

Tetrahedral Sulfur-Based Dianions Stable in the Gas Phase: Application of the Cederbaum–Dreuw Design Principles

Carl Trindle*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904

Ayşe Yumak

Department of Physics, Marmara University, Istanbul, Turkey

Received December 14, 2004

Abstract: Cederbaum and Dreuw [*Chem. Rev.* **2002**, *102*, 181–200] developed an extensive set of examples of small dianions generally stable to autoionization and in some cases to dissociation as well. Their design principles include arranging alternating positive and negative charges in roughly spherical shells, as in the alkaline earth tetrahalides MX_4^{2-} . This principle embraces a series of surprising tetrahedral oxygen-centered dianions of $\text{O}(\text{C}_2)_4$, $\text{O}(\text{BN})_4$, and $\text{O}(\text{BeO})_4$. These systems are stable with respect to autoionization (their vertical ionization energy is positive) but are metastable with respect to dissociation into monoanions. We present a family of dianions with sulfur cores which are stable both with respect to autoionization and dissociation. The shell charge alternation still contributes to stability, but these systems have a positive core in contrast to the oxo systems' negative core.

Introduction

Small molecules with high negative charge may be anticipated to be unstable simply by considering the repulsions among the excess charges. There are a number of departures from this reasonable prediction however. The way toward construction of species with positive second electron affinities (i.e., which form stable dianions) was indicated by a general analysis¹ of MX_k electron affinities, where X may be F, Cl, or CN. Experimentally realized examples include dianions of heavy metal hexahalides MX_6^{2-} (M = Re, Os, Ir, and Pt; X = chloride or bromide),² alkaline earth tetrahalides such as BeF_4^{2-} and congeners,³ and even octahalides of Se and Te.⁴ These and other experimentally characterized systems share a structure Cederbaum and Dreuw⁵ call a “Center-Ligand Sphere” which enjoys a favorable charge arrangement of concentric shells with alternating positive and negative charges.

Other means of stabilization of dianions by charge arrangement have been modeled, including linear forms

XMX and XMXMX . Here X can be assigned a formal charge of -2 , and M a charge of $+2$. SMgSMgS dianion seems to be the smallest such system which might be stable with respect to electron detachment.⁶ Longer dianions such as S_n^{2-} can be stable if n is greater than 7.⁷ In this case charge alternation may not be so important as simple separation in space of the two excess negative charges. Long-chain alkyl dicarboxylates⁸ are examples of systems in which the separation between excess negative charges is of paramount importance. Catenated systems with metal centers such as $\text{M}_2\text{X}_4^{2-}$ enjoy both the advantages of the center-ligand sphere and charge separation modes of stabilization.⁹ Dreuw and Cederbaum^{4,10} have reviewed other dianion-stabilizing structures as well as the possibility of stabilization of a dianion by a very large dipole moment and the extension of the lifetime of a metastable system by the Coulomb barrier. The general guide to design articulated by these authors can be paraphrased: doubly negatively charged species are stable when the charges are separated from one another and each occupy an electrophilic environment, i.e., a region of very positive electrical potential.

* Corresponding author e-mail: cot@virginia.edu.

Table 1. Oxo Systems: Reported and Computed Energy Differences between Tetrahedral Oxo Dianions and Monoanions (Energies in eV)

species	Koopmans ^a	Koopmans ^a	ΔSCF^9	$\Delta\text{R}(\text{O})\text{HF}^a$	ΔMP2^9	ΔDFT^a	ΔCCSD^9
$\text{O}(\text{CC})_4^{2-}$	2.63	1.96	1.66	1.41	2.33	0.73	2.06
$\text{O}(\text{BN})_4^{2-}$	2.77	2.08	2.07	0.58	2.14	0.62	2.03
$\text{O}(\text{BeO})_4^{2-}$		2.96 ^a		0.90		0.74	

^a This work: ΔE refers to monoanions' optimized structures. The DFT functional is B3LYP, basis is always 6-31G(d).

