based on oxygen attack on arylmethyl radical fragments (as evidenced in the case of substrates **1**–**5** and **9**–**11**) may be operative in the case of the bibenzyls, but these are yet to be worked out.

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Hypermetalation Involving Sodium: ONa_3, ONa_4, $HONa_2$, and $HONa_3$[1]

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Abstract: In contrast to stoichiometries expected on the basis of the octet rule, but in agreement with experimental observations, ONa_3 (**1**, D_{3h}) and ONa_4 (**2**, T_d) are found by ab initio theory to be highly stable as isolated molecules toward all possible dissociation reactions, e.g., loss of a sodium atom or an Na_2 molecule. The calculated Na–O bond lengths are only slightly longer than those in Na_2O and NaOH. $HONa_2$ (**3**) and $HONa_3$ (**4**) provide further examples of hypermetalation. The ninth and tenth valence electrons in these effectively hypervalent molecules, **1**–**4**, are involved in metal–metal rather than in oxygen–metal bonding. The central oxygen atoms are content with the usual complement of electrons and do not have an expanded valence shell. Hypermetalation is predicted to be a very general phenomenon involving all the alkali metals in combination with many if not most of the other elements in the periodic table.

"Hypermetalated" molecules violate stoichiometries based on the octet rule.[1-3] Stimulated by the experimental observation of OLi_3 in the gas phase,[4] we examined not only this species, but also OLi_4, OLi_5, OLi_6, and a large number of analogous molecules calculationally.[1,2] These effectively hypervalent molecules are comprised of a first-row central atom and a "hyperstoichiometric" number of lithium substituents, e.g., FLi_3, NLi_5, CLi_6,[3] BLi_5, and $BeLi_6$.[1] As isolated entities, all are indicated to be highly stable thermodynamically toward all possible dissociation modes. Following our predictions, OLi_4 and OLi_5 were observed experimentally.[5] We now report that sodium can function in the same way as lithium. There are experimental precedents for similar hypermetalated species involving the heavier alkali metals, e.g., the "curious suboxides"[6] O_2Rb_9 and O_3Cs_{11} for which X-ray crystal structures are available.[7] During the course of our work on ONa_3 (**1**)[8] and ONa_4 (**2**),[1] their experimental detection in the gas phase was reported.[8] Ionization potentials were determined as well as similar measurements on K_3O and K_4O. However, neither geometries nor bonding information is available from experimental sources. This paper reports a calculational investigation of the sodium oxides, Na_nO (n = 1-4), as well as $HONa_2$ (**3**) and $HONa_3$ (**4**) and a number of related species. Comparisons are made with the closely related lithium molecules, e.g., OLi_3, OLi_4, and $HOLi_2$.

Computational Methods and Comments on Technical Details

Ab initio molecular orbital calculations were carried out with restricted and unrestricted Hartree–Fock theory using the GAUSSIAN 76[9] and 82[10] series of programs. The VAX version of the latter was adapted to the Erlangen CYBER 173 computer by Dr. A. Sawaryn. The structures of all molecules were optimized within the indicated point group using analytical force evaluation routines[11] and the 3-21G split valence basis set.[12] Improved energies were obtained from higher level single point calculations employing the polarization 6-31G* basis set which includes six *d* functions on all nonhydrogen atoms.[13] Valence electron correlation corrections were obtained for the smaller species with second-order (MP2) Møller–Plesset perburbation theory.[14] These results are designated 6-31G*//3-21G and MP2/6-31G*//3-21G, respectively.

A technical problem arose with the geometry optimization of ONa_3. With the small 3-21G basis set, the UHF wave function was spin contaminated; this increased with T-shaped C_{2v} distortion from D_{3h} symmetry ($\langle S^2 \rangle = 0.845$ at D_{3h} and 1.592 at C_{2v}) and the energy was lowered artificially. Single point calculations at 6-31G* on the C_{2v} and D_{3h} 3-21G ONa_3 geometries indicated the latter to be lower in energy. Spin contamination was minimal ($\langle S^2 \rangle = 0.795$ at C_{2v} and 0.782 at D_{3h}). Hence, we only report details for D_{3h} ONa_3 (I) here, but do not exclude the possibility of small C_{2v} distortions (as reported for OLi_3)[2,15]

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Table I. Total Energies (au) of Hypermetalated Sodium Oxygen Compounds and Reference Molecules

