Inorganic Chemistry

Communication

Ozonic Acid and Its Ionic Salts: Ab Initio Probing of the O_4^{2-} Dianion

Ben M. Elliott and Alexander I. Boldyrev*

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300

Received May 4, 2004

The pyramidal O_4^{2-} dianion is valence isoelectronic to the well-known ClO_3^- and SO_3^{2-} anions, and yet it has not been observed. The synthesis of any molecule containing such a dianion would represent a major breakthrough in making molecules containing more than three covalently bound oxygen atoms. We found that the parent H_2O_4 ozonic acid is unstable in the form of the valence isoelectronic sulfurous acid H_2SO_3. Our quantum chemical probing of the Li_2O_4 ionic salt molecule is inconclusive. However, we found that the specially designed FLi_3O_4 gas phase molecule is a true metastable species and could be considered as the first molecule containing the O_4^{2-} dianion. Our theoretical prediction of the first compound containing the tetraatomic covalently bound O_4^{2-} dianion opens the possibility to even more oxygen rich compounds, which will have a great potential as high density oxygen storage.

Until very recently, only diatomic and triatomic covalently bound nitrogen (N_2 and N_3^-) and oxygen (O_2, O_2^-, O_2^{2-}, O_3, and O_3^-) species were known in an isolated state or as building blocks of ionic solids. There has been remarkable progress made by Christe and co-workers[1,2] who synthesized covalently bound N_5^+ and N_5^- species. This reveals the possibility that oxygen compounds with more than three covalently bound oxygen atoms may also be made. Some covalently bound tetraatomic neutral oxygen species have already been theoretically predicted. Adamantidies et al.[3] theoretically predicted the covalently bound cyclic (D_{2d}) form of O_4. Subsequent theoretical studies[4,5] have also identified a D_{3h} form analogous to SO_3. However, both of these structures are highly unstable and were found to be ~5.3 and ~6.5 eV higher in energy, respectively, than two separate O_2 molecules. None of the predicted covalent O_4 structures have yet been experimentally observed.[6] A large number of matrix isolation works have been devoted to $M^+O_4^-$ (M =

Na, K, Rb, Cs) molecules and the isolated O_4^- anion over the past 25 years (see ref 7 and references therein). On the basis of a good agreement between quantum chemical calculations and observed infrared spectra of the O_4^- anion in Ar matrices, Chertihin and Andrews concluded[7] that O_4^- has a rectangular structure with two short O–O distances (1.267 Å) and two long O–O distances (2.073 Å). Such an anion was found in gas-phase mass spectrometric studies,[8,9] and its photoelectron spectra have been reported by Hanold and Continetti.[10] The O_4^- anion was found to be stable with respect to $O_2 + O_2^-$ by about 0.46 eV.[9] Aquino, Taylor, and Walch[11] have performed the most accurate ab initio calculations on O_4^-. Their results agree well with the infrared spectra of O_4^- in Ar matrices[7] and the photodissociation and photodetachment data.[10] We recently probed[12] the two oxygen dianions, O_4^{2-} and O_5^{2-}, which could be a part of MO_4^- and MO_5^- ions. O_4^{2-} is valence isoelectronic to ClO_3^- and SO_3^{2-}, and O_5^{2-} is valence isoelectronic to ClO_4^- and SO_4^{2-}, which are all well-known anions in solutions and inorganic salts. However, experimental spectra[12] did not produce convincing proof that covalently bound oxygen O_4^{2-} and O_5^{2-} dianions were actually assembled in molecular beams containing MO_4^- and MO_5^- ions. In this Article we present ab initio results that, even though Li_2O_4 and Na_2O_4 parent molecules may not be stable, a specially designed FLi_3O_4 molecule is a stable species, against all gas-phase dissociation channels, containing the O_4^{2-} dianion. This presents a possibility for the synthesis of the first compound with the structural unit composed of four covalently bound oxygen atoms.

We initially studied H_2O_4, ozonic acid, which is valence isoelectronic to sulfurous acid, H_2SO_3. It is interesting to mention that the H_2O_4 acid and K_2O_4 salt were considered first by Mendeleev in his milestone book *The Principles of Chemistry*.[13] We found upon optimization that the sulfurous

* Author to whom correspondence should be addressed. E-mail: boldyrev@cc.usu.edu.

