J. Phys. Chem. A **1997,** *101,* 3607−3612

Ab Initio Calculations on the Structures and Energetics of Li_4OH, Li_3NaOH, and Li_2Na_2OH Isomers

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Received: December 4, 1996; In Final Form: February 26, 1997[⊗]

We performed ab initio electronic structure calculations on the structures and energetics of the mixed hyperalkaliated hydrogen oxides Li_4OH, Li_3NaOH, and Li_2Na_2OH. Five equilibrium geometries exist for each complex of Li_4OH and Li_3NaOH, and seven minima were located for Li_2Na_2OH. The calculated dissociation energies for the possible dissociation pathways are all endothermic. The global minimum structures of the three complexes have C_{2v} symmetry and contain a hydrogen-bridged, Li−H−Li, three-centered skeleton. We also investigated the charge redistribution within these complexes in their ionic forms. The energetic factors governing the construction of the equilibrium structures and their bonding properties are analyzed.

Introduction

The structures of hypermetalated molecules attract much interest from experimentalists and theoreticians because the stoichiometries of these compounds violate the octet rule.[1−2] The hypervalent lithium oxides OLi_3, OLi_4, and OLi_5 have been observed experimentally[3−4] as have the hypervalent sodium and potassium oxides ONa_3, ONa_4,[5] OK_3, and OK_4. Theoretical calculations of hypermetalation involving sodium[6] predicted that the outer valence electrons contribute in metal−metal rather than in oxygen−metal bonding. Potassium-containing hypermetalated compounds and their water complexes such as K_2OH, K_3OH, $K_4(OH)_2$, and $K_2(OH)(H_2O)$ are observed experimentally.[7−8] It was also expected that the lighter alkali metals (Na, Li) would behave similarly in forming hypermetalated hydroxyl compounds, although direct observation of these compounds has not yet been reported. Schleyer et al. pointed out[1] that the hypervalent species OH_3 and OH_4 appear to be only very weak van der Waals complexes between H_2O and H or H_2, which implies that these species follow the octet rule perfectly. However, if the bonded atom is lithium rather than hydrogen, the situation is completely different. Both OLi_3 and OLi_4 are indicated as thermodynamically quite stable toward dissociation or loss of an electron, despite the fact that both lithium and hydrogen have similar outer electronic structures. The alkali metals do not respect the octet rule at all. The strong metal−metal bonding calculated for these hypermetalated oxides is believed to be the major contributor to the increased stability in these compounds, which differ greatly from the hyperhydrogen analogues. It would be of interest to study the bonding character of the two similar outer-electronic-structure atoms (Li and H) toward the oxygen atom if one hydrogen atom is added to the hypermetalated oxide to form a hypermetalated hydroxyl compound (OLi_4H or Li_4OH). Na_3OH was first treated by Wurthwein, Schleyer, and Pople[6] using the 3-21G basis set. Two possible geometries (C_{2v} and C_{3v}) were described. Besides these two geometries, we obtained another local minimum (also C_{2v}) for both Li_3OH and Na_3OH molecules, with H bridging two alkali atoms. This structure was found to be the global energy minimum structure in Li_3OH, but turned out to have the highest energy in Na_3OH. The ground state properties and optical response of a series of mixed lithium/sodium clusters Li_xNa_{4-x} ($x = 0-4$) were investigated intensively both experimentally[9−13] and by ab initio calculations.[14] We reported[15] the calculated geometries and bonding properties of mixed hypermetalated lithium/sodium hydroxyl compounds (Li_2NaOH, $LiNa_2OH$). In this study we focus on Li_4OH, Li_3NaOH, and Li_2Na_2OH. Detailed conclusions about the effect of the Li/Na substitution on the electronic and geometric structures in this type of compound are drawn from the calculations.

Method of Calculations

The equilibrium structures of Li_4OH, Li_3NaOH, Li_2Na_2OH and other related species were first calculated at the Hartree−Fock (HF) level by complete optimization using analytical gradients and the basis set 6-31G*.[16] Several isomers were examined for the molecules considered. The harmonic vibrational frequencies were calculated at both the HF and MP2 level, which enabled us to screen out some structures not located in a local minimum region on the potential energy surfaces. Electron correlation corrections with Moller−Plesset perturbation theory (MP4)[17] were performed for these hypermetalated molecules at optimized geometries. Diffuse and polarization functions for both alkali and hydrogen atoms were also added to the basis set for further energy minimization. No corrections were made for the basis set superposition error[18] in the calculations.