species	state	symmetry	3-21G/3-21G	6-31G*//3-21G	MP2/6-31G*//3-21G
Na^+	^1S	K_h	−160.673 75	−161.659 29	−161.659 29
Na	^2S	K_h	−160.854 06[a]	−161.841 44	−161.841 44
NaH	$^1\Sigma^+$	$C_{\infty v}$	−161.381 18[a]	−162.372 45[a]	−162.387 97[a]
Na_2^+	$^2\Sigma_g^+$	$D_{\infty h}$	−321.563 36	−323.535 96	−323.535 96
Na_2	$^1\Sigma_g^+$	$D_{\infty h}$	−321.708 78[a]	−323.681 69	−323.699 52
O	^1D	K_h	−74.267 45[a]	−74.656 60[a]	−74.769 95
O	^3P	K_h	−74.393 66[a]	−74.783 93[a]	−74.880 04
H_2O	$^1A_1$	C_{2v}	−75.585 96[a]	−76.010 75[a]	−76.196 49
NaO^+	$^1\Pi$	$C_{\infty v}$	−234.958 79	−236.327 09	−236.442 33
NaO^+	$^3\Pi$	$C_{\infty v}$	−235.071 63	−236.455 21	−236.553 14
NaO	$^2\Pi$	$C_{\infty v}$	−235.253 63	−236.638 66	−236.788 99
NaOH	$^1\Sigma^+$	$C_{\infty v}$	−235.868 88[a]	−237.271 32	−237.469 50
$NaOH_2$ (**9**)	$^2A_1$	C_{2v}	−236.468 70	−237.861 85	−238.051 56
$NaOH_3$ (**10**)	$^1A_1$	C_{3v}	−236.906 50	−238.285 18	−238.505 81
Na_2O^+	$^2\Sigma_g$	$D_{\infty h}$	−396.045 95	−398.386 62	−398.535 93
Na_2O	$^1\Sigma_g$	$D_{\infty h}$	−396.104 78[a]	−398.485 58	−398.727 90
Na_2OH (**3**)	$^2A_1$	C_{2v}	−396.786 64	−399.161 99	−399.363 70
Na–Na–OH bent	$^2A_1$	C_s	−396.731 84	−399.116 90	−399.316 54
Na_2OH_2 (**11**)	$^1A_1$	C_{2v}	−397.321 03	−399.693 03	−399.909 57
Na_2OH_2 (**12**)	$^1A_1$	C_s	−397.331 47	−399.708 17	−399.913 91
Na_2OH_2 (**13**)	$^1A_1$	C_{2v}	−397.351 38	−399.731 48	−399.946 28
Na_3O^+	$^1A_1$	D_{3h}	−556.924 67	−560.284 16	
Na_3O (**1**)	$^2A_1$	C_{2v}	(−557.046 38)[b]	−560.389 24	
	$^2A_1$	D_{3h}	−557.035 47	−560.391 59	
Na_3OH (**4**)	$^1A_1$	C_{3v}	−557.662 68		
Na_3OH (**6**)	$^1A_1$	C_{2v}	−557.657 55		
Na_4O (**2**)	$^1A_1$	T_d	−717.935 69		
Na_4O (**5**)	$^1A_1$	C_{2v}	−717.902 25		
Na_4O^{2+}	$^1A_1$	T_d	−717.575 03		

[a] Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A., Carnegie-Mellon Quantum Chemistry Archive; Carnegie-Mellon University: Pittsburgh, PA, 1981. [b] Strongly spin contaminated wave function $\langle S^2 \rangle = 1.592$. This value is unreliable. See text.

Table II. Na–O and Na–Na Bond Lengths (3-21G) and Mulliken Population Analysis

species	state	bond lengths, Å		charges 6-31G*(3-21G)		overlap population 6-31G* (3-21G)	
		Na–O	Na–Na	O	Na	ONa	NaNa
NaO^+ ($C_{\infty v}$)	$^1\Pi$	2.475		0.057 (0.078)	0.943 (0.922)	0.90 (0.110)	
NaO^+ ($C_{\infty v}$)	$^3\Pi$	2.629		0.060 (0.045)	0.940 (0.956)	0.095 (0.067)	
NaO ($C_{\infty v}$)	$^2\Pi$	2.015		−0.729 (−0.624)	0.729 (0.624)	0.334 (0.336)	
NaOH($C_{\infty v}$)[a]	$^1\Sigma^+$	1.869		−1.062 (−0.926)	0.694 (0.631)	0.385 (0.423)	
$NaOH_2$[c] (C_{2v}) (**9**)	$^2A_1$	2.117		−0.903 (−0.743)	−0.052 (−0.098)	0.028 (0.138)	
Na_2O^+ ($D_{\infty h}$)	$^2\Sigma_g^+$	2.072	4.144	−0.730 (−0.621)	0.810 (0.865)	0.185 (0.229)	0.066 (0.015)
Na_2O ($D_{\infty h}$)	$^1\Sigma_g^+$	1.928	3.855	−1.013 (−0.872)	0.507 (0.436)	0.473 (0.439)	−0.005 (0.040)
Na_2OH (C_{2v})[b] (**3**)	$^2A_1$	2.037	3.135	−1.049 (−0.903)	0.328 (0.290)	0.219 (0.254)	0.270 (0.130)
Na_3O^+ (D_{3h})	$^1A_1'$	2.017	3.494	−1.047 (−0.931)	0.682 (0.644)	0.346 (0.328)	−0.005 (−0.004)
Na_3O (D_{3h}) (**1**)	$^2A_1$	2.013	3.487	−1.010 (−0.865)	0.337 (0.288)	0.327 (0.306)	0.081 (0.095)
$NaOH_3$[d] (C_{3v}) (**10**)	$^1A_1$	2.409		−0.704 (−0.654)	−0.601 (−0.718)	−0.638 (−0.424)	
Na_2OH_2[e] (C_{2v}) (**11**)	$^1A_1$	2.307	3.168	−0.882 (−0.719)	−0.038 (−0.077)	−0.059 (0.029)	0.745 (0.701)
Na_2OH_2[f] (C_s) (**12**)	$^1A_1$	2.185	3.274	−0.908 (−0.735)	0.053 (0.096)	0.079 (0.210)	0.772 (0.585)
					−0.114[c] (−0.127)	−0.012[c] (−0.020)	0.724 (0.585)
Na_2OH_2[g] (C_{2v}) (**13**)	$^1A_1$	2.048	2.790	−1.056 (−0.902)	−0.517 (0.488)	0.224 (0.258)	−0.128 (−0.625)
Na_3OH[h] (C_{3v}) (**4**)	$^1A_1$	2.139	2.748	(−0.864)	(0.172)	(0.168)	(0.192)
Na_3OH[i] (C_{2v}) (**6**)	$^1A_1$	2.040 × 2	3.694 × 2	(−0.902)	(0.484 × 2)	(−0.032 × 2)	(0.346 × 2)
		4.712	3.061		(−0.388)	(0.009)	(−0.268)
Na_4O (C_{2v}) (**5**)	$^1A_1$	2.038 × 2	3.664 × 2	(−0.907)	(0.400 × 2)	(0.333 × 2)	(0.042 × 2)
		1.974	3.679		(0.504)	(0.360)	(−0.252)
		4.713[j]	3.034 × 2[j]		(−0.398)[i]	(−0.026)[k]	(0.292 × 2)[j]
Na_4O (T_d) (**2**)	$^1A_1$	2.079	3.395	(−0.895)	(0.223)	(0.239)	(0.157)
Na_4O^{2+} (T_d)	$^1A_1$	2.139	3.492	(−0.935)	(0.734)	(0.267)	(−0.005)
Na_2^+ ($D_{\infty h}$)	$^2\Sigma_g^+$		3.708		0.500 (0.500)		0.372 (0.382)
Na_2 ($D_{\infty h}$)	$^1\Sigma_g^+$		3.228		0.000 (0.000)		0.759

