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Article

Molecular Oxygen Dianions Trapped in Lithium Cluster Cages

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In an important recent report, Coles and Hitchcock (*Chem. Commun.* **2005**, 3165) have synthesized a unique compound of the form $Li_9O_2(hpp)_7$, with an O_2 unit encapsulated in the Li cluster. The group hpp is the bicyclic guanidinate 1,3,4,6,7,8-hexahydropyrimido[1,2-*a*]pyrimidinate. Coles and Hitchcock raise the interesting possibility that the trapped species is the O_2 dianion. We have theoretically investigated (with full geometry optimization) the structural, vibrational, and electronic properties of this fascinating system with 165 atoms. Every indication supports the qualitative conclusion that this system is best represented as an O_2 dianion embedded in a Li cluster. Several smaller model systems, including replacement of the hpp ligands by Cl atoms, are also examined and provide some interesting comparisons.

Introduction

Stoichiometries such as OLi_3, OLi_4, and OLi_5 seemed to be excluded by the octet rule until these compounds were observed by Wu and co-workers[1−3] in 1978. The theoretical studies of Schleyer and co-workers[4,5] elucidated the electronic structures of these "hypermetalated" species; they have a negatively charged O bound electrostatically inside a cationic Li cage, e.g., $O^-Li_3^+$ and $O^-Li_4^+$.

Additional LiO clusters were discovered subsequently. Some of these have been found in more elaborate complexes. Octahedral Li_6O^{4+} cores are present in Clegg et al.'s[6] cage molecule $[(c\text{-}C_5H_9)N(H)]_{12}(O)Li_{14}$ as well as in the $Li_{26}(PR)_{12}(O)$ $\{R = Si[C(^iPr)Me_2]_3Me_2\}$ complex.[7] The Li-containing organometallic compounds are known for their oxophilicity, and Wheatley has discussed the structural motif for such metal organo- and inorganooxides, including those with the Li_2O, or Li_6O^{4+} core.[8] In 1999, Lievens et al.[9] produced many naked monoxide clusters Li_nO ($2 \leq n \leq 70$) through laser vaporization and time-of-flight mass spectrometric selection. The accompanying density functional theory (DFT) computations provided evidence for the importance of rigid geometrical structures for the small Li_nO clusters ($2 \leq n \leq 8$). The results for Li_7O and Li_8O suggested that O may prefer penta- over tetracoordination.[9] Viallon et al.'s[10] recent investigation of the Li_nO_m ($1 < m < 15$, $2 < n < 58$, $m < n$) lithium oxide clusters (with more than one O atom) revealed that all of the O atoms are separated from one another. Each O atom is apparently present as O^{2-} and utilizes largely ionic bonding to bind to several surrounding Li atoms.

We focus here on the important recent report of Coles and Hitchcock,[11] who described a fascinating new system, $Li_9O_2(hpp)_7$, in which the O atoms are bound to one another

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(the hpp ligand is the bicyclic guanidinate 1,3,4,6,7,8-hexahydropyrimido[1,2-*a*]pyrimidinate). A monocapped Li_9O_2 cubic-cage structure comprises the center of this $Li_9O_2(hpp)_7$ complex, and unlike previous Li_nO_2 examples, the two encapsulated O atoms are in proximity. Coles and Hitchcock draw the intriguing conclusion that the O_2 unit in their new compound is a dianion. It is of interest to see if this conclusion can be justified by detailed theoretical investigation. Therefore, we have investigated the nature of the bonding between these encapsulated O atoms, as well as between O and Li.

Computational Methods

The B3LYP method is a hybrid Hartree-Fock DFT method incorporating Becke's three-parameter functional[12] (B3) with the Lee−Yang−Parr (LYP) correlation functional.[13] The basis sets employed here are of double-ζ plus polarization (DZP) quality for all atoms except O, which has additional diffuse s and p functions. The diffuse functions on the O atom reflect our subsequent finding that the negative charge in this system resides largely on the two O atoms.

The DZP basis set for Li was composed of Thakkar's double-ζ contraction.[14] The DZP basis sets for C, N, O, and H in this paper are the standard Huzinaga−Dunning[15,16] double-ζ sets plus polarization functions [$\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, $\alpha_d(O) = 0.85$, and $\alpha_p(H) = 0.75$]. One set of s and p diffuse functions [$\alpha_s(O) = 0.082\,27$; $\alpha_p(O) = 0.065\,08$] was added to O atoms to describe the O_2 negative ion. The final contracted basis, denoted as DZP(++), is designated Li(9s5p/4s2p), C(9s5p1d/4s2p1d), N(10s6p1d/5s3p1d), O(10s6p1d/5s3p1d), and H(4s1p/2s1p). There are 165 atoms and 1598 basis functions for this rather large system. The $Li_9O_2(hpp)_7$ geometry was fully optimized. All computations employed the *Gaussian03* program suite.[17] The default integration grid (75, 302) was applied. Natural bond orbital (NBO) analysis[18] gave bond orders and natural charges, which provide critical information about the bonding in these molecules.

