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THEORETICAL INSIGHTS INTO THE PROPERTIES OF THE XY≡YX…M^{n+} COMPLEXES (X = H, F, Cl; Y = C, Si; M = ALKALINE AND ALKALINE EARTH METALS)

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The character of alkaline (M^+= Li, Na, K) and alkaline earth metal ions (M^{2+}= Be, Mg, Ca) interactions with disilyne and acetylene has been studied by using high-level *ab initio* computations. The interaction energies were calculated at MP2/6-311++G(2*d*,2*p*) level. These calculations show that the size and charge of cation are two significant factors that affect the character of interaction. AIM and NBO analyses of M^{n+}…X_2Y_2 interactions specify that the variation of densities and the extent of charge transfers upon complexation correlate well with the obtained interaction energies.

K e y w o r d s: disilyne, disilyne complexes, interaction energy, NBO, AIM.

1. INTRODUCTION

A variety of new compounds containing triple bonded silicon have been synthesized and studied for their chemistry [1]. The first successful synthesis was conducted in 1994; HSi≡N was prepared by matrix isolation and identified by UV and IR spectroscopy [2]. While the formation of adducts of the form RSi≡SiR (R = Me [3] and $Tip_2C_6H_3$ [4]; Tip is 2,4,6-triisopropylphenyl)) was suggested, no conclusive evidence has been presented in their support. Only Karni *et al*. have demonstrated the existence of stable FSi≡CH and ClSi≡CH under gas-phase conditions [5]. This success followed previous theoretical predictions [6]. The computational studies [7—9] have shown, however, that HSi≡CH and HSi≡SiH possess a *trans*-bent geometry in contrast to the linear geometry of acetylene.

This paper reports studies on the complex formed upon interaction between XY≡YX (X = H, F, Cl; Y = C, Si) and alkaline or alkaline earth metal ions. The optimized structures, the interaction energies and the natural population analysis (NPA) are discussed. For comparison, the properties of the M^+…Y_2X_2 and M^{2+}…Y_2X_2 complexes are calculated. The ″atom in molecules″ (AIM) methodology of Bader is also applied to study the properties of the bond critical point of metals and Y_2X_2 contacts to analyze dependencies between topological, energetic, and geometrical parameters of the complexes.

2. COMPUTATIONAL METHODS

The structures of the XY≡YX…M^{n+} complexes (X = H, F, Cl; Y = C, Si; M = alkaline and alkaline earth metals) and the corresponding monomers were optimized by the MP2 method, and 6-311+ +G(2*d*,2*p*) was chosen as a basis set.

The optimization was done along with a frequency calculation for each complex to verify that the geometry was a real minimum without any imaginary frequency.

The interaction energy, IE, can be evaluated from the difference between the energy of the complex and the sum of the energies of the Y_2X_2 and metal ions:

$$\mathrm{IE} = E(\text{complex}) - [E(X_2Y_2) + E(M^{n+})].$$

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The calculated interaction energies were corrected for basis set superposition errors (BSSE), which were computed for all calculations using the counterpoise correction method of Boys and Bernardi [10].

All electronic structure calculations were performed using the Gaussian 2003 program [11].

The population analysis has also been performed by the natural bond orbital method [12] at MP2/6-311++G(2*d*,2*p*) level of theory using NBO program [13] under Gaussian 2003 program package.

The AIM methodology was applied to analyze the electron density and its corresponding Laplacian at the critical point M^{n+}…X_2Y_2 contact from the optimized structures of M^{n+}…X_2Y_2 at the MP2/6-311++G(2*d*,2*p*) level. The topological analyses have been performed with the AIM 2000 program [14] using the MP2/6-311++G(2*d*,*p*) wave functions as input.