[a] OH = 0.961 Å; H charge = 0.368 (0.296); HO overlap population 0.507 (0.499). [b] OH = 0.967 Å; H charge = 0.394 (0.322); HO overlap population 0.487 (0.481). [c] OH = 0.967 Å; H charge = 0.478 (0.421); HO overlap population 0.511 (0.519). [d] OH = 1.027 Å; H charge = 0.435 (0.543); HO overlap population 0.070 (0.262). [e] OH = 0.979 Å; H charge = 0.479 (0.437); HO overlap population 0.448 (0.477). [f] OH = 0.966 Å; H charge = 0.485 (0.427); HO overlap population 0.510 (0.510). [g] OH = 0.965 Å; H charge = 0.388 (0.316); HO overlap population 0.494 (0.487). Na–H = 3.136 Å; H(–Na) charge = −0.367 (−0.392); overlap population −0.006 (−0.006). [h] OH = 0.975 Å; H charge = −(0.350); HO overlap population −(0.467). [i] OH = 0.966 Å; H charge = −(0.323); HO overlap population −(0.483). [j] Values involving the remote Na atom.

at higher levels. Even at 3-21G, the spin contaminations for the other open-shell doublet and triplet species were insignificant.

The absolute energies (au) are summarized in Table I. The Na–O and Na–Na bond lengths and Mulliken population analyses are given in Table II. The deficiencies of Mulliken populations for such ionic systems have been emphasized by Streitwieser,[16] but we feel that comparisons involving closely related species should reveal trends or significant dif-

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(15) However, further calculations on OLi_3 now suggest that the D_{3h} geometry may be the global minimum at higher theoretical levels: Würthwein, E.-U.; Schleyer, P. v. R.; Pople, J. A., to be published.

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Table III. Theoretical and Experimental Dissociation Energies (kcal/mol)

reaction	3-21G//3-21G	6-31G*//3-21G	MP2/6-31G*//3-21G	exptl
$Na_2 \rightarrow 2Na$	$(0.41)^a$	$(-0.75)^a$	10.44	$16.6,^b$ 16.87^c
$NaO \rightarrow Na + {}^3O$	$(3.71)^a$	$(8.34)^a$	42.36	$60.0,^b$ 59.29^c
$NaOH \rightarrow Na + OH$	$(27.98)^a$	$(29.87)^a$	67.40	83.5^c
$NaOH_2 \rightarrow Na + OH_2$	18.00	6.06	8.55	
$NaOH_3 \rightarrow NaOH + H_2$	−53.55	−70.89	−67.66	
$Na_2O \rightarrow Na + NaO$	$(1.83)^a$	$(3.44)^a$	61.16	58.8^c
$Na_2O \rightarrow Na_2 + {}^3O$	$(1.46)^a$	$(12.52)^a$	93.08	101.2^c
$Na_2OH \rightarrow NaOH + Na$	39.97	30.89	33.11	
$Na_2OH \rightarrow Na_2O + H$	116.51	111.15	85.66	
$Na_2OH \rightarrow Na_2 + OH$	67.54	61.51	90.07	
Na_2OH_2 (**13**) $\rightarrow Na_2 + H_2O$	35.54	24.50	31.54	
Na_2OH_2 (**13**) $\rightarrow NaH + NaOH$	63.58	55.04	55.73	
Na_2OH_2 (**13**) $\rightarrow Na_2O + H_2$	77.58	74.72	46.58	
Na_3O (D_{3h}) $\rightarrow Na_2O + Na$	54.94	40.52		
Na_3O (D_{3h}) $\rightarrow NaO + Na_2$	52.69	44.70		
Na_3OH (C_{3v}) $\rightarrow NaOH + Na_2$	53.35			
Na_4O (T_d) $\rightarrow Na_3O + Na$	$(22.12)^a$			
Na_4O (T_d) $\rightarrow Na_2O + Na_2$	76.64			

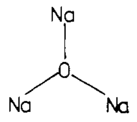
[a] Because of differences in spin multiplicity on both sides of the equation, these values are grossly underestimated at noncorrelated levels. [b] $D°_0$ values from Huber, K. P.; Herzberg, G. "Constants of Diatomic Molecules"; Van Nostrand Reinhold: New York, 1979. [c] Values calculated from data in the NBS Tables. See footnote *c*, Table IV.

ferences. Calculated dissociation energies and electron affinities are summarized in Tables III and IV; values obtained using Hartree–Fock theory are inadequate when species with different multiplicities are involved. Energies obtained with electron correlation corrections should be employed for comparison with experimental measurements, but this was not possible technically for **1** and **2**.