Table 2. Oxo Systems: R(O)HF/6-31G(d) and B3LYP Stability with Respect to Fragmentation^a

species	RHF dianion	fragments	ΔE_{fr}	B3LYP dianion	fragments	ΔE_{fr}
$\text{O}(\text{CC})_4$	-376.8727496	-376.994469	-3.31	-379.1958120	-379.313962	-3.21
$\text{O}(\text{BN})_4$	-391.0549096	-391.148000	-2.53	-393.3837715	-393.432997	-1.34
$\text{O}(\text{BeO})_4$	-433.0303083	-433.008572	+0.59	-435.3891784	-435.348205	+1.11

^a Energies in Hartrees, energy differences in eV.

Table 3. Energies (in eV) Required To Remove an Electron from a SR_4 Dianion

species	Koopmans IE	$\Delta E_{\text{R}(\text{O})\text{HF}}$ (ionization)	ΔE_{B3LYP} (ionization)
$\text{S}(\text{C}_2)_4^{2-}$	2.46	0.618	0.734
$\text{S}(\text{BN})_4^{2-}$	2.56	0.929	0.952
$\text{S}(\text{BeO})_4^{2-}$	3.47	1.143	1.154

The presumptive instability of small dianions can be moderated and even overcome in some cases by substituents that change the electrophilicity of the excess electrons' environment. Stabilization by solvent or counterions is most common; familiar species such as sulfate and carbonate are observed in the gas phase only when solvated.¹¹ Electron-acceptor substituents such as CN and BO can stabilize local negative charges, as in the carboranes¹² for which the substituent is essential to the stability of $\text{B}_6(\text{CN})_6^{2-}$.

Dianions may be unstable with respect either to autoionization or fragmentation into monoanions (or both). Familiar dianions such as CO_3^{2-} ,¹³ SO_4^{2-} ,¹⁴ and PO_4^{3-} ¹⁵ spontaneously lose an electron in the gas phase. Some dianions that appear to be stable with respect to autoionization may still be unstable with respect to dissociation, so to produce separated monoanions. This possibility has sometimes been overlooked in modeling studies, but is the case, for example, for the important class of alkaline earth tetrahalides.¹⁶

A distinct class of stable dianions incorporates the C_2 fragment and isoelectronic variants BN and BeO; e.g., $\text{Be}(\text{C}_2)_n^{2-}$ with $n = 2$ to 7; $\text{Si}(\text{C}_2)_3^{2-}$, $\text{C}(\text{C}_2)_3^{2-}$, and $\text{O}(\text{C}_2)_3^{2-}$ as well as the surprising $\text{O}(\text{C}_2)_4^{2-}$ and a number of isomers.¹⁷ As the latter example proves, the center can be negatively charged if the ligand provides a positively charged shell around that core. Isoelectronic substitution of C_2 by BN and BeO produces stable tetrahedral dianions of form OX_4^{2-} . The four-coordination of oxygen in these systems is remarkable, but one may see that the $\text{O}(\text{BN})_4^{2-}$ system is derivable from the more familiar-seeming $\text{Be}(\text{CN})_4^{2-}$ system by a kind of isoelectronic argument. Here CN is a pseudohalide so the analogy with the established BeF_4^{2-} is plain. To obtain the novel system $\text{O}(\text{BN})_4^{2-}$ from more familiar-seeming $\text{Be}(\text{CN})_4^{2-}$, transfer an electron from each CN to the core atom; then increase its atomic number from 4 (Be) to 8 (O) to compensate for the charge reassignment, and finally alter C to B to balance the loss of negative charge. This example

merely illustrates the chemical argument; $\text{Be}(\text{CN})_4^{2-}$ is not stable with respect to electron loss according to Koopmans' theorem, although the larger $\text{Mg}(\text{CN})_4^{2-}$ and the analogous $\text{Be}(\text{CNO})_4^{2-}$ (which see below) are both stable by this criterion.

Here we characterize the thia analogies to the oxo systems, SX_4^{2-} . The thia systems might be expected to be more stable than the oxo systems since the negative charges are dispersed over a larger volume, particularly when X is larger than the well-known diatomic fragments already mentioned, but the lesser electronegativity of sulfur might oppose that apparent advantage. We also discuss the possibility of stabilizing dianionic species through coordination by Lewis acids BH_3 and BF_3 .

