

Theoretical Studies on MXO_4 ($M=\text{Li, Na, K}$ and $X=\text{F, Cl, Br, I}$) Salt Ion Pairs

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The series of alkali metal perhalogenates, MXO_4 ($M=\text{Li, Na, K}$ and $X=\text{F, Cl, Br, I}$) were theoretically studied with the help of MP2 methods. Bidentate as well as tridentate structures were found to be stable minima. The bidentate structures are becoming preferred as the size of halogen increases and as the size of metal decreases. Geometrically, the M-O and M-X distances of both bidentate and tridentate structures, increase with the size of metal. Generally, the M-O₁ distances of tridentate forms are longer than the corresponding distances of bidentate forms, while the M-X distances of tridentate forms show the opposite trend. Similarly, the X-O bonds increase with the size of halogens except MFO_4 pairs, where the X-O bonds are unusually long due to the enhanced oxygen-oxygen repulsions. In short, the relative energetics as well as the geometrical parameters are found to be strongly dependent on halogen and metal elements.

Key Words: Bidentate, Tridentate, Ion pair, Alkali metal perhalogenate

Introduction

The structures and bonding characteristics of metal-anion ion pairs have been a major focus of research,¹⁻³ since contact ion pairs are important in electrolyte solutions and play significant roles in determining the stability, structure, and function of biomolecules and many other systems.⁴ Experimental data for ion pairs such as metal nitrates,⁵ sulfates,^{3,6} chlorates,^{7,8} chlorite^{1d} and perchlorates^{9,10} has been derived primarily from infrared absorption and/or Raman spectroscopic investigations, and the information extracted from such studies includes preferred coordination mode(s) by the respective anions (i.e., bidentate *versus* tridentate).

NaClO_4 is one of the most frequently used salt due to its high solubility^{2c,11-14} and is one of the least associating anions in aqueous solution which requires solvents of much lower dielectric permittivity than that of water to induce formation of contact ion-pairs and aggregates.^{9,10} Perchlorate ClO_4^- is one of the strong destabilizing inorganic anions in the Hofmeister series,¹⁵ and well-known thyroid disruptor.¹⁶ Chabanel *et al.*⁹ pointed out that the ClO_4^- groups prefer C_{3v} symmetry in LiClO_4 and at most C_{2v} symmetry in NaClO_4 . Mitterböck *et al.*¹⁰ studied aqueous D_2O solutions of lithium and sodium perchlorate by FTIR in their glassy states and found the evidence for strongly increasing contact-ion pairing in going from ambient temperature to the glassy state especially in the case of sodium perchlorate. They also reported that the spectral features of contact-ion paired perchlorate are consistent with at most C_{2v} symmetry with bidentate conformation.

In spite of their importance, the basic structures and conformations of alkali metal-perchlorates were not thoroughly understood. In this paper, comprehensive *ab initio* investigations of MXO_4 ($M=\text{Li, Na, K}$ and $X=\text{F, Cl, Br, I}$) were performed to obtain structural and energetic features of these contact ion pairs.

Computational Details

The second order Møller-Plesset Perturbation¹⁷ theory (MP2) level in conjunction with aug-cc-pVTZ and 6-311G (d) basis sets was used throughout this study. It is noted that the aug-cc-pVTZ basis set does not have basis set definitions for K and I elements. All calculations reported here were performed with the general atomic and molecular electronic structure system (GAMESS) electronic structure program.¹⁸

Results and Discussion

Relative energies of MXO_4 . Full geometry optimizations were performed with MP2 methods in combination with aug-cc-pVTZ and 6-311G(d) basis sets. Since there are no aug-cc-pVTZ basis set definitions for K and I, the corresponding calculations of contact ion pairs of LiIO_4 , NaIO_4 , KFO_4 , KClO_4 , KBrO_4 and KIO_4 were not performed with aug-cc-pVTZ basis sets. Our calculations yielded both bidentate and tridentate isomeric