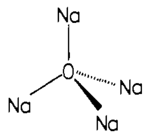
We note that the 3-21G basis set does not have any *d* functions, so that the involvement of d orbitals in hypermetallic bonding is not indicated to be essential by our results. In fact, the dissociation energies (Table III) are generally *lower* at 6-31G* than at 3-21G. This is due to the better description of oxygen with the larger basis; the extra sodium basis functions help to alleviate the oxygen 3-21G deficiencies (basis set superposition error)[17] which artificially raise the dissociation energies given by the smaller basis.

Results and Discussion

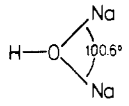
Structures and Bonding. The hypermetalated molecules, ONa_3 (**1**), ONa_4 (**2** and **5**), $HONa_2$ (**3**), and $HONa_3$ (**4** and **6**), are of central interest. Geometrical and bonding details for related species also are provided in Table II. Although NaOH and Na_2O are classical octet molecules, both favor linear structures because of their ionic character. The 3-21G and 6-31G* Mulliken populations indicate high negative charges on oxygen; nearly the same values are obtained at each level for all species in Table II with eight or more valence electrons: NaOH, Na_2O, Na_2OH, Na_3O^+, Na_3O, Na_3OH, and Na_4O. As in the case of the lithium oxides, Li_nO (n = 2–6),[1,2] "saturation" occurs when more valence electrons than eight are present, and oxygen appears to be content with its usual octet. The "extra" electrons are involved in Na–Na bonding.



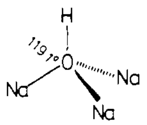
1 (D_{3h})



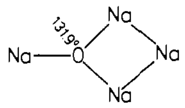
2 (T_d)



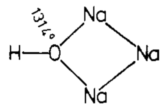
3 (C_{2v})



4 (C_{3v})



5 (C_{2v})



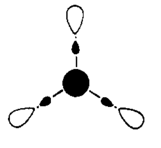
6 (C_{2v})

Table IV. Comparison of Calculated Adiabatic Ionization Potentials with Experimental Appearance Potentials

	adiabatic ionization potentials, eV			
species	3-21G// 3-21G	6-31G*// 3-21G	MP2/ 6-31G*// 3-21G	exptl appearance potentials, eV
Na	4.91	4.96	4.96	5.14^c
Na_2	3.96^b	3.97^b	4.45	4.87^c
NaO^a	4.95^b	4.99^b	6.42	$6.5 \pm 0.7,^d$ 7.1^c
Na_2O	1.60^b	2.69^b	5.22	5.06 ± 0.04^e
Na_3O (D_{3h})	3.02	2.92		3.90 ± 0.15^e
Na_4O				3.95 ± 0.10^e
Li_3O	3.22^f	3.15^g	3.37^g	4.54 ± 0.2^h

[a] Ionization to triplet NaO^+ assumed. [b] Because of changes in the number of paired electrons, noncorrelated values are expected to be underestimated. See text. [c] "The NBS Tables of Chemical Thermodynamic Properties": Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2. [d] Hildenbrand, D. L.; Murod, E. *J. Chem. Phys.* **1970**, *53*, 3403. [e] Reference 8. [f] Reference 2. [g] Reference 15. [h] Reference 4.

ONa_3 (1). Comparison of the two D_{3h} species, ONa_3^+ with eight valence electrons, and ONa_3 (**1**) with nine, is instructive. What does the extra electron in the latter do? The key result is the increase in the Na–Na overlap population in ONa_3. The sodiums in ONa_3 are mutually binding, but do not interact in ONa_3^+. As is generally true, the hypervalent (ninth as well as tenth) electrons occupy an a_1 orbital (**7**) with a radial node essentially metal–metal bonding in character. Judging from the decrease in the ONa overlap population, sodium–oxygen bonding is somewhat less favorable in going from ONa_3 to ONa_3^+. Owing to the Na–Na vs. Na–O compensation, the O–Na bond length hardly changes. Even greater metal–metal bonding is also indicated (Table II) in $HONa_2$ (**3**), where the extra valence electron is shared by only two sodiums, and in ONa_4 (**2**) and $HONa_3$ (**4**), which have ten valence electrons.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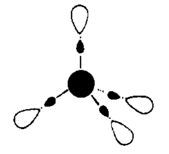
8

At the 3-21G level a C_{2v} ONa_3 isomer with one large Na–O–Na bond angle was slightly lower in energy than the D_{3h} structure. However, single-point 6-31G*//3-21G calculations favor the D_{3h} structure by 1.47 kcal/mol. Other minima (e.g., a C_{3v} structure which might have facilitated Na–Na overlap) were sought, but

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(17) (a) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553–566. (b) See: Bentley, J. *J. Am. Chem. Soc.* **1982**, *104*, 2754–2759, for an analysis of $NaOH_2$. (c) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 2283–2287.

were not found on the hyperface.

