J. Am. Chem. Soc. 1982, 104, 5839-5841

with Pt–P = 2.224 (4) Å while the three equatorially bridging ligands are symmetrically disposed with Pt–Sn = 2.680 (1) Å and Pt–Sn–Pt = 57.87 (3)°. This beautiful geometry represents the face-sharing of two distorted tetrahedral $PPtSn_3$ fragments, which constitute a series with the P_2PtSn_2 configuration (**1**) and with the corresponding P_3PtSn species (**3**), which we have also identified using NMR spectroscopy. The two Pt atoms are within bonding distance,[18] and the strong coupling between them [^1J(Pt–Pt) = 4663 Hz] is consistent with some degree of metal–metal bonding,[19] as is ^2J(P–Pt) = 82 and ^3J(P–P) = 81 Hz. As for complex **1**, nonplanar coordination is characteristic of Pt(0) while the ^{119}Sn chemical shift (−563 ppm) is indicative of Sn(II). The narrow angle at the latter and the lengthening of Pt–Sn (0.12 Å) between compounds **1** and **2** incline us toward an interpretation based on delocalization of electron density between the five metal centers. Expressed in simple qualitative terms, this situation corresponds to interaction between three hybrid orbitals on each Pt with a single hybrid per Sn to give three bonding, three nonbonding, and three antibonding levels. The Pt(0) nuclei then retain "closed-shell" d^{10} character while the Sn(II) atoms each contribute an electron pair to fill the three delocalized bonding orbitals. Superficially there is a resemblance between structure **2** and that of $[Me_2SnFe(CO)_4]_2$, but the latter clearly incorporates quadrivalent tin and accordingly the angle at Sn is almost tetrahedral[20] with that at Fe quite narrow (77.4°). The electron count in another Sn(IV) derivative[21] $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2Sn_2Fe_3(CO)_9]$ is exact in terms of isolobal relationships[22] for a closo cluster, but delocalized metal–metal bonding tentatively proposed in a somewhat similar platinum–tin(IV) cluster[23] $[(C_8H_{12})_3Pt_3(SnCl_3)_2]$ does not appear to have been discussed further. A more realistic molecular orbital description of the intermetallic bonding in compound **2** will necessarily take account of interaction involving overlap of unfilled orbitals of comparable energy with the Pt filled-shell orbitals, similar to that put forward by Dedieu and Hoffmann[24] for unbridged Pt(0)–Pt(0) complexes of the type Pt_2L_4.

A comprehensive investigation of the properties of compounds typified by **1**–**3** is in progress, including development of related Ni and Pd chemistry. Since methanolic solutions containing chloroplatinic acid and stannous chloride provided the first effective catalyst for the reduction of ethylene under ambient conditions[25] and polynuclear Pt–Sn species have been implicated[26] in similar behavior, the possibility that the Pt(0)/Sn(II) systems will demonstrate parallel catalytic reactivity is being explored.

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Registry No. 1, 82918-18-1; **2**, 82918-19-2; $Sn(acac)_2$, 16009-86-2; $(PPh_3)_2Pt(\pi\text{-}C_2H_4)$, 12120-15-9; $Pt(PPh_3)_4$, 14221-02-4; Pt, 7440-06-4; Sn, 7440-31-5.

Supplementary Material Available: Listings of crystallographic data for $PtSn_2(acac)_4(PPh_3)_2$ and $Pt_2Sn_3(acac)_6(PPh_3)_2$ (29 pages). Ordering information is given on any current masthead page.