We should make explicit that the species considered here are far from the thermodynamically most stable form of their respective collections of atoms. To take an extreme view, all species discussed in this paper are unstable with respect to their thermodynamic elements. On the other hand, unstable species can be very long-lived if there is no open channel leading toward energetically preferable products, or if (as we suspect is the case for many species considered here) a coulomb or other barrier slows passage and ensures kinetic stability. Each species described here occupies its local minimum on the potential surface, and thus we can refer to its kinetic stability. When we compare two species' energies we can refer to the relative stability of the less energetic species or to the instability or metastability of the more energetic species. A referee has pointed out that C_{3v} -symmetric dianion $\text{OCC}(\text{C}_2)_3$ is much more stable than $\text{O}(\text{C}_2)_4$ dianion. This is an important observation. The rearrangement path deserves careful study. But we can defer that study since it does not bear directly on the question of the kinetic stability of the systems under examination with respect to autoionization or dissociation to monoanionic fragments.

Methods

We have employed the Spartan software suite on PC Windows, SGI IRIX and PQS Linux systems,¹⁸ and the Gaussian 03W¹⁹ software suite on Windows.

It is essential to ascertain that the methods we use are capable of representing the molecules already known to be stable with respect to autoionization and sometimes dis-

Table 4. Thia Systems: R(O)HF/6-31G(d) and B3LYP/6-31G(d) Stability with Respect to Fragmentation^a

species	dianion	fragments	ΔE_f	dianion T_d	fragments	ΔE_f
S(CC) ₄	−699.806949	−699.771653	0.960	−702.418241	−702.403936	0.389
S(BN) ₄	−713.747796	−713.728799	0.517	−716.399604	−716.392214	0.201
S(BeO) ₄	−755.648911	−755.543245	2.875	−758.321603	−758.267402	1.475

^a Energies in Hartrees, energy differences in eV.**Table 5.** Bond Distances (Å) and Mulliken Atomic Charges (millielectrons) for Oxa-Kernel Systems O(XY)₄^{2−}

model	properties				
	R _{OX}	R _{XY}	Q _O	Q _X	Q _Y
O(CC) ₄ ^{2−}					
RHF	1.4584	1.2207	−765	−028	−280
B3LYP	1.5082	1.2524	−530	+075	−443
O(BN) ₄ ^{2−}					
RHF	1.5203	1.2272	−717	+197	−518
B3LYP	1.5271	1.2551	−472	+098	−480
O(BeO) ₄ ^{2−}					
RHF	1.6151	1.3276	−740	+214	−471
B3LYP	1.6111	1.3503	−509	+034	−407

Table 6. Bond Distances (Å) and Mulliken Atomic Charges (millielectrons) for Thia-Kernel Systems S(XY)₄^{2−}

model	properties				
	R _{SX}	R _{XY}	Q _S	Q _X	Q _Y
S(CC) ₄ ^{2−}					
ROHF	1.6266	1.2308	+1163	−545	−246
B3LYP	1.6819	1.2569	+623	−247	−408
S(BN) ₄ ^{2−}					
ROHF	1.8585	1.2305	+252	−008	−495
B3LYP	1.8514	1.2589	+319	−115	−464
S(BeO) ₄ ^{2−}					
ROHF	2.0747	1.3241	−623	+206	−550
B3LYP	2.0473	1.3459	−311	−011	−412

sociation. The simplest diagnosis of stability with respect to autoionization is provided by Koopmans' theorem, by which the energy of the highest occupied MO is an approximation to the ionization energy. A negative HOMO energy suggests that the dianion is stable with respect to loss of an electron. This estimate is a first-order estimate with no recognition of electronic relaxation or correlation and has failed in the important case of sulfate dianion.²⁰ More accurate estimates can be obtained by outer-valence Green's function methods²¹ or by comparison of separate Hartree–Fock or correlation-corrected computations on the dianion and monoanion.