(1) Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2004.

(2) Vij, A.; Pavlovich, J. G.; Wilson, W. W.; Christe, K. O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3051.

(3) Adamantidies, V.; Neisius, D.; Verhaegen, G. G. *Chem. Phys.* **1980**, *48*, 215.

(4) Roeggen, I.; Nilssen, E. W. *Chem. Phys. Lett.* **1989**, *157*, 409.

(5) Hotokka, M.; Pyykko, P. *Chem. Phys. Lett.* **1989**, *157*, 415.

(6) Cacace, F.; Petris, G. de; Troiani, A.; *Angew. Chem., Int. Ed.* **2001**, *40*, 4062.

(7) Chertihin, G. V.; Andrews, L. *J. Chem. Phys.* **1998**, *108*, 6404.

(8) Conway, D. C.; Nesbit, L. E. *J. Chem. Phys.* **1968**, *48*, 509.

(9) K. Hiroaka, *J. Chem. Phys.* **1988**, *89*, 3190.

(10) Hanold, K. A.; Garner, M. C.; Continetti, R. E. *Phys. Rev. Lett.* **1996**, *77*, 3335.

(11) Aquino, A. J. A.; Taylor, P. R.; Walch, S. P. *J. Chem. Phys.* **2001**, *114*, 3010.

(12) Zhai, H.-J.; Yang, X.; Wang, X.-B.; Wang, L. S.; Elliott, B.; Boldyrev, A. I. *J. Am. Chem. Soc.* **2002**, *124*, 6742.

(13) Mendeleeff, D. I. *The Principles of Chemistry*, 2nd Engl. ed.; P. F. Collier & Son: New York; footnote 27, p 212, 1901.

Table 1. Optimized Geometries and Harmonic Frequencies for the O_4^{2-} (C_{3v}, $^1A_1$) Structure

molecular parameter	B3LYP/ 6-311+G*	CASSCF(8,8)/ 6-311+G*	MP2/ 6-311+G*	MP4/ 6-311+G*	CCSD/ 6-311+G*	CCSD(T)/ 6-311+G*
E_{tot}, au	−300.55753	−299.17346	−299.83192	−299.88200	−298.836599	−299.87566
$R(O_1-O_{2,3,4})$, Å	1.465	1.476	1.439	1.466	1.447	1.469
$\angle O_2O_1O_{3,4}$, deg	110.7	110.1	110.2	110.1	110.4	110.3
$\omega_1(a_1)$, cm^{-1}	772 (0.3)	714	823 (1.8)	746	797	756
$\omega_2(a_1)$, cm^{-1}	535 (5.1)	521	589 (6.3)	548	563	531
$\omega_3(e)$, cm^{-1}	634 (155.0)	846	797 (169.2)	640	758	625
$\omega_4(e)$, cm^{-1}	398 (30.8)	446	479 (3.2)	422	454	395
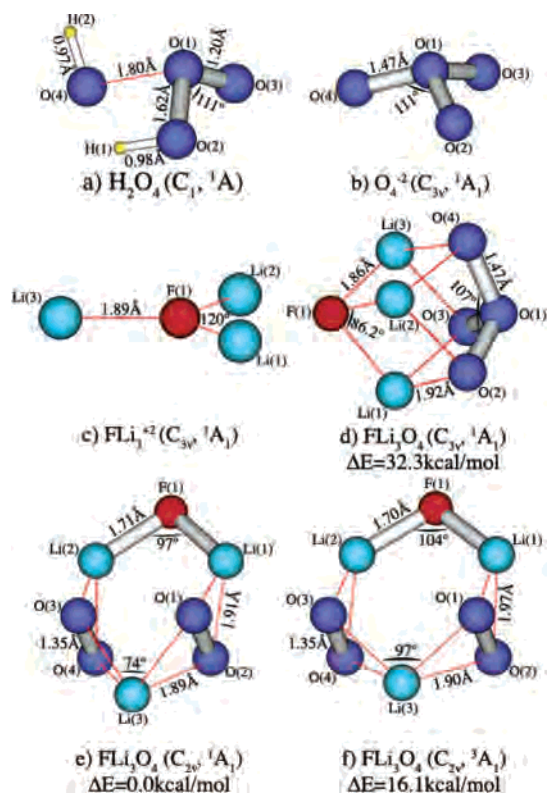
Figure 1. Structures of (a) H_2O_4, (b) O_4^{2-} (c) FLi_3^{2+}, (d) FLi_3O_4 (C_{3v}, $^1A_1$), (e) FLi_3O_4 (C_{2v}, $^1A_1$), and (f) FLi_3O_4 (C_{2v}, $^3A_1$) optimized at the B3LYP/6-311+G* level of theory.

