Molecular Electrostatic Potential Map Analysis of Metal Cation Interaction with Nucleophilic Molecules

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Synopsis. The interactions between metal cations, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, and Al^{3+} and nuleophilic molecules, NH_3, H_2O, HF, PH_3, H_2S, and HCl were calculated by the ab initio method with the MIDI-4 basis set and were analyzed on the basis of the molecular electrostatic potential (MEP) maps of the nucleophilic molecules. The position where each cation is expected to be trapped by the nucleophilic molecule can fairly be estimated as the distance from the MEP minimum point using the ionic radius of the cation, irrespective of the nucleophiles and cations.

Molecular electrostatic potential (MEP) maps are useful in understanding molecular interactions in various chemical systems, especially in biological systems.1) MEP maps can be used to compare reactivities among a set of compounds or among different conformations of a large molecule. In order to make good use of MEP maps in quantitative structure property relationship (QSPR) analysis, it is necessary to find out the appropriate quantities which describe the molecular interaction from an MEP map. The potential mimimum in the MEP map and the shape of the MEP surface can be such descriptors and have been used in QSPR analysis.2) MEP maps were also used to measure molecular similarity.3) However, attempts of quantifying MEP maps are very limited. The analysis of the metal cation–nucleophile interaction is appropriate to clarify the relation between the shape of the MEP map of a nucleophile and the interaction energy, since the interaction is expected to be mostly electrostatic. Recently, several ab initio studies on the interactions between metal cations and nucleophilic molecules have been reported.4,5) In the present study, the interactions between nucleophilic molecules and metal cations were analyzed on the basis of the MEP maps of the nucleophilic molecules.

Method

NH_3, H_2O, HF, PH_3, H_2S, and HCl were used as the model nucleophilic molecules and Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, and Al^{3+} were used as the counter cations. The interaction energy between them was calculated along the 7 directions indicated in Fig. 1, and the lowest-engrgy structure of the interacting system and the corresponding interaction energy were determined by using the MIDI-4 basis set.6) Although the MIDI-4 basis set is expected to be appropriate for the interaction energy calculation for the molecular systems involving the metal cations,5,6) two potential minima which are characteristic of the MEP map for H_2O7) are not reproduced by the MIDI-4 basis set. For the MEP calculation, we used here the STO-5G basis set8) which has been widely used in the MEP calculation.1,9) Calculations were carried out on the HP-730 workstations using ABINIT program written by our group.10)

Results and Discussion

The MEP maps of six nucleophiles are shown in Fig. 1. The energy minimum points in the MEP maps, which are shown by closed circles, and the corresponding MEP values are listed in Table 1. The locations of the metal cations, which correspond to the most stable structures of the metal–nucleophile interacting system along the fixed direction, are shown by open circles. In the H_2O MEP map, two minima are found along the directions which are 37° with respect to the C_{2v} axis. The minimum MEP along the b direction (-69 kcal mol^{-1}) is slightly lower than that along the a direction (-67 kal mol^{-1}). For the HF molecule, the MEP is axially symmetric and the minimum area is located at 1.06 Å from the F atom in direction of 119° with respect to the H–F bond. The potential wells in the MEP maps of PH_3, H_2S, and HCl are more shallow and located at a longer distance from the nucleophilic atom than those of the corresponding molecules which have second row nucleophilic atoms.

The distance between the nucleophilic atom and the metal cation in the most stable conformation, R_{X-M}, and the corresponding interaction energies are listed in Table 2. The interaction energies of the divalent cations are larger than those of the monovalent cations and become twice at a long X–M distance. For the H_2O–cation system, the interaction energies for the a direction are larger than those for the b direction, although the MEP minimum on the b direction is deeper. Figure 1 and Table 2 indicate that the R_{X-M} value depends on the ionic radius of the cation, R_{ion}. Two sets of the ionic radii were used to analyze the relationship between R_{ion} and

Table 1. Distance between the MEP Minimum Point and the Nucleophilic Atom and Minimum MEP Energy

	Distance a)	Energy b)
NH_3	1.02	−109.7
H_2O (a)	1.03	−67.2
H_2O (b)	1.03	−69.4
HF	1.06	−32.2
PH_3	1.54	−31.6
H_2S	1.52	−27.0
HCl	1.61	−20.4

a) in Å. b) in kcal mol^{-1}.