ONa_4 (2 and 5). As with OLi_4,[2] we found two minima for ONa_4 on the potential energy surface. With both metals, the hypermetalated tetrahedral arrangements (**2** for ONa_4) are more stable than "ion pair" C_{2v} forms (**5**). The latter, can be represented according to Mulliken charges as $ONa_3^+Na^-$. (A negatively charged sodium has been found in an X-ray structure.[18]) However, **5** is 21.0 kcal/mol higher in energy than **2**; in the lithium series this difference was 18.2 kcal/mol (both with the 3-21G basis set). The dipole moment of **4**, 9.1 D, is remarkably large and indicates the unbalanced nature of the charge distribution. This is partially overcome by the rather strong Na–Na binding involving the negatively charged sodium and its two nearest neighbors.

The charge distribution in ONa_4 (**2**, T_d) shows the favorable electronic arrangement. The oxygen charge, only −0.9 at 3-21G, is about the same as in ONa_2 and the other molecules at the same level and much less than would be anticipated if oxygen truly had an expanded valence shell. The relatively small sodium charge of +0.22 is evenly distributed. The sodium (ONa_4, **2**) and lithium (OLi_4, T_d) species are analogous. In general, their structures, energies, and electron distributions indicate that bonding in the sodium and in the lithium oxides is similar. While the influence of *d* functions was not studied with **2**, sodium d orbitals are expected to be of little importance in such highly polar compounds. Furthermore, the ONa_4 HOMO, **6**, which is responsible for the hypervalent bonding, has a_1 symmetry and would not be affected by inclusion of *d* functions in the oxygen basis set. "Hypervalent bonding" utilizing d orbitals is not involved. Other geometries with all four sodium atoms on one side of the oxygen, e.g., a C_{3v} inverted tetrahedron or a C_{2v} oxygen-capped rhomboid, do not correspond to minima at 3-21G but convert on optimization to T_d symmetry. The comparison with the dication ONa_4^{2+} (T_d), which has the usual valence octet, clearly shows that the two extra electrons in Na_4O are not involved in Na–O bonding. The Na–O bond length, the charge on oxygen, and the Na–O populations are very similar in both ONa_4 and ONa_4^{2+}. The two positive charges in ONa_4^{2+} are completely distributed on the four sodium atoms. The Na–Na interactions, bonding in ONa_4, are nonbonding in ONa_4^{2+}.

$HONa_2$ (3). The simplest hypermetalated molecule in this set, $HONa_2$ (**3**), has a small NaONa angle (100.6° at 3-21G), a short Na–Na distance (3.14 Å vs. 3.23 Å in Na_2 at the same level), and a large Na–Na overlap population (0.270 at 6-31G*). The OH moiety in **3** is very little different from that in NaOH, but the O–Na overlap population in the latter is significantly higher than in **3**. The extra sodium atom in $HONa_2$ binds both to oxygen and to sodium. The four doubly occupied MO's of **3**, as in **1**, have the character usual for planar AB_3 or HAB_2 species.[19] The singly occupied HOMO of **3**, which accomodates the ninth valence electron, is similar in character to **7** and **8**. The 3s functions on sodium dominate and are responsible for the Na–Na bonding, but Na 3p components aligned along the O–Na bond axes ameliorate the antibonding O–Na character. This is the general characteristic of hypermetallic bonding.[1-3]

One can also represent **3** as an interaction complex between HO^- and Na_2^+. However, the 3-21G dipole moment of $HONa_2$ (2.29 D) is modest when compared with that of HONa (5.47 D) so that a description of $HONa_2$ as a complex between an HO radical and Na_2 also is appropriate. Note that the binding energy of Na_2 to OH (90 kcal/mol, 6-31G*//3-21G, Table III) is extremely large.

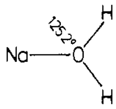
$HONa_3$ (4 and 6). Just as $HONa_2$ can be considered to result from the interaction of NaOH with a sodium atom, $HONa_3$ results when the interaction involves a Na_2 molecule. As with ONa_4 (**2** vs. **5**), two geometries are expected, a "tetrahedral" (C_{3v}) arrangement, **4**, and an ion pair $HONa_2^+Na^-$ form, **6**. In this case, the two isomers are close in energy, but **4** is still 3.2 kcal/mol more stable at 3-21G//3-21G. The dipole moment of **4** (3.49 D) is now higher than that of **6** (1.98 D). As the remote Na in **6** bears about the same negative charge as its counterpart in **5**, the much higher dipole moment in **5** (9.1 D) is due to the presence of a more electropositive atom (Na vs. H) at the opposite end of the molecule. Otherwise, the geometries, charges, and overlap populations in **5** and **6** are very similar.

The more stable $HONa_3$ isomer, **4**, also exhibits the by-now familiar hypermetallic structural and bonding features. As the oxygen and hydrogen charges (at least according to the Mulliken analysis) remain more or less constant along the series NaOH, Na_2OH, and Na_3OH (**4**), the sodium charges decrease and actually become smaller than hydrogen in the last instance. The 3-21G Na–O bond length (2.14 Å) is relatively long, and the corresponding overlap population is small. On the other hand, the Na–Na bonding in **4** (overlap population 0.192) is indicated to be the strongest in the set **1**–**4**.

$HONa_3$ (**4**) can also be regarded as an HO radical bound symmetrically to a Na_3 cluster. Hence, **4** models a hydroxyl group bound to a metallic sodium surface.[20] Additional sodium atoms are expected to bind to **4** (and the other hypermetalated species) and to form a second "layer" more distant from the electronegative atom. Such arrangements, suggested by **5** and **6**, have not yet been explored in the present instance, but OLi_5 and OLi_6 are indicated calculationally to prefer such geometries.[1,15]

Other Related Molecules: $NaOH_2$, $NaOH_3$, and Na_2OH_2. To complete the combinations of small tetra- and pentaatomic molecules containing oxygen and sodium and the necessary number of hydrogen atoms, we also examined $NaOH_2$, $NaOH_3$, and Na_2OH_2 in various geometries. Although of interest in other contexts, we do not consider these to be "hypermetalated" species.

