been explained by a certain amount of bonding occurring between the metals.[6] In the $Al_2H_7^-$ anion, no such bonding takes place and, as a result, the central Al–H–Al bond assumes a linear structure. Since a split-valence basis set without polarization functions proved unreliable in the boron case, the 3-21G results for aluminum[4] could be questioned, but since the X-ray data experiments have been confirmed, it seems safe to assume them to be correct.

An explanation for the different structure of the $B_2H_7^-$ and $Al_2H_7^-$ anions could be found in the higher electronegativity of boron and in the higher metallicity of aluminium, which would lead to a larger positive charge accumulation on the aluminium atoms and consequently a greater repulsion between them, favoring a linear Al–H–L bond. When the Mulliken overlap population is examined, the B–B region shows a 0.03-eu charge in the 6-31G** level calculations, indicative of a slight B–B bonding, while in the calculations carried out on the bent B–H–B bond with the 6-31G basis set, the B–B overlap is of only 0.01 eu. The reason for this difference can be found by examining the composition of the molecular orbitals. Upon such examination, one notices a small bonding participation by the d orbitals on the borons to be present in the ninth MO (HOMO) as well as in the seventh occupied MO. We also considered another possible explanation for the bent structure, by the examination of molecular orbitals related to the central hydrogen–boron bond. Those are the third and seventh MO's. In both of them, as expected, the largest contribution is provided by the 1s hydrogen atomic orbitals. As far as the boron atoms are concerned, in the third MO their 2s orbital contribute the most, while in the seventh MO the greatest contribution belongs to the p_y orbitals (y being the B–B axis). One notices, though, a mixing of the p_x orbital of the hydrogen (x being the axis perpendicular to the B–B bond and contained in the B–H–B plane) in the third orbital. The p_x orbital of hydrogen participates also in the seventh MO, and in both cases, it is of a bonding nature, providing additional stabilization for a bent structure. This effect might be contributing factor to the bending of the B–H–B linkage, but not the essential one. Indeed, as shown by Schleyer et al.[7] the 6-31G* basis set calculations also predict a bent structure for the anion, thus proving that the addition of p orbitals on the hydrogen is not mandatory.

The results obtained for the geometry of the $B_2H_6F^-$ anion show more clearly the importance of occupied p orbitals in producing a nonlinear structure. Indeed, the results show beyond any doubt a bent B–F–B central linkage, both through the use of 6-31G and 6-31G** basis sets. It is evident in this case that the increased stabilization that occurs for a molecular orbital of a_1 asymmetry (C_{2v}) upon bending supersedes the repulsion between the borons, which in the $B_2H_6F^-$ anion features a positive charge of about 0.5 eu and, as such, is much higher than the 0.2 eu present in the B_2H_7 anion.

In conclusion, the $B_2H_7^-$ structure, as described by the 6-31G** basis set, features a bent B–H–B central linkage, in agreement with the X-ray data of Shore et al.[1] However, there are differences between the experimental findings[1] and the theoretical results: the difference between B_1–H_1 and B_2–H_2 is only 0.02 Å in this work while the experimental result shows a 1.27-Å difference. Also, the B_1–H_1–B_2 angle is slightly larger according to our calculations (150° vs. the experimental 136°). The theoretical model also features a larger B_1–B_2 distance than the experimental boron–boron distance. The main issue, though, is the fact that theoretical Hartree–Fock calculations with a 6-31G** basis set predict a bent structure for the anion. We find however the energetic advantage of the bent structure over the linear one to be quite small (below 1 kcal/mol). This is in agreement with the results of Schleyer et al.[7] who also find a small value for the energy difference of the two species.

Registry No. $B_2H_7^-$, 27380-11-6; $B_2H_6F^-$, 82630-61-3.

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(7) A simultaneous study by K. Raghavachari, P. v. R. Schleyer, G. W. Spitznagel, and J. A. Pople reaches the same conclusions, with the use of the 6-31G** and MP2 calculations. The MP2 term modifies only slightly the geometry of the anion.

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High-Pressure Synthesis and Magnetic Properties of MMnSb (M = Ti, V, Cr) with Ni_2In Type Structures

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Pnictides with a chemical formula of MM′X (M and M′ are 3d transition metals) are intermetallic compounds, and concepts of classical valency are not easily applied to them. Although most of these compounds are metallic, they exhibit a variety of magnetic properties such as ferromagnetism, ferrimagnetism, antiferromagnetism, and Pauli paramagnetism. Unlike the phosphides and arsenides, systematic investigations of antimonides have rarely been carried out.[1] Figure 1 shows the crystal structures of the MM′Sb compounds previously synthesized.[2-4] As seen in this figure, all of them except for CoNiSb and Mn_2Sb take a MgCuSb ($C1_b$) type structure. Since the MgCuSb and the Ni_2In type structures are not found in the phosphides and arsenides,[5] it is expected that there exists a discontinuity in crystal structure between arsenides and antimonides. We have tried to synthesize antimonides in order to increase our understanding of the crystal structures and magnetic properties that they exhibit. During our synthetic studies of antimonides, it was found that high-pressure transformation of VCoSb and VFeSb from the MgCuSb type structure to the Ni_2In type structure occurred under high temperature–pressure conditions.[6]

In this study, new antimonides of TiMnSb, VMnSb, and CrMnSb with the Ni_2In type structure were synthesized under high temperature–pressure conditions and their magnetic properties were examined.

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