For initial surveys we use uncorrelated methods for which Koopmans' theorem applies. The stability with respect to ionization and dissociation for promising species can also be characterized by energy differences estimated by R(O)HF, MP2, and density functional methods. The adequacy of DFT methods must be established, particularly owing to the self-repulsion in available functionals. Galbraith and Schaefer's assurance²² that this flaw in local density functional methods does not impede the description of strongly bound anions does not guarantee that the methods are suitable for dianions. DFT's failure to describe weak

long-range interactions is not an immediate problem for our purposes, but reminds us that calibration is required. We therefore report DFT characterization of the well-defined stable dianionic species O(CC)₄^{2−}. As Tables 1 and 2 show, our simple methods capture major features of these systems' stability in an approximate way. It appears that compared with reported R(O)HF and correlation-corrected calculations²³ which deploy large flexible basis sets, our R(O)HF/6-31G(d) and especially the B3LYP/6-31G(d) calculations seriously underestimate the stability of the dianions relative to the monoanions (this would be consistent with an overestimate of electron repulsion in the DFT functional). Nonetheless the method affords reliable qualitative diagnoses of stability (i.e., the signs of the energy differences between dianion and monoanion are correct). One detail which complicates these comparisons is that if the tetrahedral structure of the dianion is assumed for the monoanions as well, as must be the case in the report of vertical ionization energies, the monoanion's electronic state is degenerate and must be subject to Jahn–Teller spontaneous distortion. Our energy differences refer to relaxed monoanions. For the most part the optimized geometry of these monoanions is of *C*_{2v} or *C*_s-symmetry with rather modest distortions from *T*_d, but in a few cases the optimization leads to dissociation. O(CC)₄^{1−} dissociates both in ROHF and DFT models. Some details of the optimized monoanions' structures and energies are collected in the Supporting Information.

Frequency calculations in RHF/6-31G(d) and B3LYP/6-31G(d) assure us that the dianions occupy relative minima on their potential surfaces. The detailed pathways and rates of dissociation remain to be addressed.

A Simple Extension

The most elementary extension of this family is to thia-analogues, in which the central kernel is sulfur. All species show stability with respect to autoionization but are now also stable with respect to dissociation into monoanions. Table 3 shows that Koopmans' theorem values are overestimates of the ionization energies compared with the differences in estimates by differences of either uncorrelated or correlated energies for the dianion and the associated monoanion. A part of the difference is that our monoanion structures are relaxed. Table 4 shows that the thia systems are stable with respect to dissociation into monoanionic fragments. The versatility of the sulfur kernel, which can tolerate both positive and negative local charge, is a part of the story of the stability of these systems (see Tables 5 and 6 and discussion below.) We conjecture that the thia-kernel can be the core of a variety of tetracoordinate stable dianions, assuming the ligands are strong π acids, which we explore in the next section or σ pair acceptors which we describe in the final section.

Table 7. Energies (in eV) Required To Remove an Electron from a $M(\text{XYZ})_4$ Dianion and To Dissociate into Two Monoanions XYZ^{-1} and $M(\text{XYZ})_3^{-1}$

species	Koopmans IE	$\Delta E_{\text{R(O)HF}}$ (IE: vert)	$\Delta E_{\text{R(O)HF}}$ (IE: rel)	$\Delta E_{\text{R(O)HF}}$ (diss'n)	ΔE_{B3LYP} (IE: vert)	ΔE_{B3LYP} (IE: rel)	ΔE_{B3LYP} (diss'n)
$\text{Be}(\text{CNO})_4^{2-}$	3.25	2.96	1.86	-0.55	0.83	0.76	-0.84
$\text{Mg}(\text{CNO})_4^{2-}$	3.61	3.34	1.67	0.00	1.20	1.15	-0.23
$\text{O}(\text{BNO})_4^{2-}$	1.77	1.42	diss ^a	-3.95	-0.35	diss ^a	-3.09
$\text{S}(\text{BNO})_4^{2-}$	1.39	1.58	1.13	-0.47	-0.15	diss ^b	-0.82

^a Monoanion dissociates spontaneously to $\text{O}(\text{BNO})_2$ and ONBBNO^{1-} . ^b Monoanion dissociates spontaneously to $\text{S}(\text{BNO})_2$ and ONBBNO^{1-} .