Our calculations on the weakly bound sodium atom–water complex, $NaOH_2$ (**9**), may be compared with the prior literature.[17b,21] Most likely because of a basis set superposition error,[17b] the 3-21G Na–O separation (2.18 Å) is shorter than the results with larger basis sets (2.32–2.38 Å).[17b,21] The 6-31G*//3-21G dipole moment (5.38 D) is also larger than the literature values (3.25–3.39 D). The enhancement over the dipole moment for water (2.20 D at 6-31G*//6-31G*) is due to a small electron donation to sodium, which is indicated to have a small negative charge. The negative charge on oxygen is somewhat smaller than the other sodium species with eight or more valence electrons (Table II). The Na–O overlap population also is quite small; note the more meaningful result at 6-31G*. The "extra" electron in $NaOH_2$ (**9**) occupies an orbital largely centered on sodium which has the same character as that shown on one of the individual sodium atoms in **7** and **8**. This can be considered to be a nonbonding lone-air type orbital on sodium oriented away from oxygen. Since no second metal atom is present, hypermetallic bonding involving the interaction of two or more orbitals of this type is not possible. Hence, the binding energy of Na with H_2O is much less than Na with NaOH or with Na_2O.



9 (C_{2v})

The second species of this type, $NaOH_3$, was constrained in "tetrahedral" (C_{3v}) symmetry (**10**) in order to compare the results with those of **2** and **4**. This constraint was quite artificial, since a $HNa-OH_2$ complex is 63.3 kcal/mol (MP2/6-31G*//3-21G) more stable, and the separated components, NaOH and H_2, lie

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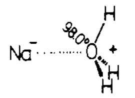
[18] Schindewolf, U.; Le, L. O.; Dye, J. L. *J. Phys. Chem.* **1982**, *86*, 2284–2286. Dye, J. L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 587–598.

[19] Gimarc, B. M. "Molecular Structure and Bonding"; Academic Press: New York, 1979.

[20] For theoretical studies of oxygen-based radicals on model lithium surfaces, see: McLean, W.; Schultz, J. A.; Pedersen, L. G.; Jarnagin, R. C. *Surf. Sci.* **1979**, *83*, 354–366. Schultz, J. A.; McLean, W.; Pedersen, L.; Jarnagin, R. C. *Chem. Phys. Lett.* **1979**, *64*, 230–233. Schultz, J. A.; Gates, S.; Pedersen, L. G., Jarnagin, R. C. *Ibid.* **1980**, *72*, 156–160.

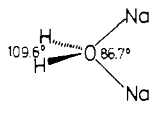
[21] Trenary, M.; Schaefer, H. F., III.; Kollman, P. A. *J. Am. Chem. Soc.* **1977**, *99*, 3885–3886; *J. Chem. Phys.* **1978**, *68*, 4047–4050. Also see: Bentley, J.; Carmichael, I. *J. Phys. Chem.* **1981**, *85*, 3821–3826. Singh, U. C.; Kollman, P. A. *J. Comput. Chem.*, in press.



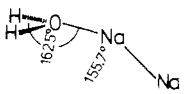
10 (C_{3v})

67.7 kcal/mol (MP2/6-31G*//3-21G) lower in energy. Nevertheless, the bonding in **10** is revealing, and corresponds to a $Na^-OH_3^+$ ion pair with a rather flattened OH_3^+ moiety (∠HOH = 98°). The negative charge on sodium is quite large (−0.60 at 6-31G*//3-21G) and the Na–O interaction is strongly antibonding. Instead, the Na–H overlap population (0.320) is favorable. A small dipole moment (0.4 D at 6-31G*//3-21G) results.

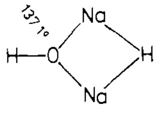
The remaining species examined, Na_2OH_2, seemed more promising than it proved to be. A "tetrahedral" (C_{2v}) geometry (**11**) was assumed initially for comparison purposes. However, a bent, end-on H_2O–Na–Na approach (**12**) is 2.7 kcal/mol (MP2/6-31G*//3-21G) more favorable than **11** and the global minimum with the same composition is **13**, a mixed NaH-NaOH "dimer", some 23.0 kcal/mol lower in energy than **11**. This Coulomb-stabilized[22] species (**13**) will be discussed in another context elsewhere.



11 (C_{2v})



12 (C_s)



13 (C_{2v})

The side-on (C_{2v}) approach of a Na_2 molecule to H_2O (**11**) is not very favorable energetically (see Table III and below), and the nature of this weak H_2O–Na_2 complex is further reflected in the Mulliken populations. The sodiums in **11** again are slightly negative and the Na–O interactions are antibonding. On the other hand, the Na–Na overlap population (0.745 at 6-31G*//3-21G) is nearly as large as that in Na_2 (0.759). A dipole moment of 3.30 D is calculated at the same level. In the end-on molecule, **12**, a C_s structure with ∠Na–Na–O = 155.7° is prefered (3-21G//3-21G) over the C_{2v} geometry. The negative oxygen polarizes the Na_2 molecule; the far Na atom becomes slightly negative and the Na near the oxygen slightly positive. The Na–O bonding is weak, but the Na–Na overlap population again is near that in Na_2. The dipole moment (6.4 D) is quite large. H_2O–Li–Li prefers a similar bent, end-on structure.[22d]