Results and Discussion

Na_3OH and Li_3OH. The optimized Hartree−Fock 6-31G* stable structures of Na_3OH and Li_3OH are displayed in Figure 1. The absolute energies (au) are summarized in Table 1. For Na_3OH, structure **1** is lower in energy than **2** by 2.95 kcal/mol (MP4/6-31G*, with zero-point energy (ZPE) correction[19]). The energy difference between these two structures is very similar to the one obtained by Wurthwein *et al.*,[6] in which only **1** and **2** were found in HF/3-21G calculations. In this paper, structure **3** is a third entity that was proved to be thermodynamically stable toward all possible dissociation modes, despite having an energy 15.76 kcal/mol higher than that of **2**. The calculations of Li_3OH exhibited three stable optimized geometries (**4**, **5**, **6**) similar to Na_3OH. However, structure **6** is the energy minimum 15.72 kcal/mol lower than that of **5**. The energy of **4** was slightly higher than that of **5** by 1.23 kcal/mol. It is interesting

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[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1997.

S1089-5639(96)03978-3 CCC: $14.00

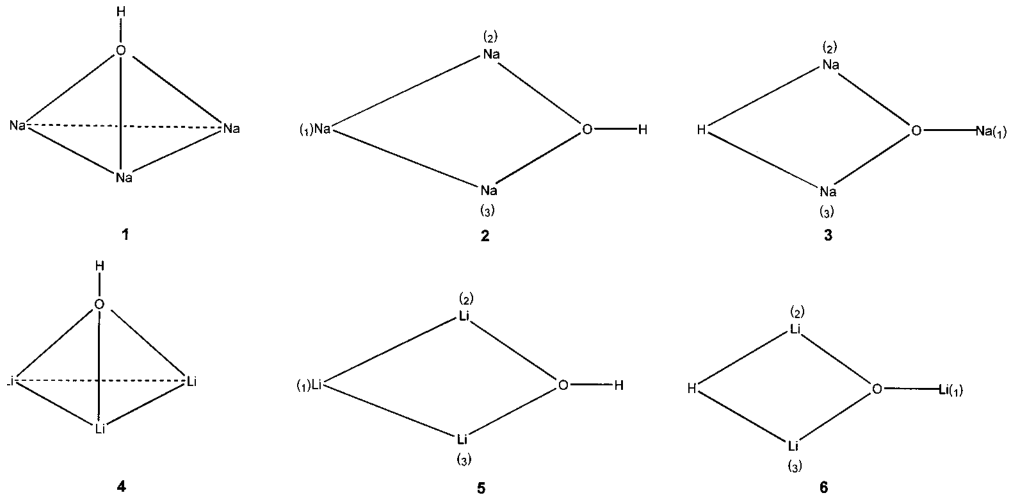


Figure 1. Calculated stable structures for Na_3OH and Li_3OH.

TABLE 1: Calculated Absolute Energies (au) of Possible Stable Structures for Li_3OH, Na_3OH, and K_3OH

species	symmetry point group	*E* (HF/6-31G*) (au)	*E* (MP2/6-31G*) (au)	*E* (MP4/6-31G*) (au)	ZPE (kcal/mol)
Li_3OH	**4** (C_{3v})	−97.836 25	−98.066 36	−98.084 44	11.00
	5 (C_{2v} I)	−97.846 37	−98.067 80	−98.085 73	10.53
	6 (C_{2v} II)	−97.853 93	−98.093 97	−98.107 06	7.94
Na_3OH	**1** (C_{3v})	−561.015 52	−561.241 94	−561.258 27	9.22
	2 (C_{2v} I)	−561.018 48	−561.236 88	−561.253 05	8.85
	3 (C_{2v} II)	−560.953 34	−561.203 08	−561.222 88	5.32
K_3OH	(C_{3v})	−1755.708 96	−1755.708 72	−1755.718 85	
	(C_{2v} I)	−1755.544 29	−1755.694 39	−1755.707 60	
	(C_{2v} II)	−1755.442 20	−1755.625 07	−1755.635 88	

to note that the absolute energy sequence of Li_3OH isomers is opposite to that of the analogous structures of Na_3OH.