Table 8. Bond Distances (Å) and Mulliken Atomic Charges (millielectrons) for Oxa-Kernel Systems $\text{O}(\text{BNO})_4^{2-}$ and Thia-Kernel Systems $\text{S}(\text{BNO})_4^{2-}$

model	properties						
	R_{OB}	R_{BN}	R_{NO}	Q_{O}	Q_{B}	Q_{N}	Q_{O}
$\text{O}(\text{BNO})_4^{2-}$							
ROHF	1.5110	1.2024	1.2551	-695	+129	+768	-1223
B3LYP	1.5113	1.2024	1.2548	-470	+037	+181	-600
$\text{S}(\text{BNO})_4^{2-}$							
ROHF	1.8292	1.2127	1.2406	+1574	-529	+1027	-1391
B3LYP	1.8120	1.2507	1.2474	+297	-167	+155	-560

Potential New Dianionic Species: $\text{Q}(\text{XYZ})_4^{2-}$

One of the first stable dianions predicted to be stable with respect to autoionization was BeF_4^{2-} . This species falls clearly into the class of center-ligand species in which stabilization arises from concentric shells of alternating charges. Simple chemical arguments suggest that all alkaline earth tetrahalides or pseudohalides would be reasonable candidates as stable dianions. We point out here that Koopmans' theorem has been a reliable guide to stability even if it systematically overestimates ionization energies. According to this criterion, $\text{Be}(\text{CNO})_4^{2-}$ and $\text{Mg}(\text{CNO})_4^{2-}$ are stable dianions. We can conjecture that the family derived from "isoelectronic" $\text{O}(\text{BNO})_4^{2-}$ might also contain stable dianions. Our preliminary calculations of Koopmans' estimate of vertical ionization energies suggest that some of these systems will be resistant to autoionization. (See Tables 7 and 8.) Vertical energy differences between RHF dianions and ROHF monoanions confirm this view. B3LYP calculations again produce smaller values for vertical ionization energy; $\text{O}(\text{BNO})_4^{2-}$ dianion in B3LYP/6-31G(d) is predicted to be unstable with respect to autoionization and also unstable with respect to distortion. B3LYP/6-31G(d) produces small imaginary e , t_1 , and t_2 frequencies. Neither of these instabilities obtains in RHF, but MP2 also maintains that the system is marginally unstable (-0.35 eV) with respect to autoionization. Curiously, an outer valence Greens' function estimate²⁴ of the ionization energy in 6-31G(d) and at the RHF/6-31G(d) optimized geometry is unambiguously positive, ca. 0.90 eV. In view of the fact that the Green's function methods include higher order corrections than MP2, one would receive these estimates with respect. Optimization of $\text{S}(\text{BNO})_4^{2-}$ in B3LYP/6-31G(d) leads to a structure of borderline instability with respect to autoionization; the vertical energy difference between the dianion and the monoanion at the geometry for the dianion optimized in T_d

Table 9. Properties of BX_3 -Stabilized Thia-Kernel Dianions^a

no. of coordinated acids	Koopmans IE	R(O)HF VIE	RHF Ediss	DFT VIE	DFT Ediss
BH_3-Stabilized Thia Dianions					
4	2.15	1.11	1.498	0.755	1.988
3	-0.18	-1.49	2.015	-1.139	2.510
2	-2.43	-3.46	2.628	-2.890	3.176
1	-3.97			-4.380	
BF_3-Stabilized Thia Dianions					
4	4.35	3.039	0.763	+2.601	1.192
3	2.01	0.568	1.477	+0.908	1.742
2	-0.47	-1.743	2.534	-1.152	2.798
1	-3.01			-3.371	

^a All energies in eV. KIE = Koopmans ionization energy, VIE = vertical ionization energy, and Ediss = dissociation energy of the n acid cluster to BX_3 and the $n-1$ acid cluster.

symmetry is -0.35 eV. This system has corresponding e , t_1 , and t_2 modes with real but very small frequencies. MP2/6-31G(d) modeling of $\text{S}(\text{BNO})_4^{2-}$ also produces small imaginary frequencies at the geometry optimized in T_d ; the vertical energy difference between the dianion singlet in MP2 and the monoanion doublet in RMP2 is -0.19 eV, confirming the B3LYP prediction of borderline instability with respect to autoionization. Again, an outer valence Greens' function estimate of the ionization energy in 6-31G(d) and at the RHF/6-31G(d) optimized geometry is unambiguously positive.