acid like structure is not a minimum on the potential energy surface and the H_2O_4 ozonic acid breaks into two fragments weakly bound to each other (Figure 1a). The sulfurous acid structure of the H_2O_4 ozonic acid may be stabilized in solution, but it would be hard to prove this computationally.

Next we studied an isolated O_4^{2-} dianion. We found that it has a minimum at the pyramidal C_{3v} ($^1A_1$) structure (Figure 1b) similar to its valence isoelectronic relatives, the SO_3^{2-} and ClO_3^- well-characterized anions. The geometric parameters optimized at many levels of theory are presented in Table 1. Optimized $R(O-O)$ and $\angle OOO$ agree very well at all post Hartree−Fock methods. The calculated $R(O-O) = 1.44-1.47$ Å bond length is close the $R(O-O)=1.452$ Å bond length in H_2O_2. The $R(O-O)$ bond in O_4^{2-} is longer than in O_4 (D_{3h}, $^1A_1'$) by about 0.16 Å at the same level of theory. This elongation is somewhat larger than in the $SO_3^{2-}-SO_3$ pair, where it is just 0.12 Å. We believe that this elongation occurs because of the extra charge in the dianion, which increases repulsion in the dianion. In addition, the lone pair at the central atom in the dianion has some residual antibonding character in the O−O bonds. However,

the O_4^{2-} dianion is not stable toward spontaneous electron ejection: "Coulomb explosion". The O_4^{2-} dianion should be dressed in order to be stable. Pyykko and co-workers (see ref 14 and references therein) have shown through numerous examples that the calculated geometric parameters and harmonic frequencies of similar unstable multiply charged anions agree reasonably well with the corresponding anions in the solid state or in solution. This is due to the existence of a local minimum separated from the products by a Coulomb barrier on the electron ejection trajectory.[15−17] Wang and co-workers proved that such metastable multiply charged anions can be experimentally observed and their properties studied.[16] Thus, our proof that the pyramidal O_4^{2-} dianion is a local minimum, while a challenging task, may be tested in the gas phase.

In our previous work[12] we found that, in the presence of one M^+ (M = Li, Na, and K) cation, anionic LiO_4^-, NaO_4^-, and KO_4^- species containing the pyramidal C_{3v} O_4^{2-} dianion correspond to true local minima. The geometrical parameters of the dianion inside of the MO_4^- anions were found to be distorted compared to their isolated parameters, but this distortion was found to be reasonable and in line with the distortion of the isoelectronic and isostructural SO_3^{2-} in $NaSO_3^-$, suggesting that chemical species containing an O_4^{2-} dianion may be viable.

Our current calculations have shown that, in the presence of the second cation, the covalently bound O_4^{2-} dianion may not be stable as a part of the gas-phase M_2O_4 species (M = Li, Na). At some levels of theory (B3LYP/6-311+G*, MP2/6-311+G*, CCSD/6-311+G*) the Li_2O_4 (C_s, $^1A'$) structure containing the pyramidal dianion was found to be a minimum, while at the others (CASSCF(8,8)/6-311+G* and CCSD(T)/6-311+G*) it dissociated without a barrier (see Table S3 in Supporting Information). Thus our results for Li_2O_4 (C_s, $^1A'$) (similar results were obtained for Na_2O_4) are inconclusive. We hope that in the solid state some additional stability may be derived from the Madelung field, which is absent in the gaseous anions and may help to stabilize the M_2O_4 solid salts. This would make such salts at least metastable, similar to $N_5^+SbF_6^-$ and $N_5^+Sb_2F_{11}^-$.[18] However, the metastability of the O_4^{2-} dianion, as a part of the MO_4^- anions,[12] hints that we may be able to stabilize the dianion