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Effectively Hypervalent First-Row Molecules. 1. Octet Rule Violations by OLi_3 and OLi_4

Paul von Ragué Schleyer* and Ernst-Ulrich Würthwein

Institut für Organische Chemie der
Friedrich-Alexander-Universität
Erlangen-Nürnberg, D-8520 Erlangen
Federal Republic of Germany

John A. Pople

Department of Chemistry, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15235

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We have discovered calculationally a large number of AX_n molecules comprised of first-row elements whose unusual stoichiometries suggest violations of the octet rule.[1] The equilibrium geometries of these species involve polycoordinated central atoms, A, which therefore appear to have some hypervalent character. This communication deals with preliminary results on two such molecules, OLi_3 and OLi_4. The former is known experimentally; gas-phase energies are available but not the geometry.[2]

The octet rule is very effective in predicting the optimum stoichiometry of AX_n first-row molecules if X is hydrogen or an element (or group) toward the right of the periodic table. Thus, addition of a hydrogen atom to an oxygen atom to give the OH radical is exothermic by 101 kcal/mol; addition of a second hydrogen atom to give H_2O is even better, releasing 118 kcal/mol.[3] However, 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.[4]

If the bonded atom X is lithium rather than hydrogen, the situation is completely different. To illustrate this, we consider the compounds OLi_n for n = 1–4. Table I gives calculated dissociation energies for $OLi_n \rightarrow OLi_{n-1} + Li$. (These results were obtained by minimizing the Hartree–Fock/3-21G[5] energy to give the structure and then using the larger 6-31G* basis[6] for MP2 correlated calculations[7] at these geometries. Zero-point corrections were made by using harmonic frequencies from the HF/3-21G surface[8,9] (see Table II). Clearly lithium does not respect the octet rule at all! The sequential addition of lithium atoms continues perfectly well after the second step and both OLi_3 and OLi_4 are indicated to be quite stable thermodynamically toward dissociation or loss of an electron. In further work to be described subsequently, OLi_5 and OLi_6 are also indicated to be stable molecules.

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Table I. Theoretical and Experimental Dissociation Energies for OLi_n Compounds (kcal/mol)

	3-21G//3-21G	6-31G*//3-21G[a]	MP2/6-31G*// 3-21G[a]	zero point corrected	exptl[b]
$OLi\ (C_{\infty v}) \rightarrow O + Li$	33.4	37.0	71.0	69.7	80.5 ± 1.5
$OLi_2\ (D_{\infty h}) \rightarrow OLi + Li$	48.5	39.8	88.0	85.8	97.8 ± 2.6
$OLi_3\ (C_{2v}) \rightarrow OLi_2 + Li$	54.6	45.9	44.8	43.7	50.7 ± 10
$OLi_4\ (T_d) \rightarrow OLi_3 + Li$	28.9			27.6[c]	
$OLi_2\ (D_{\infty h}) \rightarrow O + Li_2$	78.0	74.3	144.7	141.7	152.8 ± 2.6
$OLi_3\ (C_{2v}) \rightarrow OLi + Li_2$	106.6	83.1	118.6	115.8	123.0 ± 10
$OLi_4\ (T_d) \rightarrow OLi_2 + Li_2$	79.5			77.6[c]	

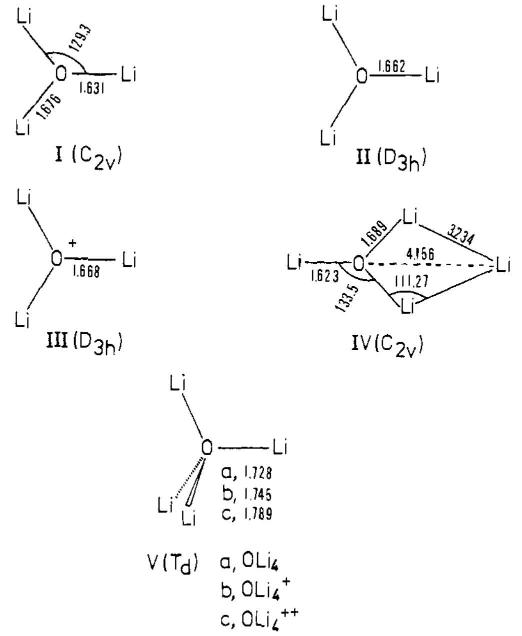
[a] Uses Hartree-Fock 3-21G geometries. [b] Data from ref 2. [c] 3-21G values.