Results and Discussion

We fully optimized the geometry of the $Li_9O_2(hpp)_7$ molecule by using the B3LYP DFT functional with the DZP(++) basis set. The fully optimized structure of $Li_9O_2(hpp)_7$ is a minimum with C_2 symmetry (Figure 1). Starting from a structure with no symmetry, the geometry reverts to the same C_2 structure. Our geometric parameters for the central Li_9O_2 fragment are compared with experimental parameters in Figure 2; the good match is apparent. In particular, the computed O−O bond distance, 1.491 Å, is close to the experimental result, 1.501 Å.[11] This O−O distance in $Li_9O_2(hpp)_7$ is much longer than that of the isolated oxygen molecule O_2 (1.219 Å computed at the same theoretical level or 1.208 Å from the experiment[19]) and is also longer than that of the O_2^- radical anion (predicted here to be $r_e = 1.351$ Å in its ground X $^2\Pi_g$ state, compared with the experimental result 1.35 Å[20]). Furthermore, our theoretical O−O distance in $Li_9O_2(hpp)_7$ is somewhat shorter than the theoretical O−O distance (1.542 Å) for the hypothetical isolated dianion O_2^{2-} (Table 1). Note that while O_2^{2-} spontaneously decays to $O_2^- + e^-$ in the gas phase, the present DZP++ basis set does not allow the "last" electron of O_2^{2-} to escape. The present theoretical

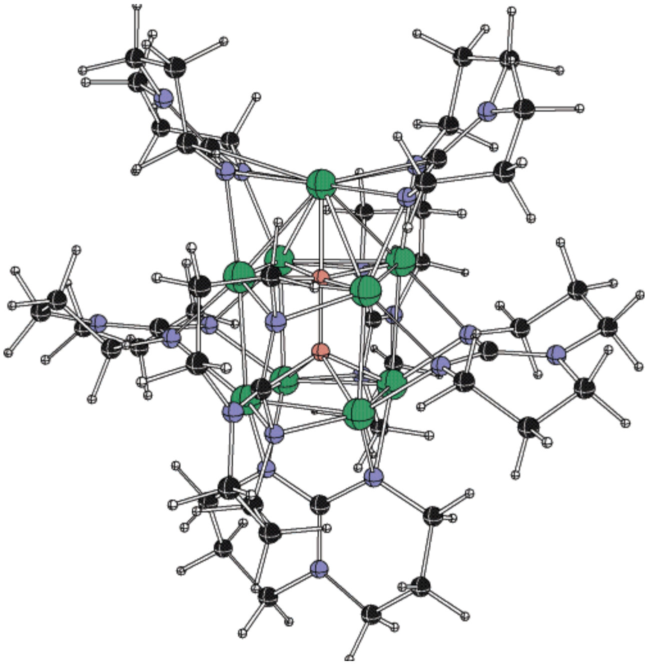

Figure 1. Optimized structure of $Li_9O_2(hpp)_7$.

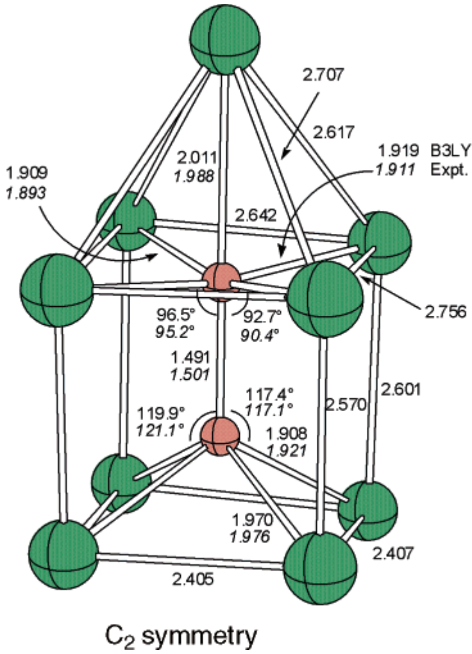

Figure 2. Geometric parameters of the centric Li_9O_2 structure.