3. RESULTS AND DISCUSSION

3.1. Energetics. Table 1 presents the computed interaction energies for the XY≡YX…M^{n+} complexes (X = H, F, Cl; Y = C, Si; M = alkaline and alkaline earth metals). These values show that for a given complex IE is greater for less electropositive alkaline and alkaline earth metals. On the other hand, IE values increase in halogenated complexes and they are greater in chlorinated complexes rather than fluorinated.

Table 1

Calculated energy E(Hartree), *interaction energy* IE (kcal/mol), BSSE (kcal/mol) *and corrected interaction energy* $IE^{corrected}$ (kcal/mol) *for the* Y_2X_2…M^{n+} *complexes by the method* MP2 *with* 6-311++G(2*d*,2*p*) *basis set*

M^{n+}	Y	*E*(Hartree)		IE		BSSE		$IE^{corrected}$	
		Si	C	Si	C	Si	C	Si	C
H^+	H	–579.435	–77.377	–204.1	–154.6	2.74	1.78	–201.36	–152.82
	F	—*	–275.489	—	–138.6	—	1.95	—	–136.65
	Cl	—*	–995.503	—	–153.5	—	2.31	—	–151.19
Li^+	H	–586.389	–84.399	–27.3	–20.0	1.08	1.66	–26.22	–18.34
	F	–784.715	–282.519	–25.3	–9.5	0.96	1.41	–24.34	–8.09
	Cl	–1504.642	–1002.522	–26.2	–17.6	1.29	2.86	–24.91	–14.74
Na^+	H	–740.803	–238.815	–18.2	–12.5	0.90	1.23	–17.3	–11.27
	F	–938.4840	–436.940	–18.8	–4.6	0.87	0.92	–17.9	–3.68
	Cl	–1659.056	–1156.939	–17.2	–10.5	1.00	2.04	–16.2	–8.46
K^+	H	–1178.306	–676.323	–11.7	–8.7	0.55	0.89	–11.15	–7.81
	F	–1376.632	–874.451	–9.8	–3.0	0.59	0.71	–9.21	–2.29
	Cl	–2096.559	–1594.449	–10.7	–8.0	0.65	1.52	–10.05	–6.48
Be^{2+}	H	–593.034	–90.944	–197.0	–127.2	1.86	1.22	–195.14	–125.98
	F	—*	–289.041	—	–102.0	—	2.60	—	–99.4
	Cl	–1511.313	–1009.092	–212.3	–140.4	2.18	4.63	–210.12	–135.77
Mg^{2+}	H	–778.111	–276.057	–111.9	–64.8	1.30	0.83	–110.6	–63.97
	F	–976.444	–474.162	–114.3	–44.3	1.57	1.77	–112.73	–42.53
	Cl	–1696.381	–1194.190	–121.5	–68.2	1.47	3.39	–120.03	–64.81
Ca^{2+}	H	–1255.525	–753.509	–61.7	–38.2	0.86	0.57	–60.84	–37.63
	F	–1453.851	–951.620	–59.8	–22.1	1.06	1.32	–58.74	–20.78
	Cl	–2173.784	–1671.641	–64.5	–41.3	0.94	1.15	–63.56	–40.15

* These complexes are not stable.

Table 2

Electron densities ρ (e/a_0^3) *and Laplacians* $\nabla^2\rho$ (e/a_0^5) *at bond critical points of* $X_2Y_2\ldots M^{n+}$ *interaction and variation of electron density at the bond critical point of* YY, *calculated at the* MP2/6-311++G(2*d*,2*p*) *level within the* AIM *theory*