Sodium atoms and Na_2 molecules thus bind to water and other lone-pair donor bases. The binding energies are moderate, somewhat smaller than those for Li or Li_2, but much larger than those found in the very weak H_2O–H or H_2O–H_2 van der Waals complexes. Since the H_2O–Na_2 complexes **11** and **12** involve metal-metal but no appreciable Na–O bonding, we do not consider them to be examples of hypermetalation.[23]

The finding that the best Na–Na–OH_2 geometry is a bent end-on arrangement prompted us to examine similar structures for Na–Na–O–H and for Na–Na–ONa. Apparent minima were found in both cases, but these are only weak complexes. Thus, the bonding energy of Na to the sodium atom in NaOH to give a planar, cis-bent complex is only 3.5 kcal/mol at MP2/6-31G*//3-21G (see Table I for data). The energies of both bent isomers are not competitive with the hypermetalated forms, **3** for Na_2OH and **1** for Na_3O; the relative energy of **3** is 29.6 kcal/mol (MP2/6-31G*//3-21G) lower.

Energies. In their theoretical study of the interaction of alkali metal atoms with n-donor bases, Trenary, Schaefer, and Kollman calculated a bonding energy of 5.2 kcal/mol for the Na–OH_2 complex.[21] A similar value, 6.1 kcal/mol, was obtained by Bentley[17b] with the 6-31G** basis set after counterpoise corrections. We employed the 3-21G optimized geometries (the basis set superposition error at that level is responsible for the large dissociation energy in Table III), but no counterpoise or zero-point corrections. Nevertheless, our MP2/6-31G*//3-21G value, 8.6 kcal/mol, probably will not change appreciably with fuller treatments. The binding of a sodium atom to electron donor bases is weak when no other sodium already is present. The same is true of a Na_2 molecule when oriented "tetrahedrally" (C_{2v}) as in the H_2ONa_2 complex, **11**. The $H_2O + Na_2$ binding energy to give **11** again is quite modest, 8.5 kcal/mol (MP2/6-31G*//3-21G, Table III).

The bonding in hypermetalated species is much stronger (Table III). The 6-31G*//3-21G bonding energies of a Na atom to NaOH or to Na_2O (to give **1** and **3**) are 30.9 and 40.5 kcal/mol, respectively. The binding energies of Na_2 to NaOH and to Na_2O (to give **4** and **2**) are even larger, 53.4 and 76.6 kcal/mol. Obviously, the presence of more than one metal atom in hypermetalated molecules is decisive in accomodating "extra" valence electrons.

The binding energy of Li to Li_2O to give Li_3O (45.9 kcal/mol at 6-31G*//3-21G)[2] is only slightly larger than that of the sodium analogue. The same is true of the reaction $Li_2 + Li_2O \rightarrow Li_4O$ (T_d), −79.5 kcal/mol at 3-21G//3-21G.[2] This demonstrates that sodium and lithium both can participate in hypermetallic bonding equally well. Since experimental examples involving oxygen and the heavier alkali metals, potassium, rubidium, and cesium, already are known,[6-8] we conclude that hypermetallic bonding should be a very general phenomenon.

During the course of our work, Castleman et al.[8] reported the preparation of metal oxide clusters, Na_nO and K_nO (n = 2–4), in molecular beam experiments. Metal clusters were oxidized in the gas phase by reaction with an appropriate gas, like N_2O, and the appearance potentials of the resulting products were measured. The experimental data for Na_nO (n = 1–4) are given in Table IV, along with our calculated values. Unfortunately, these are incomplete for Na_3O and Na_4O, although reasonably good agreement is obtained for NaO and Na_2O at MP2/6-31G*//3-21G. Subsequent to our earlier publication,[2] we have now calculated the vertical IP of OLi_3 at MP2/6-31G*//3-21G. The value, 3.37 eV,[4] does not agree well with the experimental appearance potential, 4.54 ± 0.2 eV. We are investigating possible causes of this discrepancy further.

Conclusions

The "octet rule" does not predict the stoichiometries of alkali metal compounds satisfactorily; more than the expected number of Li, Na, K, Rb, or Cs atoms may be present. Na_2OH (**3**), Na_3OH (**4**), Na_3O (**1**), and Na_4O (**2**) may now be added to the growing list of molecules[1-8] which, at least as isolated species, are thermodynamically very stable toward all possible dissociation processes and are the global potential energy minima for each chemical composition.

However, the octet rule is not really violated in such hypermetalated compounds.[23] The ninth (in **1** and **3**) and tenth (in **2** and **4**) valence electrons are not associated with oxygen, which contents itself with the usual eight, but participate in Na–Na bonding. In effect, a metallic cage surrounds or partly surrounds the central atom, but the binding of metal atoms to such clusters is much stronger than to clusters comprised only of metal atoms, e.g., the binding of Na to Na_n ($n > 2$).[24]

While single alkali metal atoms, M, or diatomic species, M_2, do bind to water and to molecules with lone-pair electrons, the

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[22] See: (a) Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* **1983**, *105*, 2502–2503. (b) Schleyer, P. v. R.; Kos, A. J.; Kaufmann, E. *Ibid.* **1983**, *105*, 7617–7623. (c) Kaufmann, E.; Clark, T.; Schleyer, P. v. R. *Ibid.* **1984**, *106*, 1856–1857. (d) Kaufmann, E., unpublished calculations.