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Table 1. Theoretical O−O Distance (R), the O−O Stretching Vibrational Frequency (ω), and the O−O Stretching Force Constant (F_{ii}) for $O_2Li_9(hpp)_7$ Predicted by the DZP(++) B3LYP Method, Compared with the Same Properties for the Isolated O_2, O_2^-, and O_2^{2-} Molecules at the Same Level (in Parentheses Are the Experimental Data)

	R (in Å)	ω (in cm^{-1})	F_{ii} (in aJ/Å^2)
O_2	1.219 (1.208[a])	1646 (1580[a])	12.77
O_2^-	1.351 (1.35[b])	1181 (1090[b])	6.58
O_2^{2-}	1.543	721	2.45
$O_2Li_9Cl_7$	1.500	890	3.54
$O_2Li_9(hpp)_7$	1.491 (1.501[c])		4.16

[a] Reference 19. [b] Reference 20. [c] Reference 11.

results thus support Coles and Hitchcock's description[11] of "a previously unobserved array of nine lithium atoms encapsulating the O_2^{2-} dianion".

Indeed, the NBO analysis confirms this conclusion. The natural atomic charges are −0.96 and −0.90 for the two O atoms (they are inequivalent) in $Li_9O_2(hpp)_7$. The natural charges for the nine Li atoms ranging from +0.885 to +0.897 also demonstrate the ionic bonding between the encapsulated O_2^{2-} diatomic dianion and the cationic Li cage.

Mulliken charges are known to depend strongly on the basis set and may be quite misleading, especially when basis sets with diffuse functions are used. So, the Mulliken charges are not discussed here. The natural charges are much less sensitive to the level of theory. With the 3-21G basis set, the natural atomic charges for the two O atoms in our case are predicted to be −0.91 and −0.85 (compared to −0.96 and −0.90, respectively, with the larger basis; see above).

Compared with the neutral O molecule (X $^3\Sigma^-_g$), the O_2^{2-} dianion has two extra electrons occupying the antibonding π^* orbitals. This decreases the O−O bond order from 2 to 1 and, accordingly, increases the O−O bond distance from 1.219 Å for isolated O_2 to 1.501 Å for $Li_9O_2(hpp)_7$ (Table 1).

The naked Li_9O_2 cluster (i.e., without ligands) is not stable and dissociates into Li_5O and Li_4O fragments upon attempted optimization. Obviously, the hpp ligands are very important contributors to the stability of the $Li_9O_2(hpp)_7$ complex. Do the hpp ligands play a *unique* role in this system? To test this hypothesis, we examined a simple test model, $Li_9O_2Cl_7$, in which seven Cl atoms replace the seven hpp ligands. Like the hpp ligands, the Cl atoms withdraw electrons from the Li atoms and stabilize the system. Indeed, our computations with the same theoretical method show that the $Li_9O_2Cl_7$ complex is a genuine minimum with C_{2v} symmetry (Figure 3). Although the geometry of the Li cage necessarily is somewhat different from that of $Li_9O_2(hpp)_7$, the O−O distance in $Li_9O_2Cl_7$ (1.500 Å) is almost the same as that in $Li_9O_2(hpp)_7$. The natural charges for the two O atoms are both −0.93, indicating again the trapped dianionic O_2^{2-} subunit character.