M^{n+}	Y	ρ($H_2Si_2\ldots M^{n+}$)		$\nabla^2\rho$		ρ(SiSi)		Δρ(SiSi)	
		Si	C	Si	C	Si	C	Si	C
—	H	—	—	—	—	0.0881	0.4109	—	—
—	F	—	—	—	—	0.0658	0.3864	—	—
—	Cl	—	—	—	—	0.0718	0.3801	—	—
H^+	H	—	0.2056	—	–0.2529	0.0818	0.4085	–0.0063	–0.0023
	F	—	0.1975	—	–0.2107	—	0.3918	—	0.0054
	Cl	—	0.1982	—	–0.1944	—	0.3880	—	0.0079
Li^+	H	0.0169	0.0197	0.0430	0.0930	0.0888	0.4011	0.0007	–0.0098
	F	0.0155	0.0157	0.0338	0.0705	0.0691	0.3778	0.0033	–0.0087
	Cl	0.0167	0.0200	0.0400	0.0993	0.0734	0.3786	0.0016	–0.0016
Na^+	H	0.0121	0.0128	0.0320	0.0589	0.0889	0.4009	0.0008	–0.0100
	F	0.0111	0.0089	0.0268	0.0391	0.0693	0.3770	0.0035	–0.0094
	Cl	0.0119	0.0121	0.0308	0.0583	0.0731	0.3790	0.0013	–0.0011
K^+	H	0.0088	0.0104	0.0220	0.0379	0.0883	0.4005	0.0002	–0.0103
	F	0.0078	0.0073	0.0189	0.0263	0.0671	0.3762	0.0012	–0.0102
	Cl	0.0087	0.0108	0.0222	0.0422	0.0712	0.3788	–0.0006	–0.0013
Be^{2+}	H	—	0.0763	—	0.1561	0.0873	0.4115	–0.0008	0.0007
	F	—	0.0681	—	0.1090	—	0.3840	—	–0.0025
	Cl	0.0441	–0.0577	–0.0319	–0.3247	0.0612	0.3723	–0.0107	–0.0079
Mg^{2+}	H	0.0300	0.0374	0.0140	0.1414	0.0893	0.4133	0.0012	0.0024
	F	0.0252	0.0306	–0.0124	0.1083	0.0559	0.3834	–0.0099	–0.0030
	Cl	0.0263	0.0372	–0.0045	0.1624	0.0671	0.3784	–0.0047	–0.0017
Ca^{2+}	H	0.0215	0.0270	0.0270	0.0920	0.0912	0.4126	0.0031	0.0018
	F	0.0180	0.0229	0.0146	0.0715	0.0683	0.3797	0.0025	–0.0067
	Cl	0.0199	0.0327	0.0205	0.1181	0.0766	0.3881	0.0048	0.0080

Considering the magnitudes of $IE^{corrected}$, it can be found that the size and charge of the cation are important factors determining the strength of the binding in these systems.

3.2. "Atoms in molecules" analysis. The analysis of electron density by means of the Bader's methodology (AIM) provides useful tools to confirm the presence of H_2Si_2—M^{n+} interactions.

Table 2 lists the values of ρ and $\nabla^2\rho$ of the complexes and X_2Y_2 at the MP2/6-311++G(2*d*,2*p*) level. It contains the electron densities at the bond critical points of $M^{n+}\ldots X_2Y_2$ contacts and YY bonds. Several features of the electron densities analysis obtained in the AIM framework are summarized as follows:

1. All the BCPs of $M^{n+}\ldots Y_2X_2$ interactions are characterized by small ρ(*r*) values and positive Laplacian of the electron density. The sign of the Laplacian is determined by the positive curvature of ρ(r) along the interaction line, as the Pauli Exclusion Principle leads to a relative depletion of charge density in the interatomic surface. These interactions are dominated by the contraction of charge density away from interatomic surface toward each of interacting species. It has been confirmed that the electron density at the bond critical point can be used as a measure of the binding strength. Figure 1 represents the plot of calculated interaction energies of $M^{n+}\ldots Y_2X_2$ complexes versus their electron density at the BCP(SiSi).