(14) Pyykko, P.; Runeberg, N. *J. Mol. Struct. (THEOCHEM)* **1991**, *234*, 279.
(15) Scheller, M. K.; Compton, R. N.; Cederbaum, L. S. *Science* **1995**, *270*, 1160.
(16) Wang, X. B.; Wang, L. S. *Nature* **1999**, *400*, 245.
(17) Simons, J.; Skurski, P.; Barrios, R. *J. Am. Chem. Soc.* **2000**, *122*, 11893.
(18) Vij, A.; Wilson, W. W.; Vij, V.; Rham, F. S.; Sheehy, J. A.; Christe, K. O. *J. Am. Chem. Soc.* **2001**, *123*, 6308.

Table 2. Dissociation Channels and Calculated Energies of Dissociation

	ΔE (kcal/mol)	
dissociation channel	B3LYP/ 6-311+G*	CCSD(T)/ 6-311+G*
FLi$_3$O$_4$ (C_{3v},^{1}A$_1$) → O$_3$ (C_{2v},^{1}A$_1$) + LiF ($C_{\infty v}$,$^1\Sigma$) + Li$_2$O ($D_{\infty h}$,$^1\Sigma_g$)	+105.7(101.9)^a	+106.9
FLi$_3$O$_4$ (C_{3v},^{1}A$_1$) → LiF ($C_{\infty v}$,$^1\Sigma$) + 2LiO (C_{2v},^{2}A$_2$)	+51.9 (47.4)	+63.1
FLi$_3$O$_4$ (C_{3v},^{1}A$_1$) → O$_3$ (C_{2v},^{1}A$_1$) + Li$_3$OF (C_{2v},^{1}A$_1$)^b	+40.9 (39.0)	+39.4
FLi$_3$O$_4$ (C_{3v},^{1}A$_1$) → LiF ($C_{\infty v}$,$^1\Sigma$) + Li$_2$O$_4$ (D_{2h},^{1}A$_g$)^b	+27.1 (24.6)	+26.1
FLi$_3$O$_4$ (C_{3v},^{1}A$_1$) → LiOF (C_s,^{1}A′) + Li$_2$O$_3$ (C_{2v},^{1}A$_1$)^b	+80.7 (77.7)	+86.1
FLi$_3$O$_4$ (C_{3v},^{1}A$_1$) → FLi$_3$O$_3$ (C_s, ^{1}A′)^b + O (^{3}P)	+38.3 (35.1)	+33.3

^{a} Values in parentheses indicate dissociation energies adjusted for zero-point-vibrational energy. ^{b} Optimized structures given in Supporting Information.

inside of some neutral molecule if we find an appropriate doubly charged cation. This dication must have lower electron affinity than two M$^+$ cations.

About twenty years ago[19] we proposed a class of so-called superalkali cations, which have lower electron attachment energies than alkali metal cations. It was confirmed experimentally[20–23] that Li$_2$F$^+$, Li$_3$O$^+$, and other cations with the general formula XM$_{k+1}^+$ (X, halogen, chalcogen, or pnictogen atom; M, alkali metal atom; k is the formal maximal valence of the central atom X) do indeed have very low electron attachment energies (or their neutral parents have very low ionization energies), which are in fact lower than the electron attachment energies of the M$^+$ cation. In the spirit of these findings we thought that we could design a dication, which will have low electron attachment energies for two electrons.

We selected the FLi$_3^{2+}$ dication as a potential countercation with low electron attachment energy for the pyramidal O$_4^{2-}$ dianion. The isolated FLi$_3^{2+}$ dication is a local minimum with a planar triangular structure (Figure 1c). Our calculations proved that the [FLi$_3$]$^{2+}$(O$_4$)$^{2-}$ (C_{3v}, ^{1}A$_1$) salt molecule formed out of the FLi$_3^{2+}$ dication and the O$_4^{2-}$ dianion is a local minimum (Figure 1d and Table S2) and it is stable toward any dissociation channel (Table 2) at all studied theoretical levels (all dissociation energies are positive). A natural population analysis clearly shows that the pyramidal O$_4$ group carries an effective charge close to −2 e (−1.82 e at B3LYP/ 6-311+G*). The optimized geometric parameters of O$_4^{2-}$ in [FLi$_3$]$^{2+}$(O$_4$)$^{2-}$ are not distorted too much as compared to the corresponding parameters of the isolated O$_4^{2-}$ dianion (Tables 1 and S1).