The monoanions $\text{O}(\text{BNO})_4^{1-}$ and $\text{S}(\text{BNO})_4^{1-}$ both dissociate spontaneously to dissociation to $\text{O}(\text{BNO})_2 + (\text{BNO})_2^{1-}$ and $\text{S}(\text{BNO})_4 + (\text{BNO})_2^{1-}$. These products are more stable than the parent dianion or the monoanionic fragments. We noticed analogous behavior in the B3LYP treatment of $\text{S}(\text{BN})_4^{1-}$ which produced spontaneous dissociation to $\text{S}(\text{BN})_2$ and $(\text{BN})_2^{1-}$. It does not appear that the BNO-substituted oxygen or sulfur species are promising candidates as long-lived dianions, despite some promising results from Green's function and Koopmans estimates of ionization energies.

We have not established definitely that $\text{S}(\text{BNO})_4^{2-}$ dianion is stable either with respect to autoionization or dissociation (be that kinetic or thermodynamic). However we consider worth exploring a family of other pseudohalogens and isoelectronic variants. Other candidates for stable dianionic species can be derived by isoelectronic substitution. XYZ examples include isoelectronic ligands NCO, BNF, NBF, NNN, and CCF for alkaline earths and BCF, CCO, BeNF, LiOF, and NCN for the chalcogens. We will describe members of this series elsewhere.

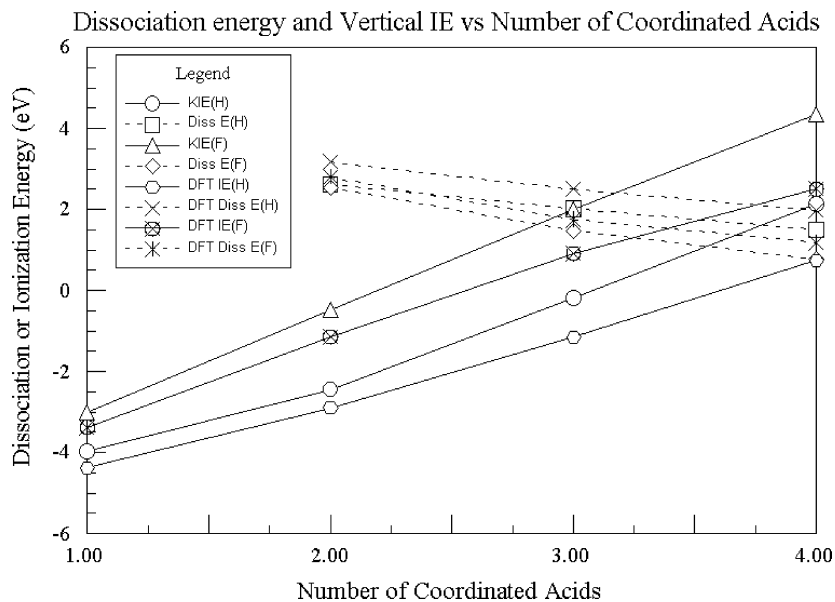


Figure 1. The dependence of vertical ionization energy and dissociation energy on the number of coordinated acids in the system $S(BX_3)_n^{2-}$. Dashed lines refer to dissociation energies, solid lines refer to vertical ionization energies, either Koopmans' estimates (KIE) or energy differences between dianion and monoanion. Positive ionization energies define stable dianions. Parenthesized (F) and (H) refer to acids BF_3 and BH_3 , respectively.

Geometry and Charges of $K(XY...)_4$ Dianions

We have collected geometric parameters of the tetrahedral dianionic species described above in Tables 4 and 5 along with Mulliken charges. For the oxo systems B3LYP displays the familiar bond-length extension relative to RHF except for the central O–Be bonds in $O(BeO)_4^{2-}$, which suggests that correlation is playing a role in that system's binding. Reports⁴ of the structures of the tetrahedral dianions $O(C_2)_4^{2-}$ and $O(BN)_4^{2-}$ show that our B3LYP/6-31G(d) bond lengths agree within 0.01 Å with CCSD calculated values; in the CCSD calculation a Dunning double- ζ basis was employed, augmented by diffuse functions.

Mulliken charges are to be considered only semiquantitative, but values collected here for oxo systems seem to suggest that B3LYP favors a more uniform distribution of charge than does RHF and assigns less negative charge to the central oxygen. Charge alternation is plain, with the central and peripheral atoms unambiguously negative. The intervening atoms are positively charged except for the C in $O(CC)_4^{2-}$, for which the charge alternation is least marked.