Table II. Absolute Energies (au)

species	state	3-21G//3-21G	6-31G*//3-21G	MP2/6-31G*//3-21G	ZPE[a]
$OLi\ (C_{\infty v})$	$^2\pi$	−81.82836	−82.27434	−82.42450	1.3
$OLi_2\ (D_{\infty h})$	$^1\Sigma_g^+$	−89.28714	−89.16918	−89.99609	3.5
$OLi_3\ (C_{2v})$ I	$^2A_1$	−96.75561	−97.27371	−97.49891	4.6
(D_{3h}) II	$^2A_1'$	−96.75483			
$OLi_4\ (T_d)$ Va	$^1A_1$	−104.18315			5.9
(C_{2v}) IV	$^1A_1$	−104.15422			
$OLi_3^+\ (D_{3h})$ III	$^1A_1'$	−96.63634			
$OLi_4^+\ (T_d)$ Vb	$^2A_1$	−104.05738			
$OLi_4^{2+}\ (T_d)$ Vc	$^1A_1$	−103.78256			
$O\ (K_h)$	^3P	−74.39366	−74.78393	−74.88004	
$Li\ (K_h)$	^2S	−7.38151	−7.43137	−7.43137	
$Li_2\ (D_{\infty h})$	$^1\Sigma_g^+$	−14.76925	−14.86692	−14.88545	0.5

[a] Zero point energy, in kcal/mol. Based on 3-21G frequencies.

Chart I



Peculiar stoichiometries do not require hypervalence. Thus, the third lithium in OLi_3 might be connected to another lithium, or to both lithiums, but not to oxygen. Such species would certainly be interesting but would not involve hypervalent oxygen. However, this is not the case. We have examined a large number of OLi_3 structures computationally. The only minimum we have been able to find at the 3-21G level is I (Chart I), with C_{2v} symmetry. The closely related D_{3h} structure, II, is only 0.5 kcal/mol higher in energy but is indicated by diagonalizing the force constant matrix to be a transition structure on the potential-energy surface. The O–Li bond lengths in I and II are shorter than in OLi_3^+ (III), an octet molecule included for comparison. Two minima have been found on the OLi_4 potential-energy surface. IV is shown by Mulliken population analysis to be best regarded as a OLi_3^+,Li^- ion pair.[10] However, this is not the most stable form; the global OLi_4 minumum, some 18.2 kcal/mol lower in energy, has a simple tetrahedral geometry (Va).

What is the nature of the "hypervalent bonding" in OLi_3 and OLi_4? Hypervalent molecules with second-row central atoms are common and use low-lying d orbitals. This cannot be the explanation in the first row since d orbitals are less readily available energetically; in any case, the phenomenon is found with the 3-21G basis, which has no d-type functions. Some indication of the nature of the bonding can be obtained from the occupied molecular oribtals and the Mulliken analysis. Consider tetrahedral OLi_4 with ten valence electrons. These occupy molecular orbitals $(3a_1)^2(2t_2)^6(4a_1)^2$. The $3a_1$ and $2t_2$ orbitals are analogous to the valence orbitals in the tetrahedral carbon molecules CH_4 and CLi_4. Occupation of these four orbitals leads to AX bonding, but net antibonding among the substituent atoms, X. The HOMO in OLi_4 is the totally symmetric orbital $4a_1$ with an additional radial node. The OLi σ^* antibonding character of this MO is reduced by some $p\sigma$ character on lithium. The computed bond lengths give evidence for some OLi bond weakening, being 1.583 Å in OLi_2, 1.661 Å (average) in OLi_3, and 1.728 Å in OLi_4.