While the [FLi$_3$]$^{2+}$(O$_4$)$^{2-}$ structure is a true minimum, it is not the most stable structure for this stoichiometry.

According to our calculations two other structures of FLi$_3$O$_4$ (C_{2v}, ^{1}A$_1$, Figure 1e, and C_{2v}, ^{3}A$_1$, Figure 1f) were found to be lower in energy. In both structures we found that the O$_4^{2-}$ dianion has a rectangular shape similar to the singly charged O$_4^-$ anion previously characterized experimentally and theoretically.[7–11] Thus our [FLi$_3$]$^{2+}$(O$_4$)$^{2-}$ structure is a metastable one. However, the metastability of the salt molecule does not mean that it cannot be made. The N$_5^+$ cation is a metastable species too, and yet their N$_5^+$SbF$_6^-$ and N$_5^+$Sb$_2$F$_{11}^-$ salts show surprising thermal stability: they decompose at 70 °C.[18]

We can speculate that the synthesis of O$_4^{2-}$ compounds should involve ozone molecules, which are already thermodynamically unstable species storing an appreciable amount of energy. This will help to make the O$_3$ + O^{2-} → O$_4^{2-}$ formation reaction favorable. While the FLi$_3^{2+}$ countercation in the [FLi$_3$]$^{2+}$(O$_4$)$^{2-}$ salt looks very exotic, a crystal salt [Li$_3$O]$^+$(NO$_2$)$^-$ containing a singly charged superalkali cation, Li$_3$O$^+$, has been known for 60 years.[24] We therefore hope that the [FLi$_3$]$^{2+}$(O$_4$)$^{2-}$ salt molecule can be prepared in matrix isolation and probably even synthesized as a solid compound with the [FLi$_3$]$^{2+}$(O$_4$)$^{2-}$ stoichiometry. Also, we believe that other salts containing the O$_4^{2-}$ dianion will be possible too.

In summary, our theoretical prediction[25] of the first compound containing the tetraatomic covalently bound O$_4^{2-}$ dianion opens the possibility to even more oxygen rich compounds, which will have great potential as high-density oxygen storage.

Supporting Information Available: Optimized geometries and harmonic frequencies of all calculated chemical species. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049418E

(19) Gutsev, G. L.; Boldyrev, A. I. *Chem. Phys. Lett.* **1982**, *92*, 262.
(20) Kappes, M. M.; Radi, P.; Schar, M.; Schumacher, E. *Chem. Phys. Lett.* **1985**, *113*, 243.
(21) Vituccio, D. T.; Herrmann, R. F. W.; Glonzka, O.; Ernst W. E. *J. Chem. Phys.* **1997**, *106*, 3865.
(22) Lievens, P.; Thoen, P.; Bouckaert, S.; Boewen, W.; Vanhoutte, F.; Weidele, H.; Silverans, R. E.; Navarro-Vazquez, A.; Schleyer, P. v. R. *J. Chem. Phys.* **1999**, *110*, 10316.
(23) Yokoyama, K.; Haketa, N.; Hashimoto, M.; Furukawa, K.; Tanaka, H.; Kudo, H. *Chem. Phys. Lett.* **2000**, *320*, 645.
(24) Zintl, E.; Morawietz, M. Z. *Anorg. Allg. Chem.* **1938**, *236*, 372.
(25) The initial search for most stable structures has been performed using a hybrid method known in the literature as B3LYP with the polarized split-valence basis sets (6-311+G*). The lowest few structures in every system were then refined using the Møller−Plesset second-order perturbation theory (MP2), complete active space self-consistent method including 8 active electrons and orbitals (CASSCF(8,8)) and coupled-cluster method with single, double, and noniterative triple excitations (CCSD(T)) with the same basis sets. Total energies of these structures were also calculated using the CCSD(T) method and extended 6-311+G(2df) basis sets. Core electrons were frozen in treating the electron correlation at the MP2, CASSCF(8,8), and CCSD(T) levels of theory. All calculations were performed using the Gaussian 98 program.[26]
(26) Frisch, M. J.; Trucks, G. M.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C., Adamo, C.; Clifford, S.; Ocheterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.