

Is TeF_8^{2-} the MX_n^{2-} dianion with the largest electron detachment energy (5 eV)

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(Received 16 March 1992; accepted 1 May 1992)

I. INTRODUCTION

Stable small doubly charged anions with the general formula MF_n^{2-} such as BeF_4^{2-} , MgF_4^{2-} , SiF_6^{2-} , etc., have been predicted by *ab initio*^{1,2} methods to be electronically stable and geometrically metastable species (i.e., not thermodynamically stable to loss of F^- , but local minima on the dissociation pathways with quite high potential barriers to dissociation). The bonding in these species can be qualitatively accounted for by allowing the two "extra" electrons to expand the valence number of the central atom and subsequently distributing, through polar bond formation, these two excess charges over n (> 2) equivalent ligands.

The reduced Coulombic repulsion resulting from delocalizing 2 charges over n symmetry-equivalent sites is a key ingredient in the local stability of these dianions. From earlier work, it is known that the first electron detachment energy (DE) is smaller for BeF_4^{2-} than for SiF_6^{2-} and smaller for BeF_4^{2-} than for MgF_4^{2-} . The higher DE of SiF_6^{2-} (compared to BeF_4^{2-}) is likely due to delocalization of the two "extra" electrons over six rather than four fluorine atoms. MgF_4^{2-} has a larger DE than BeF_4^{2-} because of the larger fluorine-fluorine distances and hence the lower Coulomb repulsion in the Mg compound (for details, see Refs. 3–5).

Recently, new salts $[\text{N}(\text{Me})_4^+]_2\text{TeF}_8^{2-}$ involving the dianion studied here have been prepared.⁶ For this TeF_8^{2-} dianion, a square antiprism geometry (of D_{4d} symmetry) was proposed on the basis of the structure found for the isoelectronic IF_8^- anion using IR and Raman spectra. The TeF_8^{2-} dianion is found to have no central-atom valence lone pair electrons although it has a closed-shell electronic structure. Therefore, delocalization of the two "extra" electrons over all eight fluorine ligands is expected.

Delocalization through this number of electronegative ligands should maximize the stability of the doubly charged anion with respect to loss of an electron. Because eight is the largest number of ligands known for such MX_n molecules, the MF_8^{2-} dianions should have the largest first DEs among all MX_n^{2-} species. Furthermore, due to the large M–F and therefore large F–F distances in TeF_8^{2-} compared, for example, to SeF_8^{2-} , the dianion studied here is expected to have the largest first DE of all such species.

The kinetic stabilities of several MF_n^{2-} dianions are discussed in Refs. 1 and 2 in terms of potential energy curves that have two parts. At long F^- to MF_{n-1}^- distances, the curve is repulsive due to the strong Coulombic repulsions between the two unit negative charges. At distances where valence interactions come into play, the curve becomes attractive due to charge transfer from F^- to

MX_{n-1}^- and redistribution of the excess electron density through the n F atoms. According to this model, all MF_k^{2-} dianions could have local minima at highly symmetric structures if they are stable to loss of extra electrons at such geometries and if the size of the central atom is adequate to overcome steric "crowding" of the n ligands.

II. THIS WORK

In this work, we optimized the geometries of the TeF_8^{2-} , TeCl_8^{2-} , and SeF_8^{2-} dianions at the self-consistent-field (SCF) level using double zeta basis sets, and examined the stabilities of these dianions to loss of extra electrons. Electron correlation has been shown to be unimportant^{1,2} in geometry optimization of this class of dianions. More specifically, we used Dunning's valence double-zeta basis set (9s5p/3s2p) for the fluorine atoms⁷ and the Hay–Wadt pseudopotential and valence 2s2p basis set for the tellurium, selenium, and chlorine atoms⁸ (this defines our "DZ" basis set). Optimized structures were also calculated with a DZ-diff (p)F basis (the diffuse functions for fluorine were taken from Ref. 9). Some calculations were carried out using our Utah MESS-KIT modular electronic codes.¹⁰ The vibrational frequencies as well as final optimized geometries we obtained using the Los Alamos pseudopotential and valence double-zeta basis sets (denoted LANL1DZ) within the GAUSSIAN-90 program suite.¹¹