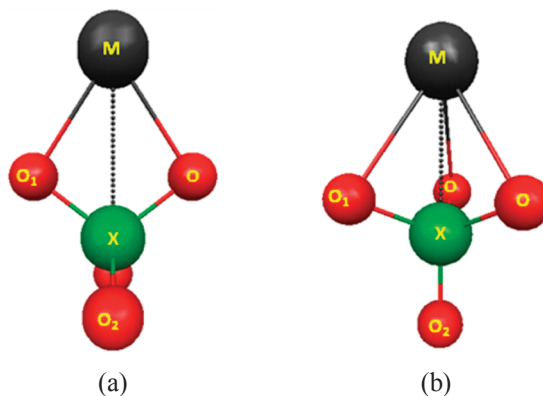


Figure 1. MXO_4 salt ion pairs of (a) bidentate and (b) tridentate structures where $M=\text{Li, Na, K}$ and $X=\text{F, Cl, Br, I}$.

Table 1. The relative energies (in kcal/mol) of the tridentate structures with respect to bidentate forms of MXO_4 (where $\text{M}=\text{Li, Na, K}$ & $\text{X}=\text{F, Cl, Br, I}$) ion pairs at MP2 level with different basis sets. See the Figure 1 for the corresponding structures.

Species		ΔE (kcal/mol)	
M	X	MP2/6-311G(d)	MP2/aug-cc-pVTZ
Li	F	-5.0	-4.2
	Cl	8.6	6.9
	Br	11.7	9.9
	I	16.7	-
Na	F	-8.0	-6.2
	Cl	1.9	1.4
	Br	4.1	3.4
	I	8.1	-
K	F	-8.7	-
	Cl	-0.1	-
	Br	1.2	-
	I	-	-

forms of MXO_4 series except the KIO_4 in which only the bidentate form was found to be stable minimum. Figure 1(a) and 1(b) correspond to the bidentate and tridentate structures, respectively. The calculated relative energies between the two forms are presented in Table 1. The oxygens are tetrahedrally bonded to the halogen, X. However, due to the steric hindrance between metal and oxygens, the oxygen conformations of tridentate structures become more like pyramidal form. It is seen that the relative energies as obtained with the two different basis sets agree with each other within 2 kcal/mol. Therefore, the diffuse functions are not essential. So the results with the 6-311G(d) basis set were mostly referred for the rest of discussions.

The tridentate forms of MFO_4 ($\text{M}=\text{Li, Na, K}$) series are more stable than the corresponding bidentate ones by 5.0, 8.0 and 8.7 kcal/mol for Li, Na and K, respectively. And in the case of KClO_4 , the bidentate and tridentate forms are nearly isoenergetic with the tridentate being 0.1 kcal/mol more stable. Other than these cases, bidentate structures are predicted to be more stable. It is noted that larger metal cations prefer the tridentate forms. This cation size effect can be attributed to the fact that larger cations can better accommodate the crowded oxygens of tridentate. The same trends of cation size effect can be seen in MClO_4 ($\text{M}=\text{Li, Na, K}$), MBrO_4 ($\text{M}=\text{Li, Na, K}$), and MIO_4 ($\text{M}=\text{Li, Na}$) series. The opposite relative stability trend is seen in LiXO_4 ($\text{X}=\text{F, Cl, Br, I}$) series. As the size of halogen increases, the tridentate forms gradually become less stable than the bidentate ones. These halogen size effects may be due to the increased strains of M-O-X angles in the pyramidal tridentate oxygen conformations with larger halogen. The same halogen size effects can be generally seen in MClO_4 and MBrO_4 as well as MIO_4 series. Therefore, with the same counter metal ion, the bidentate structure is becoming more stable with the size of halogens. In short, the relative energies between the bidentate and tridentate structures of metal-perhalogenates strongly depend on the relative size of metal and halogen elements. The bidentate structures are preferred as the size of halogen increases and as the size of metal decreases.

Table 2. The bond lengths (Å) and angles ($^\circ$) of bidentate MXO_4 (where $\text{M}=\text{Li, Na, K}$ & $\text{X}=\text{F, Cl, Br, I}$) salt ion pairs as obtained with MP2/6-311G(d) level. The corresponding structures are presented in the Figure 1(a).