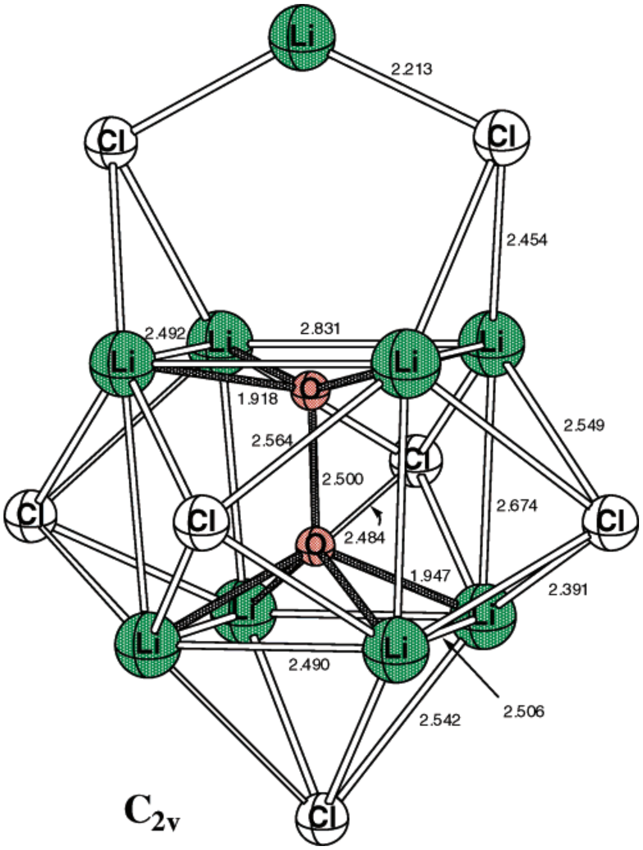

Figure 3. Geometric parameters of the optimized $Li_9O_2Cl_7$ molecule.

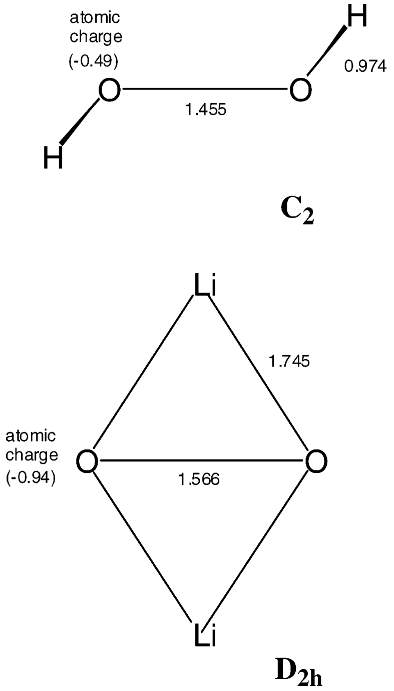

Figure 4. Bond length and atomic charge of peroxides HOOH and LiOOLi.

The vibrational frequency corresponding to the O−O stretching mode is related to the O−O bond order. The computed vibrational frequencies are 1646 cm^{-1} for the neutral O_2 molecule and 1181 cm^{-1} for the O_2^- radical anion (Table 1). These correspond to the formal bond orders of 2 and 1.5, respectively. The predicted vibrational frequency (890 cm^{-1}) for the O−O stretching mode of $Li_9O_2Cl_7$, which is a reasonable model for $Li_9O_2(hpp)_7$, is lower than both, consistent with the formal single O−O bond order for the dianionic O_2^{2-} moiety in this cluster. We could not complete the vibrational analysis directly for $Li_9O_2(hpp)_7$ because of its size. However, we have numerically evaluated the force constant of the O−O stretching for $Li_9O_2(hpp)_7$ by moving the O atoms by small (±0.005 Å) displacements while retaining the other atomic positions. For comparison, the same process is carried out for related molecules, and all of these results are listed in Table 1. Using these numerically derived force constants, we have perfectly reproduced the vibrational frequencies for O_2, O_2^-, and O_2^{2-} to within 1 cm^{-1}. Compared with the O−O stretching force constants for O_2 (12.8 aJ/Å^2), O_2^- (6.6 aJ/Å^2), and the hypothetical O_2^{2-} (2.5 aJ/Å^2), those for $Li_9O_2Cl_7$ (3.5 aJ/Å^2) and $Li_9O_2(hpp)_7$ (4.2 aJ/Å^2) are a bit larger than that of the hypothetical O_2 dianion. These values further support the contention that there is a single O−O bond in $Li_9O_2Cl_7$ and $Li_9O_2(hpp)_7$.

The O−O distance in $Li_9O_2(hpp)_7$ may also be compared with those in the HOOH or LiOOLi peroxides, predicted at the same level of theory (Figure 4). The O−O distance (1.500 Å) of $Li_9O_2(hpp)_7$ is between that in HOOH (1.455 Å) and that in LiOOLi (1.566 Å). The natural charge of each O atom of HOOH is −0.49 compared to −0.94 in LiOOLi, which has a greater degree of ionic bonding.

Our theoretical results for the large experimental $Li_9O_2(hpp)_7$ system, as well as the smaller $Li_9O_2Cl_7$ computational model, show that intact O_2^{2-} dianions can be encapsulated in Li cages provided that there is suitable overall charge balance. To preserve the single bond between the two O atoms, as well as the ionic bonding between the dianion and the cationic Li cage, electron transfer to O from the Li exterior must be limited. In effect, the systems studied here can be represented as $Li_2O_2{\cdot}(LiA)_7$, where A = hpp or Cl. The overall stability is buttressed by the ionic bonding between the Li cage and the outside ligands.

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