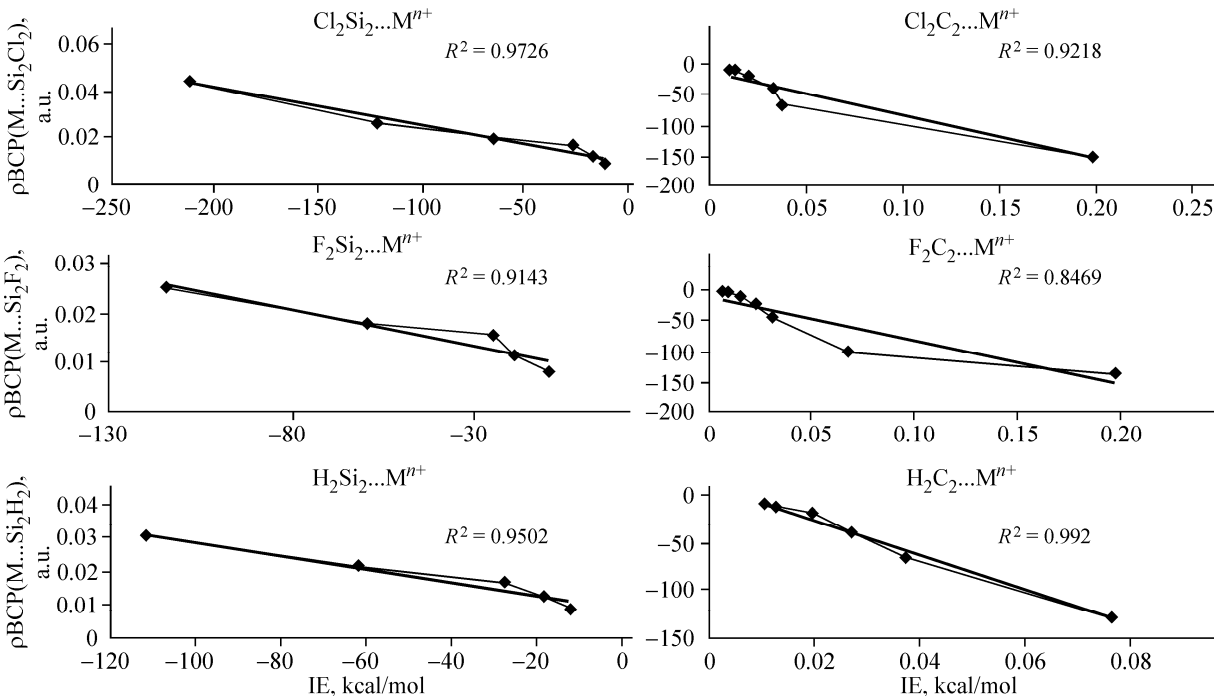

Fig. 1. Correlation between the interaction energies and the density at the BCP of Y_2X_2…M^{n+} complexes

2. Among all complexes, the obtained values for electron density are lower for the interaction of M^+ with Y_2X_2 rather than M^{2+}. Also, theses values are greater in C_2X_2…M^{n+} than in Si_2X_2…M^{n+} complexes. The decrease of these values in halogenated complexes is compatible with their electronegativity.

3. An interesting feature of H^+…Si_2H_2, Be^{2+}…Si_2H_2, Mg^{2+}…Si_2F_2, Be^{2+}…Si_2Cl_2, and Mg^{2+}…Si_2Cl_2 interactions is the formation of a ring critical point (RCP, ρ(3,+1)) along the line connecting the cation to the center of SiSi upon complexation (see Fig. 2).

4. The variation of electron density at the Si—Si bond critical points in different complexes can also present another indicator for the strength of M^{n+} … H_2Si_2 interactions. The computed variations of electron density of the Si—Si bond critical points (Δρ(SiSi)) upon complexation are given in Table 2. These values of Δρ(SiSi) show that the Si—Si strength increases little upon the complex formation, except for Si_2H_2…H^+, Si_2H_2…Be^{2+}, Si_2F_2…Mg^{2+}, Si_2Cl_2…Be^{2+}, Si_2Cl_2…Mg^{2+}. It can be seen that the maximum reduction corresponds to the case of Si_2Cl_2…Be^{2+} interaction.