However, the $4a_1$ orbital is *bonding* between all pairs of lithiums. Since the eight electrons in $3a_1$ and $2t_2$ largely fill the octet on the oxygen atom, $4a_1$ has large coefficients on the lithium atoms (particularly the diffuse outer function of the 3-21G Li basis). It follows that the contribution to Li–Li bonding from the six pair-wise combinations is quite large. These effects are reflected in the total (atom–atom) Mulliken overlap populations. The series of tetrahedral molecules OLi_4^{2+} (Vc), OLi_4^+ (Vb), and OLi_4 (Va) with 8, 9, and 10 valence electrons is instructive. For all these species, the oxygen–lithium overlap population is nearly constant (0.33 → 0.30), but the lithium–lithium overlap population increases from 0.00 for (OLi_4^{2+}) to 0.10 (OLi_4^+) to 0.16 (OLi_4) when more electrons are present. Thus the decrease in the O–Li distance along the same series (1.789, 1.745, 1.728 Å) is due to more favorable interactions among the lithium atoms rather than changes in O–Li bonding.

The Mulliken populations indicate the nature of these species in another way. The lithium in OLi has donated 0.55 electron to oxygen. In OLi_2, the total donation to oxygen has increased to 0.81 electron, and a second partially ionic LiO bond has formed. The negative charge on oxygen in OLi_3, -0.87, is only slightly larger and no further increase is indicated in OLi_4 or even in OLi_6.

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[10] See: Klimenko, N. M.; Zakzhevskii, V. G.; Charkin, O. P. *Koord. Khim.*, in press.

Similarly, there is no significant change in the oxygen changes in OLi_4^{2+} (-0.884), OLi_4^+ (-0.875), and OLi_4 (-0.871). Thus, the extra electrons in the nominally hypervalent species are not associated with oxygen but rather contribute to Li–Li bonding. The overall structure can be described in terms of an oxygen bonded within a cationic lithium cage, e.g., $O^-Li_3^+$ or $O^-Li_4^+$.

Our further calculations indicate this phenomenon to be quite general. We have already investigated hyperstoichiometric lithium species involving hydrogen and all first-row and some second-row elements.[11] The other alkali metals behave like lithium. ONa_3 and ONa_4, which were reported recently,[12] have calculated structures and bonding like OLi_3 and OLi_4.[11] "Curious suboxides in which there are covalent M–M bonds",[13] e.g., O_2Rb_9 and O_3Cs_{11}, also are known experimentally.[14] The present work also is pertinent to surface complexes between oxygen species and lithium and other metals.[15]

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Registry No. OLi_3, 69235-02-5; OLi_4, 8290-38-9.

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Evidence Implicating *cyclo*-Diphosphates as Intermediates in Reactions of Nucleoside Phosphorothioates with Cyanogen Bromide

R. Douglas Sammons,† Hsu-Tsu Ho,‡ and Perry A. Frey*‡

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210
and Institute for Enzyme Research, University of Wisconsin
Madison, Wisconsin 53706

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Adenosine 5′-(1-thiodiphosphate) (ADPαS) and adenosine 5′-(2-thiotriphosphate) (ATPβS) can be desulfurized to ADP and ATP by reacting them with cyanogen bromide. In $H_2{}^{18}O$ both the α- and β-phosphoryl groups of ADP and the β- and γ-phosphoryls of ATP become labeled with ^{18}O. The incorporation of isotope into the terminal phosphoryl groups is *at the expense* of incorporation in place of sulfur in the substrates.

Reaction of 10 mM ATPβS with 20 mM CNBr in $H_2{}^{18}O$ (95% ^{18}O) at pH 7 in 0.1 M potassium phosphate produced [^{18}O]ATP in 55% yield. [^{18}O]ATP was systematically degraded so that P_α, P_β, and P_γ were separately isolated as inorganic phosphate. These samples were analyzed for ^{18}O by ^{31}P NMR analysis of the ^{18}O-induced isotope shifts,[1a,b] which showed that P_β and P_γ contained equivalent ^{18}O enrichment while P_α was unenriched. Reaction of 100 mM ADPαS with 400 mM CNBr in $H_2{}^{18}O$ (98% ^{18}O) at pH 10.6 in 0.5 M potassium tetraborate produced [^{18}O]ADP. The proton-spin-decoupled ^{31}P NMR spectrum consisted of two doublets exhibiting the chemical shifts and coupling constants of P_α and P_β in ADP.[2] Both signals were accompanied by isotope shifted signals of approximately equal intensities attributed to the presence of ^{18}O in equal amounts of both positions.