Species		Bond lengths (Å)				Angle ($^\circ$)
M	X	M-O ₁	M-X	X-O ₁	X-O ₂	$\angle \text{M-O}_1\text{-X}$
Li	F	1.857	2.290	1.538	1.868	84.28
	Cl	1.882	2.424	1.520	1.441	90.23
	Br	1.909	2.520	1.661	1.590	89.50
	I	1.933	2.659	1.841	1.780	89.54
Na	F	2.214	2.663	1.547	1.808	88.31
	Cl	2.243	2.820	1.507	1.449	95.53
	Br	2.305	2.940	1.654	1.599	94.45
	I	2.289	3.025	1.831	1.784	93.86
K	F	2.523	3.054	1.608	1.705	92.67
	Cl	2.544	3.164	1.497	1.450	99.81
	Br	2.556	3.229	1.640	1.599	98.29
	I	2.574	3.348	1.820	1.786	97.79

Table 3. The bond lengths (Å) and angles ($^\circ$) of tridentate MXO_4 (where $\text{M}=\text{Li, Na, K}$ & $\text{X}=\text{F, Cl, Br, I}$) salt ion pairs as obtained with MP2/6-311G(d) level. The corresponding structures are presented in the Figure 1(b).

Species		Bond lengths (Å)				Angle ($^\circ$)
M	X	M-O ₁	M-X	X-O ₁	X-O ₂	$\angle \text{M-O}_1\text{-X}$
Li	F	1.983	2.047	1.602	2.049	68.67
	Cl	2.140	2.244	1.493	1.433	73.88
	Br	2.212	2.343	1.636	1.584	73.30
	I	2.294	2.491	1.820	1.776	73.51
Na	F	2.313	2.379	1.595	1.967	72.37
	Cl	2.445	2.591	1.489	1.441	78.21
	Br	2.553	2.718	1.636	1.592	77.49
	I	2.593	2.810	1.817	1.780	76.94
K	F	2.619	2.702	1.601	1.927	75.36
	Cl	2.719	2.905	1.484	1.442	81.76
	Br	2.775	2.978	1.625	1.596	80.32
	I	-	-	-	-	-

Structures of MXO_4 . The geometries of the bidentate and tridentate isomeric forms as obtained with MP2/6-311G(d) theory are presented in Table 2 and 3, respectively. The corresponding geometric parameters are also plotted in Figure 2 and 3, respectively. It is observed that as the metal size increases, the M-O₁ and M-X distances of both bidentate (Fig. 2(a) and 2(b)) and tridentate (Fig. 2(c) and 2(d)) forms linearly increases. In addition, the M-O₁ bonds of tridentate forms are generally longer than the corresponding distances of bidentate forms. This M-O₁ bond length trend is due to the increased steric hindrance of extra oxygen in between metal and halogen of tridentate form. On the other hand, the M-X distances of tridentate forms are shorter than the corresponding distances of bidentate forms. This M-X distance trends are not due to the stronger interactions between metal and halogen in tridentate form. In fact, the interaction between metal and halogen is negligibly weak. Therefore,