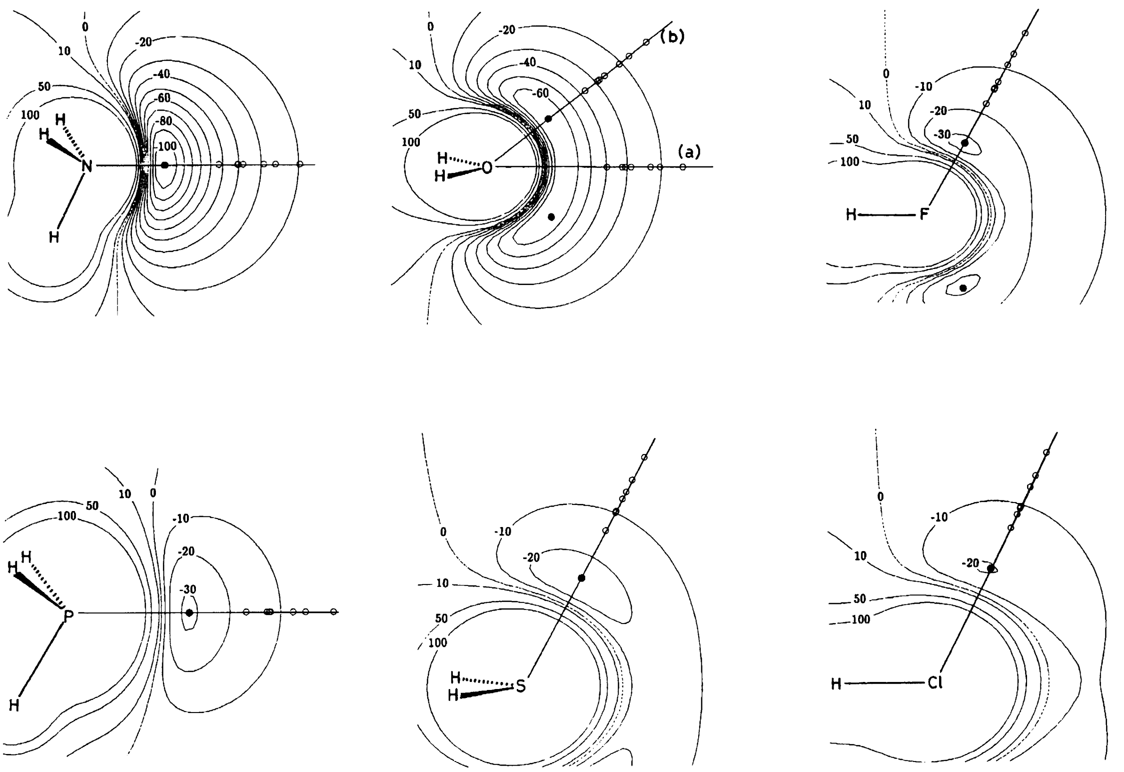

Fig. 1. MEP maps of NH_3, H_2O, HF, PH_3, H_2S, and HCl, and the direction (solid line) along which the cation interacts with the nucleophilic molecule. For H_2O, two directions, *a* and *b* are shown. For NH_3 and PH_3, the map is created on the plane which includes the C_{3v} axis and the N–H or P–H bond. For H_2O and H_2S, the map is created on the plane which includes the C_{2v} axis and bisects the HOH or HSH angle. For HF and HCl, the map is created on the plane which includes the H–F or H–Cl bond. The contour lines are drawn in every 10 kcal mol^{-1} for the negative potential region, while the lines of 10, 50, and 100 kcal mol^{-1} are shown for the positive potential area. The closed circles are the MEP minimum points and the open circles are the positions at which the cations are trapped.

Table 2. Equilibrium Distances (R_{X-M}) and Interaction Energies in Parentheses for Various Cation-Ligand Complexes$^{a)}$

	NH_3	H_2O (a)	H_2O (b)	HF	PH_3	H_2S	HCl
Li^+	1.978	1.830	1.843	1.852	2.593	2.518	2.468
	(−44.1)	(−42.8)	(−40.9)	(−21.8)	(−25.5)	(−20.3)	(−13.3)
Na^+	2.318	2.168	2.182	2.195	2.890	2.824	2.769
	(−32.5)	(−31.8)	(−30.3)	(−16.1)	(−19.7)	(−15.5)	(−10.3)
K^+	2.788	2.602	2.623	2.663	3.406	3.321	3.257
	(−21.3)	(−22.0)	(−20.8)	(−10.8)	(−12.8)	(−10.1)	(−6.9)
Be^{2+}	1.716	1.586	1.601	1.620	2.332	2.257	2.187
	(−148.2)	(−129.5)	(−125.1)	(−69.5)	(−131.5)	(−100.2)	(−64.4)
Mg^{2+}	2.030	1.906	1.920	1.945	2.607	2.545	2.489
	(−97.3)	(−88.0)	(−84.3)	(−45.0)	(−76.8)	(−57.4)	(−36.2)
Ca^{2+}	2.457	2.303	2.321	2.355	3.056	2.991	2.933
	(−60.5)	(−58.6)	(−55.5)	(−28.7)	(−41.8)	(−31.2)	(−20.5)
Al^{3+}	1.964	1.781	1.801	1.822	2.547$^{b)}$	2.696	2.370
	(−233.9)	(−195.1)	(−190.3)	(−112.7)	(−247.6)$^{b)}$	(−217.4)	(−149.4)

a) The ligand geometry was optimized in the calculation. Distances are in Å and interaction energies in kcal mol^{-1}. b) A stable complex was not obtained when the ligand geometry was optimized. If the PH_3 geometry is fixed at MIDI-4 structure and only the P–Al distance is optimized, the stable structure listed is obtained.