In thia systems this central bond shortening in B3LYP is more prominent, and the central sulfur varies strikingly in charge, ranging from very positive in $S(CC)_4^{2-}$ to unambiguously negative in $S(BeO)_4^{2-}$. Again B3LYP predicts more uniform charge distributions than does RHF.

These patterns apply as well to $O(BNO)_4^{2-}$ and $S(BNO)_4^{2-}$; the kernel of the oxo system is negative, while the kernel of the thia system is positive, and the well-established charge alternation is more prominent in the RHF representation than in the B3LYP model.

BH_3 and BF_3 as Dianion-Stabilizing Shells

A remarkable T-symmetric trianion $N(BF_3)_4^{3-}$ has been characterized by computation²⁵ and shown to be stable with respect to autoionization though not with respect to dissocia-

tion. The less dramatic dianionic analogue, $O(BF_3)_4^{2-}$, is likewise stable with respect to ionization according to the Koopmans criterion. The thia cousin $S(BH_3)_4^{2-}$ is stable not only with respect to autoionization (by Koopmans' criterion) but also with respect to dissociation into neutral BH_3 and the $S(BH_3)_3^{2-}$ dianion. (See Table 9.) That product anion $S(BH_3)_3^{2-}$ is unstable with respect to autoionization but would not dissociate into BH_3 and $S(BH_3)_2^{2-}$. This is not due to any intrinsic stability of the dianion but reflects the penalty paid in dissociation to an even smaller product dianion; the latter dianion is still more unstable with respect to autoionization according to Koopmans' theorem. Probably another decomposition channel involving the $S(BH_3)_3^{1-}$ monoanion opens. We have not pursued this possibility.

As one expects, BF_3 produces more stable thia dianions than does BH_3 ; both $S(BF_3)_4^{2-}$ dianion and $S(BF_3)_3^{2-}$ dianion are stable with respect to autoionization according to Koopmans' theorem and do not dissociate into closed shell products including a less stable (because less completely coordinated) dianion. Figure 1 provides a graphic summary of this behavior.

As the degree of coordination increases and the excess negative charge is more effectively stabilized the BH and BF distances shorten. The SB distances in $S(BF_3)_n^{2-}$ increases as the bulkier BF_3 ligands crowd the dianion's central sulfur. Sulfur donates more negative charge to ligands as their number increases. Structural details are provided in Supporting Information.

Conclusions

The design principles guiding Dreuw and Cederbaum's construction of "center-ligand" dianions stable with respect to autoionization and dissociation are easily extended to systems with sulfur cores and pseudohalogen π -acid and BX_3

Lewis acid ligands. The thia family contains many species that are likely to be stable, even when the oxo analogue is not.

Acknowledgment. This work was supported by the University of Marmara, Istanbul, The Turkepetrol Foundation, and the University of Virginia. We thank the Body Foundation for equipment, travel support, and general encouragement and wish to acknowledge the key role in making this collaboration possible of Professor Dr. Zikri Altun of the Physics Department, the University of Marmara, Istanbul.