As described by Wurthwein et al., the calculated hypervalent electron of Li_3OH molecule does not enhance the Li−O bonding. Judging from the highest occupied molecular orbital (HOMO) (a_1) orbitals of structures **4** and **5** shown in Figure 2, we found that the three s-dominated orbitals of the lithium atoms form hypermetal bonding with radial nodes between Li−O and O−H bonds. In structure **6**, the valence electron of the HOMO orbital is mainly located in the hydrogen s orbital, which forms a hydrogen-bridged three-centered bond with the two p_z orbitals of lithium atoms. This strong hydrogen-bridged bonding contributes greatly to the stabilization of the structure.[20] The two p_z orbitals of lithium atoms induce a substantial orbital overlap with the s orbital of hydrogen. The strong interaction between hydrogen and lithium atoms provides an important contribution.[21−23] In contrast, in Na_3OH structure **3** is the least stable of the three listed isomers. The Na−Na bond in **3** indicates stronger antibonding relative to that of the Na−Na bond in **2**, while structure **1** shows good equivalent metal−metal bondings. Since the Na−O−Na bond angle in **3** is bent to 79.8°, that brings the Na atoms within a 2.69 Å tight distance and the electron repulsion between two bulky Na atoms becomes dominant. Apparently the interaction between hydrogen and sodium atoms is less significant. The hydrogen-bridged sodium structure, **3**, inevitably turns out to be the least stable species.

An identical calculated energy trend as in Na_3OH was found for the three K_3OH[24] isomers. The bulky steric effect is even more pronounced. The K_3OH structure analogous to **3** has the highest energy being 52.06 kcal/mol (MP4/6-31G*) above that of C_{3v}. It might well be unstable if the products for all dissociation pathways of K_3OH were further calculated. Another structure of K_3OH (C_{2v}) similar to **2** is calculated to be 7.06 kcal/mol higher than the C_{3v} structure. The energy difference between these isomers becomes larger going from lithium to potassium. The global minimum structure of Li_3OH is different from other hyperalkaliated hydrogen compounds.

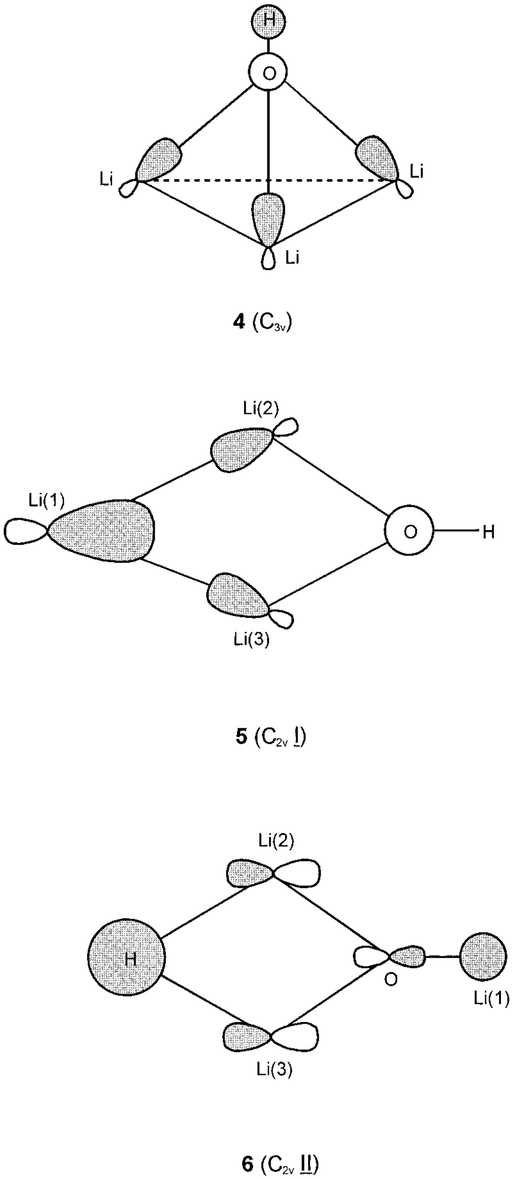
Li_4OH. Fourteen different possible structures were examined, chosen by considering two ways to form Li_4OH: one is adding one Li atom to the three stable geometries of Li_3OH, and the other is adding an H atom to the two calculated stable geometries of Li_4O.[1] Five stable structures, all with positive eigenvalues in the second-derivative matrix, are illustrated in Figure 3. They were the starting points for further calculations with electron correlation corrections included (MP4). The results are listed in Table 2. The thermal dissociation energies of several possible dissociation pathways of Li_4OH are listed in Table 3. Evidently only **7** and **8** are sufficiently stable not to dissociate. These findings supported the conclusion that these two structures are the possible stable geometries for the Li_4OH molecule. The insertion of a hydrogen atom in the molecular plane of Li_4O (C_{2v}) gives **8**, which is still higher than **7** by 14.57 kcal/mol. Structure **7** could be formed from the global minimum structure of Li_4O (T_d)[1] by adding a hydrogen atom on the axis which bisects the angle of Li−O−Li. The O−H axis becomes the rotation axis in the C_{2v} point group of structure **7**. Two additional unstable structures of Li_4OH may be constructed from Li_4O (T_d). One structure has the hydrogen connected to the Li atom at the tetrahedron corner, the other has the hydrogen connected to the oxygen atom. Actually, these two structures are transition states on the potential surface which is formed by moving the hydrogen around the sphere of Li_4O (T_d structure), and **7** locates the minimum on this potential surface. Among all the possible dissociation pathways, the product channel producing Li_3OH (**6**) and Li gives the least enthalpy change endothermically, yet it still needs 36.84 kcal/mol for **7** to dissociate. Structure **7** is the global minimum among all the possible geometries of the Li_4OH molecule.