R_{X-M}; one is Pauling's set[11)] and the other set consists of the radii which reproduce the experimental hydration energies of cations[12)] when they are used in Born's formula.[13)] The second set of radii is thus similar to that given by Latimer et al.[14)] Figure 2 shows the relation between R_{ion} and R_{X-M} for the H_2O–cation systems. Large correlation was observed between R_{ion} and R_{X-M} for both ionic radius sets. The c_1 coefficient of the lin-

Table 3. Coefficients and Constants in the Liner Relation, $R_{\text{X-M}} = c_1 R_{\text{ion}} + c_2$, for Each Ligand

		NH_3	H_2O (a)	H_2O (b)	HF	PH_3	H_2S	HCl
Pauling's set[a]	c_1	1.02	1.00	1.01	1.02	1.08	0.98	1.05
	c_2	1.40	1.26	1.28	1.29	1.95	1.99	1.84
Born's formula[b]	c_1	1.17	1.14	1.15	1.16	1.23	1.10	1.20
	c_2	0.40	0.29	0.31	0.30	0.90	1.06	0.82

a) Pauling's ionic radii/Å; 0.60 (Li^+), 0.95 (Na^+), 1.33 (K^+), 0.31 (Be^{2+}), 0.65 (Mg^{2+}), 0.99 (Ca^{2+}), 0.50 (Al^{3+}). b) Ionic radii/Å estimated from the experimental hydration energies and Born's formula; 1.32 (Li^+), 1.64 (Na^+), 2.02 (K^+), 1.12 (Be^{2+}), 1.44 (Mg^{2+}), 1.72 (Ca^{2+}), 1.34 (Al^{3+}).

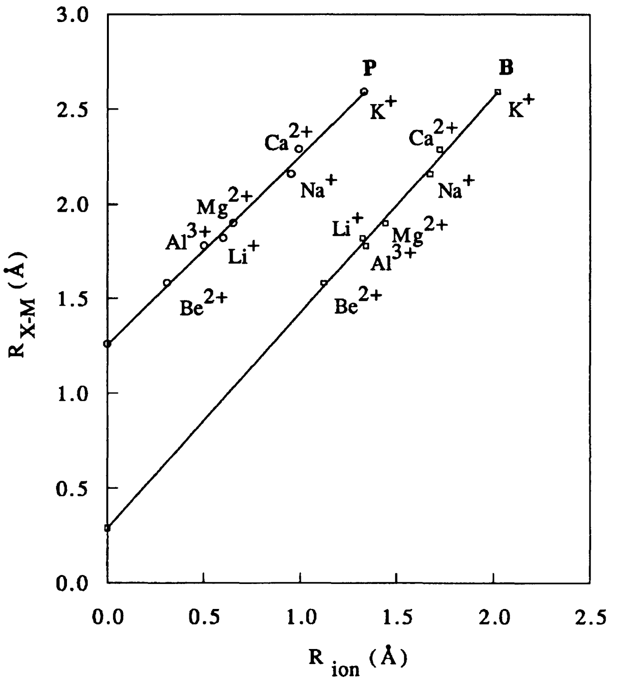

Fig. 2. Correlation between the metal–H_2O(a) distance, $R_{\text{X-M}}$, and ionic radius of the cation, R_{ion}. The Pauling's R_{ion} values are used in P, while the values derived from Born's formula and experimental hydration energies of cations are used in B. For the values of R_{ion}, see the footnote of Table 3.

ear relation, $R_{\text{X-M}} = c_1 R_{\text{ion}} + c_2$, is about 1.0 for the Pauling's set, indicating that the value of $R_{\text{X-M}} - R_{\text{ion}}$ is almost constant independent of cation species.

Table 3 shows the parameters determined for other cation–nucleophile systems. Although the c_1 coefficients of the linear relation are almost constant for all nucleophiles, 1.02 for the Pauling's set and 1.15 for the second set, the c_2 constants are larger for PH_3, H_2S, and HCl. As is shown in Table 1, the MEP minimum points of these molecules are located at a longer distance from the nucleophilic atoms than those of NH_3, H_2O, and HF. This suggests that the location of a cation along the direction indicated in Fig. 1 can be estimated successfully as the distance not from the nucleophilic atom but from the MEP minimum point. If Pauling's ionic radii are used, the distance from the MEP miuimum is expressed roughly by $R_{\text{ion}}+0.31$, irrespective of both the metal cations and nucleophilic molecules.

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