The calculated variations of electron density of the C—C bond critical points (Δρ(CC)) upon complexation are given in Table 2. These values of Δρ(CC) show that the C—C strength decreases little upon the complex formation, except for C_2F_2…H^+, C_2Cl_2…H^+, C_2H_2…Be^{2+}, C_2H_2…Mg^{2+}, C_2Cl_2…Ca^{2+}, C_2H_2…Ca^{2+}.

3.3. Natural population analysis. Natural bond orbital analysis emphasizes the role of intermolecular orbital interaction in the complex, particularly charge transfer. The analysis is carried out by considering all possible interactions between filled donor and empty acceptor NBOs and estimating their energetic importance by second-order perturbation theory. For each donor NBO (*i*) and acceptor NBO (*j*), the stabilization energy *E*(2) associated with the electron delocalization between donor and acceptor

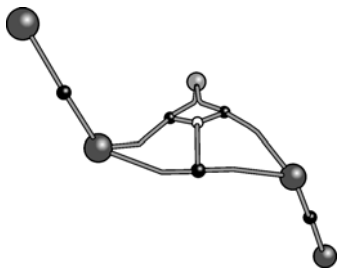

Fig. 2. The formation of a ring critical point (RCP, ρ(3,+1)) along the line connecting the cation to the center of SiSi upon complexation in H^+…Si_2H_2, Be^{2+}…Si_2H_2, Mg^{2+}…Si_2F_2, Be^{2+}…Si_2Cl_2, and Mg^{2+}…Si_2Cl_2 complexes

Table 3

The results of second-order perturbation theory analysis of the Fock matrix within the NBO *basis* (E^2 *energy values for the donor-acceptor interactions in* kcal/mol)

M^{n+}	Y	donor → acceptor		E^2		$\varepsilon_j - \varepsilon_i$		$F_{i,j}$	
		Si	C	Si	C	Si	C	Si	C
H^+	H	—	σ(C—C) → *n**(H)	—	22.81	—	1.15	—	0.175
	F	—	σ(C—C) → *n**(H)	—	21.25	—	1.12	—	0.168
	Cl	—	σ(C—C) → *n**(H)	—	20.43	—	1.15	—	0.165
Li^+	H	π(Si—Si) → *n**(Li)	π(C—C) → *n**(Li)	30.49	9.70	0.51	0.89	0.112	0.083
	F	σ(Si—Si) → *n**(Li)	π(C—C) → *n**(Li)	29.57	8.81	0.46	0.99	0.105	0.084
	Cl	π(Si—Si) → *n**(Li)	π(C—C) → *n**(Li)	32.80	7.51	0.50	1.07	0.116	0.080
Na^+	H	π(Si—Si) → *n**(Na)	π(C—C) → *n**(Na)	16.13	3.27	0.44	0.71	0.076	0.043
	F	π(Si—Si) → *n**(Na)	π(C—C) → *n**(Na)	22.97	3.41	0.43	0.78	0.091	0.046
	Cl	π(Si—Si) → *n**(Na)	π(C—C) → *n**(Na)	16.99	2.99	0.44	0.75	0.079	0.042
K^+	H	π(Si—Si) → *n**(K)	π(C—C) → *n**(K)	6.01	1.70	0.49	0.75	0.049	0.032
	F	π(Si—Si) → *n**(K)	π(C—C) → *n**(K)	6.78	1.50	0.46	0.80	0.050	0.031
	Cl	π(Si—Si) → *n**(K)	π(C—C) → *n**(K)	6.21	1.38	0.51	0.75	0.051	0.029
Be^{2+}	H	—	π(C—C) → *n**(Be)	—	102.13	—	0.70	—	0.239
	F	—	π(C—C) → *n**(Be)	—	122.42	—	0.69	—	0.259
	Cl	—	π(C—C) → *n**(Be)	—	90.10	—	0.84	—	0.245
Mg^{2+}	H	—	π(C—C) → *n**(Mg)	—	37.34	—	0.52	—	0.125
	F	—	π(C—C) → *n**(Mg)	—	40.33	—	0.57	—	0.135
	Cl	π(Si—Si) → *n*(Mg)	π(C—C) → *n**(Mg)	163.62	33.98	0.13	0.56	0.144	0.123
Ca^{2+}	H	π(Si—Si) → *n**(Ca)	π(C—C) → *n**(Ca)	57.38	13.59	0.35	0.68	0.129	0.086
	F	π(Si—Si) → *n**(Ca)	π(C—C) → *n**(Ca)	47.97	13.77	0.33	0.75	0.113	0.091
	Cl	σ(Si—Si) → *n**(Ca)	π(C—C) → *n**(Ca)	25.91	10.80	0.37	0.82	0.089	0.084