Supporting Information Available: Tables S1–S17. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Gutsev, G. L.; Boldyrev, A. I. *J. Phys. Chem.* **1990**, *94*, 2256.
- (2) Wang, X.-B.; Wang, L.-S. *J. Chem. Phys.* **1999**, *111*, 4497.
- (3) Weikert, H. G.; Cederbaum, L. S.; Tarantelli, F.; Boldyrev, A. I. *Z. Phys. D-Atoms, Molecules, Clusters* **1991**, *18*, 229. Weikert, H. G.; Cederbaum, L. S. *J. Chem. Phys.* **1993**, *99*, 8877. Observation reported by Middleton, R.; Klein, J. *Phys. Rev. A* **1999**, *60*, 3515.
- (4) Boldyrev, A. I.; Simons, J. *J. Chem. Phys.* **1992**, *97*, 2826.
- (5) Cederbaum, L. S.; Dreuw, A. *Chem. Rev.* **2002**, *102*, 181–200.
- (6) Boldyrev, A. I.; Simons, J. *J. Chem. Phys.* **1993**, *98*, 4745.
- (7) Berghof, V.; Sommerfeld, T.; Cederbaum, L. S. *J. Phys. Chem. A* **1998**, *102*, 5100.
- (8) Maas, W. P. M.; Nibbering, N. M. M. *Int. J. Mass Spec. Ion Proc.* **1989**, *88*, 257.
- (9) Scheller, M. K.; Cederbaum, L. S. *Chem. Phys. Lett.* **1993**, *216*, 441. Scheller, M. K.; Cederbaum, L. S. *J. Chem. Phys.* **1994**, *100*, 8934. Scheller, M. K.; Cederbaum, L. S. *J. Chem. Phys.* **1994**, *100*, 894. Scheller, M. K.; Cederbaum, L. S. *J. Chem. Phys.* **1994**, *101*, 3962.
- (10) Dreuw, A.; Cederbaum, L. S. In *Theoretical Prospect of Negative Ions*; Kalcher, J., Ed.; Research Signpost: Trivandrum, Kerala, India, 2002; pp 1–28.
- (11) Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **1994**, *116*, 10761.
- (12) Zint, N.; Dreuw, A.; Cederbaum, L. S. *J. Am. Chem. Soc.* **2002**, *124*, 4910.
- (13) Sommerfeld, T. *J. Phys. Chem. A* **2000**, *104*, 8806.
- (14) Janoschek, R. Z. *Anorg. Allg. Chem.* **1992**, *616*, 101.
- (15) Boldyrev, A. I.; Simons, J. *J. Phys. Chem.* **1994**, *98*, 2298.
- (16) Weikert, H. G.; Cederbaum, L. S. *J. Chem. Phys.* **1993**, *99*, 8877.
- (17) Dreuw, A.; Schweinsberg, H.; Cederbaum, L. S. *J. Phys. Chem. A* **2002**, *106*, 1406.
- (18) Spartan 2002, Wavefunction, Inc., Irvine, CA. See methods described in the following: Kong, J.; White, C. A.; Krylov, A. I.; Sherrill, C. D.; Adamson, R. D.; Furlani, T. R.; Lee, M. S.; Lee, A. M.; Gwaltney, S. R.; Adams, T. R.; Ochsenfeld, C.; Gilbert, A. T. B.; Kedziora, G. S.; Rassellov, V. A.; Maurice, D. R.; Nair, N.; Shao, Y.; Besley, N. A.; Maslen, P. A.; Dombrowski, J. P.; Daschel, H.; Zhang, W.; Korambath, P. P.; Baker, J.; Boyd, E. F. C.; Van Voorhis, T.; Oumi, M.; Hirata, S.; Hsu, C.-P.; Ishikawa, N.; Florian, J.; Warshel, A.; Johnson, B. G.; Gill, P. M. W.; Head-Gordon, M.; Pople, J. A. *J. Comput. Chem.* **2000**, *21*, 1532.
- (19) Gaussian 03, Revision B.2, Frisch, M. G.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 2003.
- (20) Boldyrev, A.; Simons, J. *J. Phys. Chem.* **1994**, *98*, 2298.
- (21) These agree closely with the vertical ionization energies estimated by MP2 according to Dreuw, A.; Sommerfeld, T.; Cederbaum, L. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1889. Dreuw, A.; Sommerfeld, T.; Cederbaum, L. S. *J. Chem. Phys.* **1998**, *109*, 2727.
- (22) Galbraith, J. M.; Schaefer, H. F. *J. Chem. Phys.* **1996**, *105*, 862; see also Tschumper, G. S.; Schaefer, H. F. *J. Chem. Phys.* **1997**, *107*, 2529.
- (23) Dreuw, A.; Schweinsberg, H.; Cederbaum, L. *J. Phys. Chem. A* **2002**, *106*, 1406.
- (24) Cederbaum, L. S.; Domcke, W. *Adv. Chem. Phys.* **1977**, *36*, 205. Implementation in Gaussian according to Zakrzewski, V. G.; Ortiz, J. V. *Int. J. Quantum Chem.* **1995**, *53*, 583. Zakrzewski, V. G.; Ortiz, J. V. *J. Chem. Phys.* **1995**, *102*, 294. Dolgounitcheva, O.; Zakrzewski, V. G.; Ortiz, J. V. *J. Chem. Phys.* **1998**, *109*, 87.
- (25) Dreuw, A.; Cederbaum, L. S. *J. Phys. Chem. A* **2001**, *105*, 10577.

CT049854Q