[23] Hypermetalated compounds are defined as molecules containing two or more metal atoms and having stoichiometries exceeding expectations based on the octet rule. Such compounds are stable thermodynamically as isolated entities toward all possible dissociation processes and are generally the global energy minima corresponding to the given chemical composition. Metal–metal bonding as well as metal–heteroatom bonding of significant magnitude is involved.

[24] See: Flad, J.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1979**, *71*, 3042. Pacchioni, G.; Beckmann, H.-O.; Koutecky, J. *Chem. Phys. Lett.* **1982**, *87*, 151. Flad, J.; Igel, G.; Dolg, M.; Stoll, H.; Preuss, H. *Chem. Phys.* **1983**, *75*, 331–345. Peterson, K. I.; Dao, P. D.; Farley, R. W.; Castelman, A. W., Jr. *J. Chem. Phys.* **1984**, *80*, 1780–1785.

association energies are much smaller than to molecules where one metallic atom already is present. This differentiates hypermetalated species, which enjoy both metal–metal and metal–central atom bonding of substantial magnitudes, from relatively weak complexes.

Since the principle of hypermetallic bonding is general,[1-3] compounds of the alkali metals with most if not all the other elements in the periodic table are expected. Alloys, surface complexes,[20] and definable entities in the solid state[7] are more familiar manifestations of the same phenomenon. Many small cluster molecules of this type have already been detected in the gas phase,[1-5,8] and should be observable in matrix isolation. Hypermetalated species already are known in condensed phases.[7,25] The $\Delta H_f°{}_{298}$ (Na_3O, crystal) value[26] is 2.5 kcal/mol more favorable than that for Na_2O.

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Note Added in Proof. The nature of the bonding in hypermetalated molecules has now been analyzed by Gopinathan and Jug[27] and by Reed and Weinhold;[28] both groups concur with our conclusions.

Registry No. 1, 87331-12-2; **2**, 89091-90-7; **3**, 92285-05-7; **4**, 92285-06-8; O_2, 7782-44-7.

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[25] See Bogdanović, B.; Wermeckes, B. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 684–686.

[26] See footnote *c*, Table IV.

[27] Gopinathan, M. S.; Jug, K. *Theor. Chim. Acta* **1983**, *63*, 511–527.

[28] Reed, A. E.; Weinhold, F., submitted for publication.

Lipophilic Crown-4 Derivatives as Lithium Ionophores

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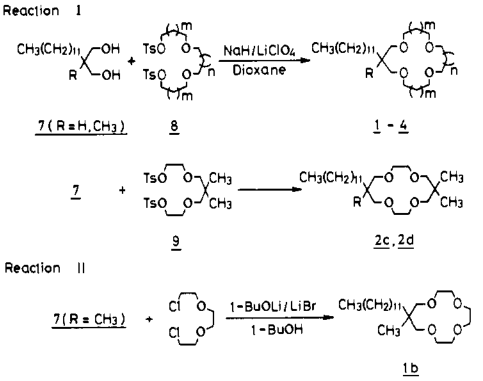
Abstract: Crown-4 derivatives of 13- through 16-member rings bearing a long aliphatic chain have been synthesized in an effort to obtain highly selective ionophores for lithium ions. The measurements of potentiometric selectivity coefficients for polymeric membranes containing the crown ethers indicated that their lithium selectivities can be explained primarily in terms of the size-fit concept, the 14-crown-4 and 15-crown-4 derivatives being much more selective for lithium than the larger and the smaller macrocycles. It was found that incorporation of a methyl group geminal to the long aliphatic chain prevents formation of sandwich-type 2:1 crown ether–metal complexes with alkali metal ions other than lithium and, therefore, enhances the lithium selectivity of the original crown ether. Some of the lipophilic 14-crown-4 derivatives possess remarkably high preference of lithium over sodium which bears importantly upon their applications.

Increasing attention is being focussed on Li^+ ionophores as tools for biological applications as well as for analyses and separation of the ion. Several Li^+ ionophores have been designed which are based on dioxadiamide derivatives.[1-4] Some of them have been applied for neutral carriers of polymeric membrane Li^+-selective electrodes,[1,2] which are very convenient tools for monitoring of Li^+ activity in environmental and biological systems. The others have been tested for Li^+ transport activity through a biological membrane.[3,4] The selectivity ratio of Li^+ over Na^+, one of the most essential factors for Li^+ ionophores, has proved to range from 10 to 100. Ionophores with still higher Li^+ selectivity are desirable for the practical applications.

Macrocyclic polyethers, referred to as crown ethers or cryptands, can complex various alkali and alkaline earth metal ions, and their ion-selectivities often depend on their cavity size. The cyclic polyethers, when dissolved in organic solvents or incorporated into membranes, can behave as ionophores selective for particular metal ions. Especially, highly lipophilic derivatives, e.g., crown ethers and cryptands bearing a long aliphatic chain(s),[5-10] may be efficient ionophores. Most of the crown ethers contain 5 or 6 oxygen atoms in the crown ring, thus being suited for preferential complexation with Na^+ or K^+. Very few crown ethers selective for Li^+ have appeared so far. In addition to cryptand [2.1.1],[11] crown

Scheme I



Crown ether	m	n	R
1a	0	0	H
1b	0	0	CH₃
2a	0	1	H
2b	0	1	CH₃
2c	0	1	H
2d	0	1	CH₃
3a	1	0	H
3b	1	0	CH₃
4a	1	1	H
4b	1	1	CH₃

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