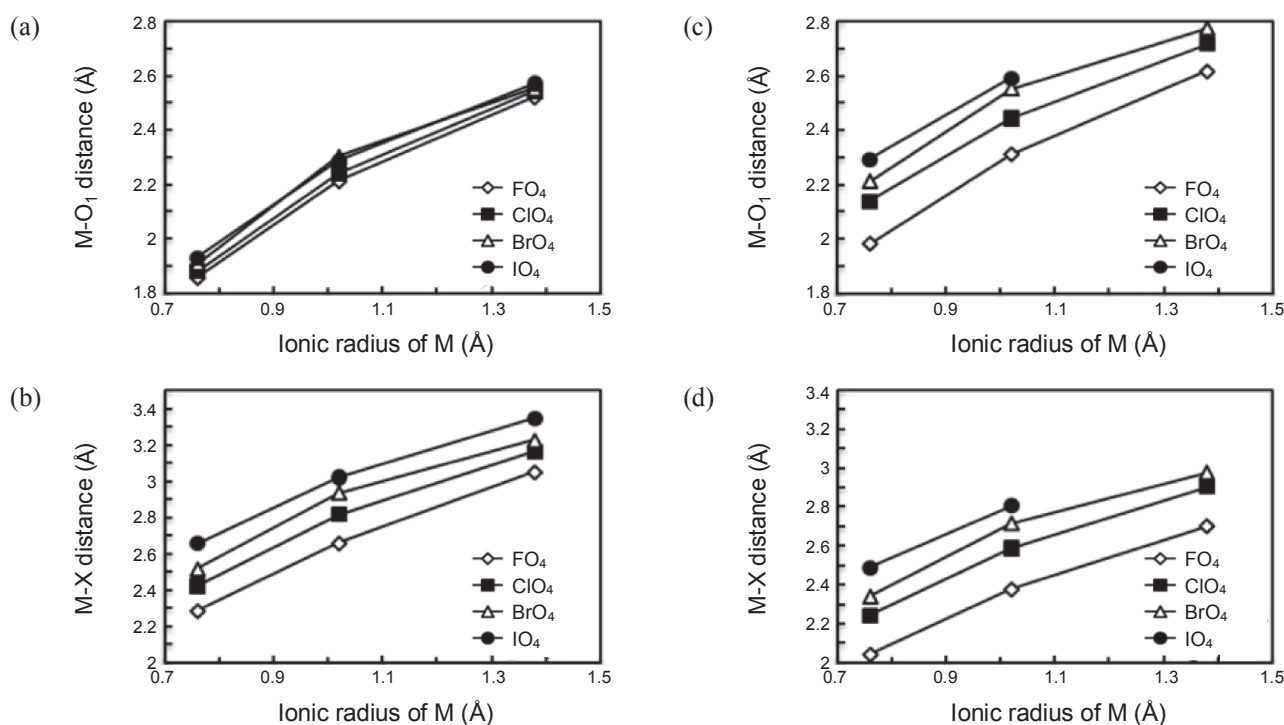


Figure 2. (a) The $M-O_1$ (b) and the $M-X$ distances of bidentate form. (c) The $M-O_1$ (d) and the $M-X$ distances of tridentate form. The distances are obtained with MP2/6-311G*, which are plotted as a function of cationic radius [$M=Li$ (0.76 Å), Na (1.02 Å) and K (1.38 Å)].