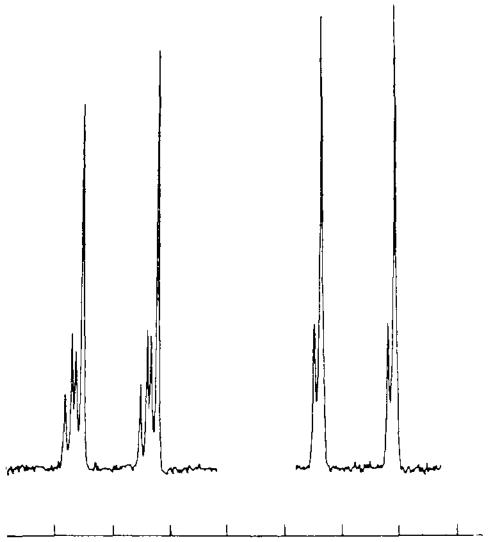
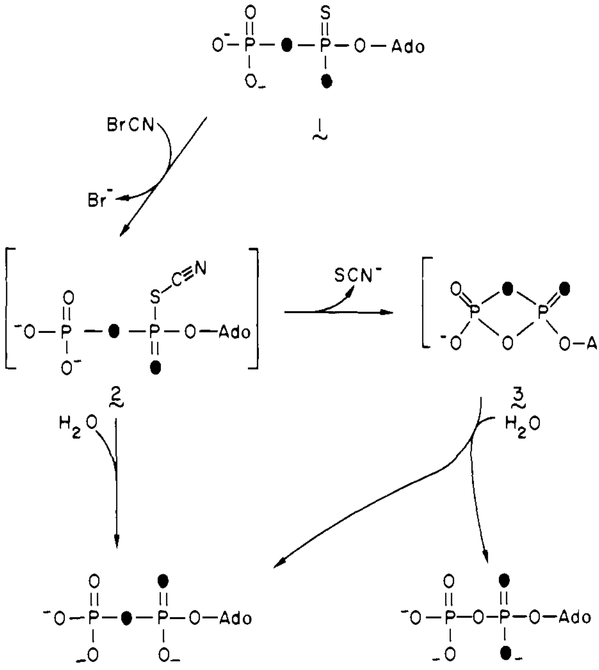


Figure 1. ^{31}P NMR spectrum of (S_P)-ADPαS($\alpha^{18}O_2$). The proton-spin-decoupled spectrum of (S_P)-ADPαS($\alpha^{18}O_2$) **1** in Scheme I, was obtained on the Bruker WM-300. The P_α signals are the doublet patterns at the left in the figure and those for P_β are the doublets at the right in the figure. The chemical shift values for the ^{18}O-containing species are given in the text. (S_P)-ADPαS($\alpha^{18}O_2$) was synthesized by specific phosphorylation of AMPS($^{18}O_2$).[2,3a–d]

Scheme I



To shed light on the basis for the dilution of isotope at the position of substitution, we investigated the reaction of ADPαS, $\alpha^{18}O_2$ (**1**, Scheme I, Ado = adenosine), with cyanogen bromide in H_2O. The ^{31}P NMR spectrum of **1** is shown in Figure 1. The signals for P_β are the upfield pair of doublets, an isotope shifted signal at δ -6.642 owing to the high ^{18}O enrichment in the bridging position, and a smaller unshifted signal at δ -6.620 reflecting the presence of some ^{16}O in the bridge. The P_α signal is more complex, consisting of four doublets representing the four possible ^{18}O

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† The Ohio State University.

‡ University of Wisconsin.

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