Li_3NaOH. On the basis of the five possible structures of Li_4OH (Figure 3), we substituted one Li atom at several

TABLE 2: Comparison of Calculated Energies of Possible Isomers for Li_4OH (7−11), Li_3NaOH (12−16), and Li_2Na_2OH (17−23)[a]

Li_4OH	MP4/6-31G*// 6-31G*	Li_3NaOH	MP4/6-31+G**// 6-31G* + ZPE × 0.9	Li_2Na_2OH	MP4/6-31+G**// 6-31G* + ZPE × 0.9
7	−105.599 83 (0.00)	**12**	−259.983 95 (0.00)	**17**	−414.365 22 (0.00)
8	−105.575 92 (15.00)	**13**	−259.978 61 (3.35)	**18**	−414.361 12 (2.57)
9	−105.533 49 (41.63)	**14**	−259.970 41 (8.50)	**19**	−414.354 66 (6.63)
10	−105.545 40 (34.15)	**15**	−259.956 20 (17.41)	**20**	−414.349 85 (9.65)
11	−105.534 84 (40.78)	**16**	−259.951 91 (20.10)	**21**	−414.345 82 (12.18)
				22	−414.344 85 (12.78)
				23	−414.341 37 (14.97)

[a] The numbers in parentheses represent the relative energy between the isomers; the unit is kcal/mol.



4 (C_{3v})

5 (C_{2v} I)

6 (C_{2v} II)

Figure 2. The shapes of the HOMO for the three stable isomers of Li_3OH.

locations by one sodium atom. More than 15 sodium-substituted structures were examined at the Hartree−Fock level with and without hydrogen polarization functions (6-31G** and 6-31G*) for geometry optimization. Only five geometries with all positive eigenvalues in the second-derivative matrix were obtained. They are illustrated in Figure 4. It is adequate to use Mulliken population analysis to reveal trends or significant differences for closely related species.[6] A natural bond orbital analysis was also performed, giving similar trends. There are only small differences in geometries and overlap populations resulting from calculations with or without the use of hydrogen polarization functions at the HF level.

TABLE 3: Theoretical Dissociation Energies of Li_4OH (7) to Several Possible Dissociation Products

		dissociation products	MP4/6-31G* (kcal/mol)
Li_4OH	→	H + Li_4O (C_{2v})	72.32
	→	H + Li_4O (T_d)	57.15
	→	Li + Li_3OH (C_{2v} I)	51.91
	→	Li + Li_3OH (C_{2v} II)	38.53
	→	Li + Li_3OH (C_{2v})	52.72
	→	Li_2OH (C_{2v} I)	62.71
	→	Li_2OH (C_{2v} II)	109.70
	→	Li_2H (C_{2v})	78.35
	→	LiH + Li_3O (C_{2v})	55.45
	→	LiOH + Li_3	105.70
	→	OH + Li_4 (D_{2h})	154.82