III. SUMMARY OF FINDINGS

At the SCF/DZ level, we find that an optimized square antiprism structure having $R(\text{Te}-\text{F}) = 1.98 \text{ \AA}$ and a F–Te–F angle of 73.0° is 37.6 kcal/mol [36.9 kcal/mol at the HF/DZ=diff, (p)F level] lower in energy than the optimized cube structure (having $R(\text{Te}-\text{F}) = 2.00 \text{ \AA}$). Therefore our calculations support the assumption made in Ref. 6 that the square antiprism structure is the most stable configuration of the TeF_8^{2-} dianion. In addition, as indicated in Table I where the vibrational frequencies are shown, all frequencies of TeF_8^{2-} are real; hence this structure is a local minimum on the ground-state potential surface. In contrast, the cubic structure of TeF_8^{2-} has two imaginary vibrational frequencies and thus is not a local minimum. Our calculated Te–F bond length for the square antiprism structure is 0.14 \AA longer than the bond length in the neutral TeF_6 molecule. This bond length difference is a typical and not unexpected result for dianions (see, e.g., Refs. 1 and 2).

The optimized antiprism structures of SeF_8^{2-} [$R(\text{Se}-\text{F}) = 1.92 \text{ \AA}$ and a F–Se–F angle of 72.8°] and TeCl_8^{2-} [$R(\text{Te}-\text{Cl}) = 2.71 \text{ \AA}$ and a Cl–Te–Cl angle of 73.2°] are

TABLE I. Calculated (SCF/LANL1DZ) and experimental vibrational frequencies (cm^{-1}) on D_{4h} TeF_8^{2-} , TeCl_8^{2-} , and SeF_8^{2-} .

Mode	TeF_8^{2-}		SeF_8^{2-}	TeCl_8^{2-}
	Calculated ^a	Experimental ^b	Calculated	Calculated
$\nu_1(a_1)$	599.2 (0.0)	582	572.6 (0.0)	248.1 (0.0)
$\nu_2(a_1)$	405.1 (0.0)	408	438.4 (0.0)	188.2 (0.0)
$\nu_3(b_1)$	206.6 (0.0)		227.9 (0.0)	103.0 (0.0)
$\nu_4(b_2)$	602.4 (183.3)	558	561.1 (284.9)	223.6 (111.9)
$\nu_5(b_2)$	409.7 (188.2)	375	466.6 (130.7)	199.4 (38.2)
$\nu_6(e_1)$	601.0 (197.5)		556.0 (257.5)	220.2 (58.0)
$\nu_7(e_1)$	422.7 (173.8)	265?	478.8 (166.0)	200.0 (92.4)
$\nu_8(e_1)$	332.3 (2.8)		362.9 (0.1)	158.0 (0.4)
$\nu_9(e_2)$	486.7 (0.0)	490	516.4 (0.0)	223.2 (0.0)
$\nu_{10}(e_2)$	446.9 (0.0)	388	381.1 (0.0)	158.0 (0.0)
$\nu_{11}(e_2)$	112.2 (0.0)		97.7 (0.0)	37.9 (0.0)
$\nu_{12}(e_3)$	519.2 (0.0)		505.0 (0.0)	220.5 (0.0)
$\nu_{13}(e_3)$	397.8 (0.0)	325	395.4 (0.0)	167.7 (0.0)
ZPE ^c	12.7		12.7	5.3

^aIR intensities (KM/mol) are given in parentheses.

^bData from Ref. 6.

^cZero-point energy corrections are given in kcal/mol.

also lower in energy than the corresponding cubic structures [$R(\text{Se}-\text{F})=1.96 \text{ \AA}$ for SeF_8^{2-} and $R(\text{Te}-\text{Cl})=2.75 \text{ \AA}$ for TeCl_8^{2-}] by 40.4 kcal/mol and 31.0 kcal/mol at the HF/DZ level, respectively. Both antiprism structures are local minima with no imaginary vibrational frequencies (see Table I).

The vibrational frequencies and IR intensities calculated for the most stable structures of TeF_8^{2-} , TeCl_8^{2-} , and SeF_8^{2-} at the SCF level are listed in Table I, where the available experimental frequencies are also given. In Table II, analogous data is given for the TeF_7^- , TeCl_7^- , and SeF_7^- anions derived by loss of a single F^- anion from the corresponding parents. These seven-coordinate anions are minima on their respective surfaces and have five equatorial and two axial M-F bonds. The latter species plus a single F^- ion lie 43, 69, and 75 kcal/mol below TeF_8^{2-} , TeCl_8^{2-} , and SeF_8^{2-} , respectively [at the SCF/DZ+diff(p)F+ZPE level]. The geometries of the seven-coordinate species are as follows.