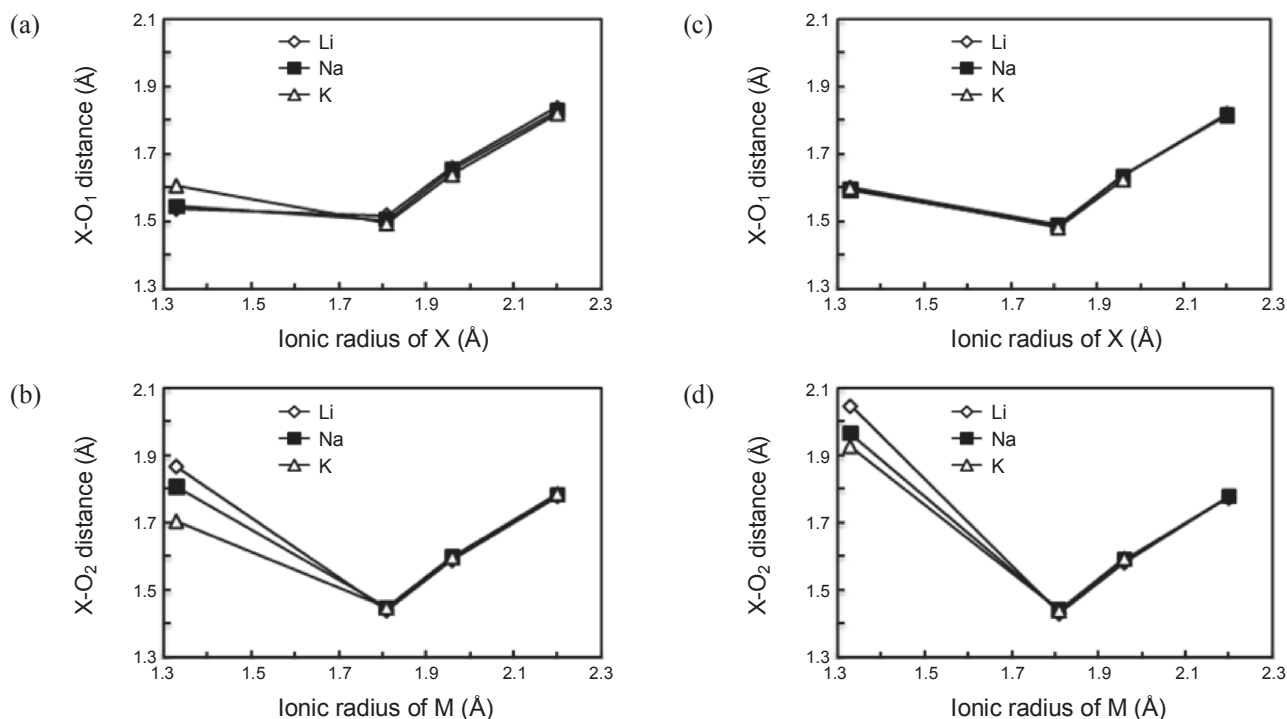


Figure 3. (a) The $X-O_1$ (b) and the $X-O_2$ distances of bidentate form. (c) The $X-O_1$ (d) and the $X-O_2$ distances of tridentate form. The distances are obtained with MP2/6-311G*, which are plotted as a function of ionic halogen radius [$X=F$ (1.33), Cl (1.81), Br (1.96) and I (2.2 Å)].

the shorter $M-X$ distances of tridentate forms are mainly due to the larger oxygen-oxygen repulsions of tridentate forms as compared to those of bidentate forms. As a result, the larger oxygen-oxygen repulsions of tridentate forms yielded longer oxygen-oxygen distances, which happened to reduce the $M-X$

distances of tridentate forms. While these two distances are highly affected by the metal size, however, the $X-O_1$ and $X-O_2$ distances which are not directly bonded to the metal, are relatively unchanged or become slightly shorter with the increasing metal size (see Table 2 and 3). The calculated $M-O_1-X$ bond

angle was found to be increased ($3 \sim 5^\circ$) with the increase of metal size from Li to K of both bidentate and tridentate forms.

X-O₁ and X-O₂ distances, which are directly bonded to the halogen, of both bidentate (Fig. 3(a) and 3(b)) and tridentate (Fig. 3(c) and 3(d)) forms were plotted as a function of halogen ionic radius. It is found that except fluorine compounds, both X-O₁ and X-O₂ distances increase with the size of halogens. However the corresponding two distances of MFO₄ pairs are abnormally longer than those of MCIO₄ pairs (see Figure 3). This anomalous behavior of perfluorinates can be attributed to the relatively small size of fluorine as compared to the other halogens. As such, the oxygen-oxygen repulsions become highly enhanced resulting much longer X-O₁ and X-O₂ distances in the case of MFO₄ pairs.

In summary, like the relative energetics, the geometrical parameters are also found to strongly depend on halogen and metal elements.

Conclusions

Structures and relative energies of alkali metal perhalogenates, MXO₄ (M=Li, Na, K and X=F, Cl, Br, I) were theoretically studied with the help of MP2 methods. Bidentate and tridentate forms were found in all alkali metal perhalogenate combinations except KIO₄, where the tridentate form of KIO₄ was not found to be minimum. The relative energies between the bidentate and tridentate structures of metal-perhalogenates depend on the metal and halogen elements. It is generally observed that the bidentate structures are preferred as the size of halogen increases and as the size of metal decreases.

It is seen that as the metal size increases, the M-O₁ and M-X distances of both bidentate and tridentate structures linearly increase. In general, the M-O₁ distances of tridentate forms are longer than the corresponding distances of bidentate forms, which is due to the increased steric hindrance of additional metal bound oxygen of tridentate. On the other hand, the M-X distances of tridentate forms are shorter than the corresponding distances of bidentate forms, which is mainly due to the larger oxygen-oxygen repulsions of tridentate forms as compared to those of bidentate forms. Except MFO₄ pairs, both X-O₁ and X-O₂ distances increase with the size of halogens. In the case of MFO₄ pairs, the two distances are abnormally longer than the corresponding distances of MCIO₄ pairs, which can be attributed to the enhanced oxygen-oxygen repulsions due to the relatively small fluorine size.

In summary, the bidentate structures are generally more stable except the cases of MFO₄ (M=Li, Na, K) and KClO₄. Overall, the relative energies and structures are highly dependent on the metal and halogen elements.

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