Improved energies were obtained from higher level (MP4) single-point calculations employing polarization functions on all atoms and diffuse functions on all non-hydrogen atoms, as shown in Table 2. Structures **12** and **13** show the lower energies at either level of calculation. There is no change in the order of energies for these five isomers at all levels of calculation employed. With the consideration of zero-point energy and single-point calculation at the MP4 level using the 6-31+G** basis set, structure **12** has the lowest minimum, 3.35 kcal/mol lower than that of **13**. Structures **12** and **13** are basically constructed from the global minimum geometry of Li_4OH (**7**). The former is built by replacing a Li atom in the Li−O−Li vertical plane by a Na atom, and the latter by a similar replacement in the Li−H−Li−O horizontal plane. Since a sodium atom is much bigger than a lithium atom, the steric effect is more enhanced in the more crowded Li−H−Na−O plane of structure **13**, thus raising the nuclear repulsion energy (69.7584 au for **12** and 70.9258 au for **13**) and decreasing the stability of **13**. The calculated dissociation energies for all the possible dissociation pathways of structure **12** are given in Table 4; they are all endothermic. For the three other geometries of Li_3NaOH (**14**−**16**), the energies are 8.50, 17.41, and 20.10 kcal/mol, respectively, above **12**. They are still smaller than the least dissociation energy of the product channel, $Li_3NaOH \rightarrow Na + Li_3OH$, $\Delta H = +20.68$ kcal/mol. It implies that, thermodynamically, the formation of Li_3NaOH in any one of these five structures could be possible, but with **12** being the most stable isomer.

Ionic Species. To understand how the extra valence electrons contribute in structure **12**, a series of geometry optimizations of several ionic species (Li_3NaOH^+, Li_3NaOH^{2+}, and Li_3NaOH^{3+} with 10, 9, and 8 valence electrons, respectively) were carried out. Using the procedures described by Wurthwein et al.,[6] the calculated atomic charges, Mulliken overlap populations, bond lengths, and bond angles are listed in Table 5. We find that the cation with three positive charges, Li_3NaOH^{3+}, is not stable; instead, it dissociates into H^+ and Li_3NaO^{2+}. Obviously, there are not sufficient electrons to bind these atoms together.

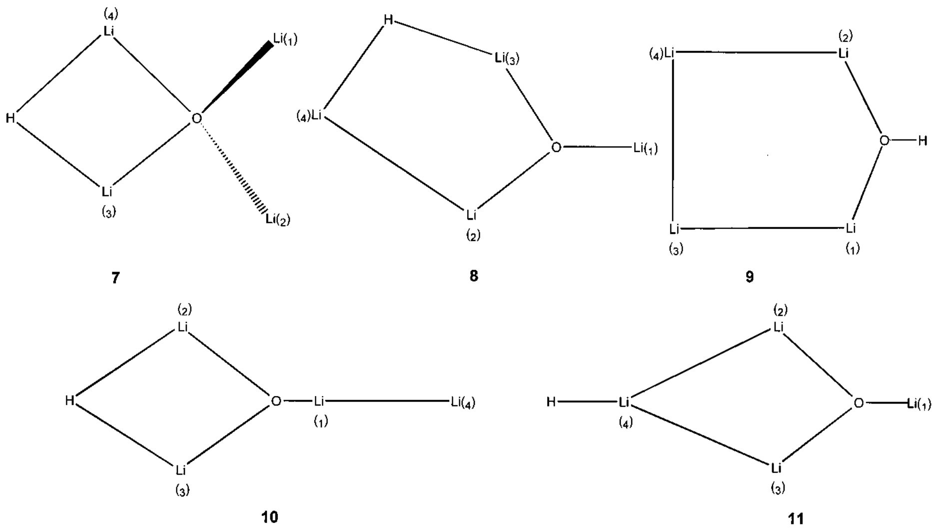


Figure 3. Calculated stable structures for Li_4OH.