(a) TeF_7^- has axial Te-F bond lengths of 1.86 \AA and equatorial lengths of 1.92 \AA .

(b) SeF_7^- has axial Se-F bond lengths of 1.76 \AA and equatorial lengths of 1.85 \AA .

(c) TeCl_7^- has axial Te-Cl bond lengths of 2.47 \AA and equatorial lengths of 2.63 \AA .

The Koopman's theorem first DE of TeF_8^{2-} is very large (6.51 eV at the DZ and 6.72 eV at the DZ+diff(p)F basis sets, respectively). Electron correlation and electron relaxation corrections to the Koopmans' DEs of BeF_4^{2-} and MgF_4^{2-} , calculated by Green's function methods, are negative (i.e., meaning the predicted DE is smaller than the Koopman's estimate) and of magnitude 1.5–1.6 eV.^{1,2} For geometrically larger and more charge-delocalized systems such as TeF_8^{2-} these corrections should be even smaller in magnitude (because the excess charges are distributed over a large space). Therefore, 1.6 eV can be taken as an upper limit to the magnitude of the relaxation and

TABLE II. Calculated (SCF/LANL1DZ) and experimental vibrational frequencies (cm^{-1}) of D_{5h} TeF_7^- , TeCl_7^- , and SeF_7^- .

Mode	TeF_7^-		SeF_7^-	TeCl_7^-
	Calculated ^a	Experimental ^b	Calculated	Calculated
$\nu_1(a_1')$	651.2 (0.0)	640	649.7 (0.0)	294.8 (0.0)
$\nu_2(a_1')$	626.7 (0.0)	597	613.5 (0.0)	268.9 (0.0)
$\nu_3(a_2'')$	725.7 (143.6)	695	767.2 (206.9)	334.5 (97.5)
$\nu_4(a_2'')$	343.1 (120.9)	332	395.8 (84.5)	164.4 (18.2)
$\nu_5(e_1')$	665.0 (146.9)	625	637.5 (200.7)	259.5 (64.4)
$\nu_6(e_1')$	413.7 (159.5)	384	480.7 (173.0)	205.9 (73.6)
$\nu_7(e_2')$	241.2 (8.1)		276.4 (1.9)	117.2 (0.2)
$\nu_8(e_1'')$	298.6 (0.0)	299	340.3 (0.0)	142.6 (0.0)
$\nu_9(e_2')$	562.4 (0.0)	458	599.2 (0.0)	267.7 (0.0)
$\nu_{10}(e_2')$	491.5 (0.0)	326	457.5 (0.0)	186.1 (0.0)
$\nu_{11}(e_2')$	26.2 (0.0)		70.1 (0.0)	32.2 (0.0)
ZPE ^c	11.1		11.6	5.0

^aIR intensities (KM/mol) are given in parentheses.

^bData from Ref. 6.

^cZero-point energy corrections are given in kcal/mol.

correlation correction for TeF_8^{2-} . If we then reduce our Koopman's DE of TeF_8^{2-} by 1.6 eV, the resulting DE is 4.9–5.1 eV, *the largest first DE of any doubly charged anion* MF_n^{2-} . The corresponding electron affinity of the TeF_8^{2-} anion is thus also very large, as a result of which this species can be termed a superhalogen^{3,4} (its electron affinity is higher than the atomic electron affinities of halogen atoms). The Koopmans' DEs of SeF_8^{2-} and TeCl_8^{2-} are also very high: 5.5 eV and 3.9 eV at the SCF/DZ [5.7 eV and 4.3 eV at the SCF/DZ+diff(p)F] levels, respectively, but they are smaller than for TeF_8^{2-} . The corresponding values for TeF_7^- , SeF_7^- , and TeCl_7^- are 11.9, 11.2, and 8.0 eV at the Koopman's theorem, SCF/DZ+diff(p)F, Cl, level.

ACKNOWLEDGMENTS

This work was supported in part by the Office of Naval Research and by NSF Grant No. CHE9116286. We also thank the Utah Supercomputer Institute for staff and computer resources.

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