is estimated as:

$$E^{(2)} = -q_i \frac{(F_{i,j})^2}{\varepsilon_i - \varepsilon_j},$$

where q_i is the orbital occupancy, ε_i, ε_j are diagonal elements and F_{ij} is the off-diagonal NBO Fock matrix element.

The results of the second-order perturbation theory analysis of the Fock matrix at MP2/6-311++G(2*d*,2*p*) level of theory are collected in Table 3. For the $M^{n+}\ldots X_2Y_2$ complexes, most charge transfer energies reported in Table 4 are related to dominant interaction which occurs between π-electrons of donor species and $n^*(M^{n+})$ (π(Y, Y = C, Si) → $n^*(M^{n+})$). There is no interaction of this type when $M^{n+} = H^+$, Be^{2+}, Mg^{2+}. The σ(Si—Si) → *n**(Li) and σ(Si—Si) → *n**(Ca) interactions occur in $Si_2F_2\ldots Li^+$, $Si_2Cl_2\ldots Ca^{2+}$ complexes, respectively. On the other hand, σ(C—C) → *n**(H) occur in $C_2X_2\ldots H^+$ complexes.

The interaction of $H^+$with Si_2H_2 has attractive aspect. The strongest interaction is between σ(Si2—H3) donor and *n**(Si2) acceptor. The hybridization coefficients for the Si2—H3 bond are:

$$\sigma(\text{Si2—H3}):0.4903(sp^{5.87}d^{0.15})\text{Si} + 0.8716(sp^{0.02})\text{H}.$$

The occupancy of this bond is 1.624.

A comparison between the results of $\text{IEs}^{\text{corrected}}$ in Table 1 and *E*(2) in Table 4 shows that although for a given cation the interaction energy is greater when the Si_2H_2 interacts with alkaline earth

Table 4

The natural population analysis for the M^{n+}…Y_2X_2

M^{n+}	Y	M		Y		M^{n+}	Y	M		Y	
		Si	C	Si	C			Si	C	Si	C
H^+	H	–0.25260	0.36165	0.77169	–0.00853	Be^{2+}	H	1.14323	1.79117	0.54634	–0.26712
	F	—	0.32726	—	0.54710		F	—	1.73197	—	0.32971
	Cl	—	0.36476	—	–0.01126		Cl	0.96337	1.79747	0.77681	–0.30492
Li^+	H	0.90849	0.97688	0.21115	–0.25799	Mg^{2+}	H	1.41188	1.89097	0.43672	–0.27147
	F	0.86405	0.97893	0.78538	0.29625		F	1.16805	1.87124	1.13221	0.30473
	Cl	0.90100	0.98275	0.41808	–0.19414		Cl	1.25289	1.88974	0.67091	–0.25624
Na^+	H	0.94041	0.99004	0.20249	–0.17288	Ca^{2+}	H	1.79084	1.95836	0.25485	–0.27768
	F	0.91463	0.98868	0.76432	0.30302		F	1.69971	1.95509	0.86538	0.28986
	Cl	0.93811	0.99051	0.41436	–0.17312		Cl	1.75114	1.95474	0.45273	–0.23485
K^+	H	0.97771	0.99539	0.19046	–0.24433						
	F	0.97288	0.99422	0.73534	0.30706						
	Cl	0.97749	0.99383	0.40877	–0.16060						

metals, especially for Be and Mg. Figure 3 represents the plot of calculated interaction energies of M^{n+}…X_2Si_2 complexes versus $E(2)$.