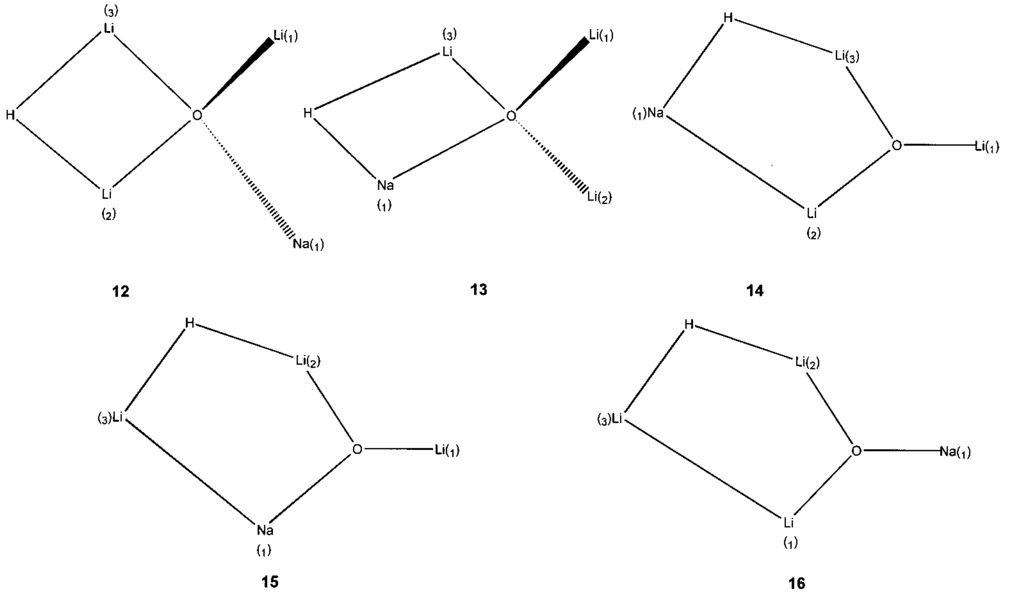


Figure 4. Calculated stable structures for Li_3NaOH.

TABLE 4: Theoretical Dissociation Energies of Li_3NaOH (12) (kcal/mol)

			MP4/6-31G**// 6-31G* + ZPE × 0.9
Li_3NaOH	→	Na + Li_3OH	+20.68
	→	Li + Li_2NaOH	+35.06
	→	LiNa + Li_2OH	+43.88
	→	Li_3O + NaH	+47.20
	→	LiH + Li_2NaO	+53.47
	→	Li_2 + LiNaOH	+54.43
	→	H + Li_3NaO	+54.56
	→	Li_2H + LiNaO	+81.86
	→	Li_3 + NaOH	+100.03
	→	OH + Li_3Na	+135.80

It is interesting, however, that the proton is removed from the group and not the alkali atom. This suggests that the alkali atom has the stronger tendency to hold electrons in forming oxides than does the hydrogen atom. When one electron is added to Li_3NaOH^{3+}, a local minimum in the potential surface can be found, indicating that these atoms can bind to form a certain structural arrangement but still not a stable one. The analysis of the bonding of Li_3NaOH^{2+} reveals that the added electron distributes most of its charge onto the hydrogen atom but helps very little in the formation of the two Li−H bonds. It still could be treated as two separate species, H and Li_3NaO^{2+}. When one more electron is added to form Li_3NaOH^{+}, the charge is mostly distributed in the formation of two Li−H bonds (overlap populations of Li^2−H and Li^3−H increase to 0.367 from 0.030) to form the hydrogen-bridged three-centered (Li−H−Li) bond. The added charge also distributes some charge onto the hydrogen atom (becoming negatively charged), and some in the Li^2−Li^3 bond (overlap population increases from 0.017 to 0.122). Interestingly, when the eleventh valence electron is added to form the neutral Li_3NaOH, the bonding nature of the hydrogen-bridged three-centered bond does not change significantly; instead, the atomic charge of sodium shifts from +0.752 to −0.063 and that of hydrogen becomes more negative (−0.199 to −0.248). The charge of this last electron contributes very little to a further strengthening of metal−metal bonding in the molecule. Meanwhile, the atomic charge of oxygen is nearly constant during the addition of these three valence electrons (−1.126 → −1.157 → −1.144 → −1.125). Obviously, the octet rule still holds in the vicinity of an oxygen atom. The three extra valence electrons are distributed mainly on the hydrogen and sodium atoms and in the hydrogen-bridged 3-center bond. This result is slightly different from that of the Li_4OH molecule in which no alkali atom carries a negative

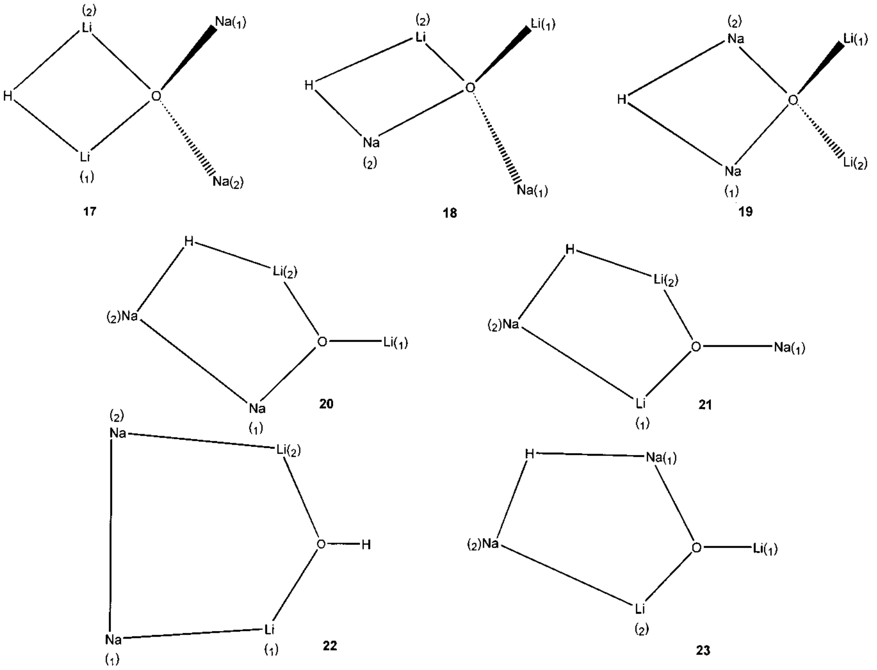


Figure 5. Calculated stable structures for Li_2Na_2OH.

TABLE 5: Comparison of Structural Parameters of Li_3NaOH (12) at Varying Numbers of Valence Electrons

	valence electrons			
	11 (Li_3NaOH)	10 (Li_3NaOH^+)	9 (Li_3NaOH^{2+})	8 (Li_3NaOH^{3+})
HF/6-31G*, E_{tot} (au)	−259.72806	−259.58913	−259.24256	−258.63777
atomic charge				
O	−1.125	−1.144	−1.157	−1.126
Li^1	0.575	0.627	0.773	0.763
Na^1	−0.063	0.752	0.835	0.864
Li^2	0.431	0.482	0.756	0.750
Li^3	0.431	0.482	0.756	0.750
H	−0.248	−0.199	0.036	1.000
overlap population				
$O-Li^1$	0.372	0.359	0.289	0.296
$O-Na^1$	0.137	0.250	0.224	0.179
$O-Li^2$	0.257	0.217	0.284	0.316
$O-Li^3$	0.257	0.217	0.284	0.316
O−H	−0.015	−0.017	−0.001	0.000
Li^1-Na^1	−0.057	0.055	0.009	0.010
Li^2-Li^3	0.103	0.122	0.017	0.011
Li^2-H	0.361	0.367	0.030	0.000
Li^3-H	0.361	0.367	0.030	0.000
bond length (Å)				
$O-Li^1$	1.713	1.709	1.783	1.820
$O-Na^1$	2.161	2.115	2.272	2.699
$O-Li^2$	1.781	1.837	1.784	1.747
$O-Li^3$	1.781	1.837	1.784	1.747
O−H	2.857	2.831	3.685	10.217
Li^1-Na^1	2.741	3.321	3.310	3.544
Li^2-Li^3	2.212	2.246	2.902	2.962
Li^2-H	1.833	1.777	3.018	9.407
Li^3-H	1.833	1.777	3.018	9.407
bond angle (deg)				
$\angle Li^1ONa^1$	89.3	120.2	108.8	101.5
$\angle Li^2OLi^3$	76.8	75.4	108.8	115.9

charge. It also deviates from those of the oxide compounds, Li_4O, Na_3O, ..., etc., in which the extra valence electrons are mostly distributed among the metal−metal bonds. The system can not be described in terms of an oxygen atom bonded within a cationic alkali cage, e.g., $O^-Li_4^+$ or $O^-Na_3^+$.[1] The substituted sodium atom withdraws more charge onto itself and leaves the lithium nucleus (Li^1) more exposed, despite the fact that lithium is considered to have the larger Pauling electronegativity.

Li_2Na_2OH. Like Li_3NaOH, many possible structures of Li_2Na_2OH were examined. Seven stationary points were obtained and all were confirmed with analytical second derivatives. They are illustrated in Figure 5. Structures **17**, **18**, and **19** are constructed from the skeleton of **7**. The formation of **17** arises from the replacement of two lithium atoms at the Li^1-O-Li^2 plane by sodium atoms, while **18** is made by the replacement of two lithium atoms located in separate planes, Li^1-O-Li^2 and $O-Li^4-H-Li^3$. The dihedral angle between these two planes is 90°. Structure **19** has two sodium atoms replacing lithium atoms located in the $O-Li^4-H-Li^3$ plane. Likewise, the geometries of **20**, **21**, and **23** are based on the skeleton of

TABLE 6: Theoretical Dissociation Energies of Li_2Na_2OH (17) (kcal/mol)