The natural population analysis shows that Be and Mg have the smallest charge (Table 4). This implies different nature for Si_2X_2…Be and Si_2X_2…Mg interaction in comparison to other interactions. It means that these interactions are more covalent.

4. CONCLUSIONS

In the present theoretical study, interaction of alkaline (M^+ = Li, Na, K) and alkaline earth metal ions (M^2 = Be, Mg, Ca) with disilyne and acetylene have been investigated. The calculations suggest that the size and charge of cation are two significant factors that affect the nature of interaction.

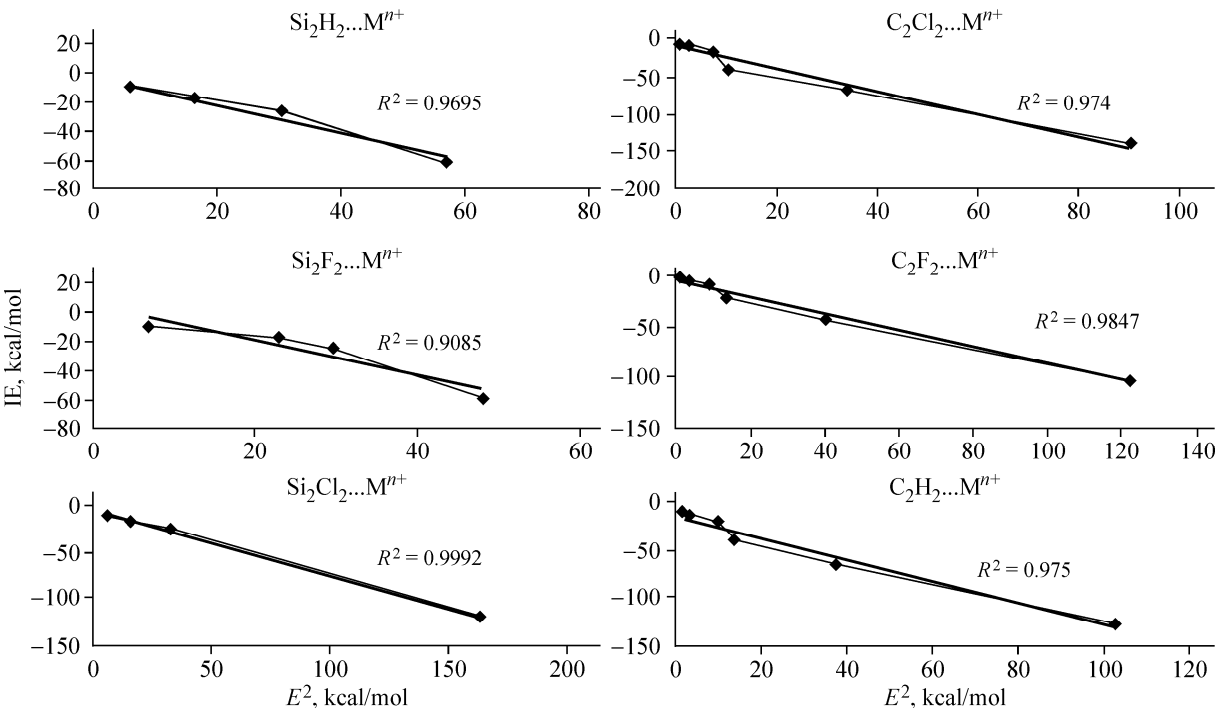

Fig. 3. Correlation between the $E^{(2)}$ stabilization energy and interaction energies of Y_2X_2…M^{n+} complexes

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