			MP4/6-31+G**//6-31G* + ZPE × 0.9
Li_2Na_2OH	→	$Na + Li_2NaOH$	+17.11
	→	$Na_2 + Li_2OH$	+28.40
	→	$Li + LiNa_2OH$	+31.83
	→	$LiNa + LiNaOH$	+39.26
	→	$NaH + Li_2NaO$	+46.73
	→	$Li_2 + Na_2OH$	+51.57
	→	$LiH + LiNa_2O$	+54.67
	→	$Li_2O + Na_2H$	+59.64
	→	$H + Li_2Na_2O$	+62.98
	→	$Li_2H + Na_2O$	+85.56
	→	$OH + Li_2Na_2$	+121.71

8, in which all the six atoms lie in the same plane. Structure **22,** constructed from the skeleton of **9**, is the only stationary point found which contains an O−H bond. All six atoms lie in the same plane. Although the structures **17**, **18**, and **19** are all constructed from the same skeleton of Li_4OH (**7**), the total electron energies are very different; **19** has the highest energy. It is most likely that the two large sodium atoms confined to the same plane $O-Na^1-H-Na^2$ cause a greater steric effect and increase the nuclear repulsion energy. In contrast, structure **17** has two sodium atoms in the less crowded Na−O−Na plane which leads to a smaller nuclear repulsion energy. The global energy minimum, **17**, has the same hydrogen-bridged skeleton as the global minimum of Li_4OH. The calculated energies for all possible Li_2Na_2OH structures at MP4/6-31+G**//6-31G* + ZPE×0.9 are listed in Table 2. The dissociation energies of the global Li_2Na_2OH to all the possible product channels are listed in Table 6. All possible dissociations are endothermic. The smallest dissociation energy to the product channel $Li_2Na_2OH \rightarrow Na + Li_2NaOH$, $\Delta H = +17.11$ kcal/mol, is still larger than the relative energy between the least stable isomer, **23**, and the global minimum. Therefore, thermodynamically, these seven geometries of Li_2Na_2OH are all possible candidates for isomer structures. From the calculated dissociation energies it follows that the binding strength of Li (31.83 kcal/mol) or H (62.98 kcal/mol) is much stronger than that of Na (17.11 kcal/mol) in the Li_2Na_2OH molecular system. In fact, Li and H bonding in hypermetallic species is more covalent in nature and that of Na bonding is more ionic.

Conclusions. A Li−H−Li hydrogen-bridged three-centered structure is common to the three calculated global hypermetalated hydrogen oxide molecules: Li_4OH, Li_3NaOH, and Li_2Na_2OH. It is surprising that hydroxide (O−H) isomers, such as **9**, are not favored. The calculated data show that the electron density of the hydrogen atom in the O−H bond is mainly confined to the oxygen and hydrogen atoms and contributes little to the metal−metal bonding. In the hydrogen-bridged structure, however, the electrons are distributed evenly between the two Li−H bonds. In addition, the properties of Li and H atoms resemble one another, and they interact strongly when the three atoms Li, H, and Li are connected together. Therefore, the hydrogen-bridged structures are preferred. However, this is not the case for sodium atoms. The sodium atom is too large to fit three atoms (Na, H, and Na) in a hydrogen-bridged three-centered skeleton. The steric effect is enhanced. In Li_2Na_2OH (**17**) which has two sodium atoms arranged in a less crowded plane perpendicular to the Li−H−Li−O plane, the nuclear repulsion energy is reduced, and the arrangement becomes the global minimum isomer. Two major factors influence the structural stability of hyperalkaliated hydrogen oxide molecules. The first and most important is the nuclear repulsion energy. It can be greatly reduced if the larger atoms are separated by a longer distance. Second is the formation of a hydrogen-bridged three-centered construction which can lower the system energy considerably, especially in the Li−H−Li skeleton. Metal−metal bonding between alkali metals contributes moderately to the stability of the structure. The stable configuration also depends on the number of mixed lithium and sodium atoms in the compound. If the atoms are arranged in accord with the above stated factors, the system energy will be considerably lowered.

Acknowledgment. Support for this research from the National Science Council of the Republic of China (NSC-85-2113-M-003-014) is gratefully acknowledged. We are also grateful to the National Center for High-Performance Computing where the Gaussian package and the computer time were provided. We are also indebted to the reviewer for helpful suggestions concerning the manuscript.

Supporting Information Available: Tables describing the calculated atomic charges, bond lengths, bond angles, and Mulliken population analysis regarding the structure of five Li_3NaOH (**12**−**16**) isomers and the calculated dissociation energies at several calculation levels and basis sets for Li_3NaOH and Li_2Na_2OH molecules (3 pages). Ordering information is given on any current masthead page.

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