Hypercoordinate atoms of second-row elements in dodecahedrane endohedral complexes

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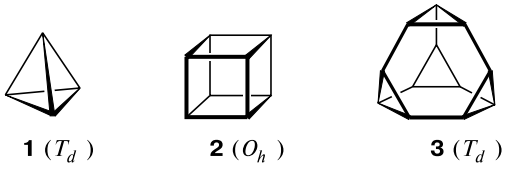
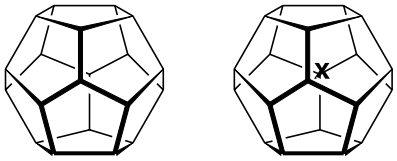
The energy characteristics and geometric parameters of the dodecahedrane endohedral complexes $X@C_{20}H_{20}$ ($X = C^{4-}$, N^{3-}, O^{2-}, F^-, Ne) were studied by the density functional theory B3LYP method with the 6-311G(d,p), 6-311+G(d,p), and 6-311G(df,p)) basis sets. In all structures the central atoms X are characterized by a coordination number of 20. The energy of formation of the complexes decreases in the order $X = C^{4-}$, N^{3-}, O^{2-}, F^-, Ne. The coordination number of the central atom remains unchanged upon adding Li^+ counterions to anionic systems.

Key words: hypercoordination, second-row elements, dodecahedrane endohedral complexes, quantum chemical calculations.

Evaluation of the coordination potential of main-group elements is one of the key issues in modern theoretical and experimental chemical research.[1,2] In addition to studies on the nature of hypercoordination and search for novel structural motiffs that provide the formation of hypercoordinate centers an important problem in chemistry of hypercoordinate compounds is to determine the maximum possible number of ligands capable of interacting with a certain atom through multicenter bonding. Recently, considerable attention has been paid to endohedral complexes of various polyhedral cage systems[3—12] in order to vary the coordination characteristics of the endohedral center by varying the molecular and electronic structure of such systems. An important feature of the formation of endohedral complexes is the size of the cage, whose interior should be large enough to accommodate an atom or ion.



1 (T_d) **2** (O_h) **3** (T_d)



4 (I_h) **5** (I_h)

For instance, the cavity volume in the simplest polyhedral system, tetrahedrane **1**, is too small to form endohedral complexes.[8] Cage extension by going to cubane **2** permits the formation of stable endohedral derivatives with small cations (Li^+ and Be^{2+}) and He atom.[8] A truncated tetrahedrane **3** can form a larger number of the complexes $X@C_{12}H_{12}$ (X = H, He, Ne, Li, Li^+, Na^+, Be^{2+}, Mg^{2+})[8]. The complexation potential significantly enhances as the cage even more extends. Some examples are provided by the theoretically studied endohedral complexes of dodecahedrane **4**, namely, structures **5** with X = H, He, Ne, Ar, Li, Li^+, Li^-, Na, Na^+, Mg, Mg^+, Mg^{2+},[9—11] and bulkier endohedral centers (X = N, P, C^-, Si^-, S^+).[12] The synthesis of a dodecahedrane complex with helium, $He@C_{20}H_{20}$, was reported.[5]

The stability of endohedral complexes can be significantly enhanced upon formation of chemical bonds between the central atom and the cage atoms. For instance, in complex $X@C_{20}H_{20}$ ($X = C^{4-}$) the filled p-orbitals of the central atom X with the closed eight-electron shell interact with the vacant σ*-orbitals of C—H bonds in the molecular cage. This results in the formation of the carbon center that has a coordination number (CN) of 20 and forms chemical bonds with all carbon atoms in the cage, as confirmed by the results of the natural bonding orbital (NBO) analysis and topological analysis of the electron density distribution according to Bader.[13] One can expect the formation of endohedral centers with CN = 20 in the isoelectronic systems $X@C_{20}H_{20}$ ($X = N^{3-}$, O^{2-}, F^-, Ne)

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containing central atoms with the closed eight-electron shells.

In this work we carried out a quantum chemical study of geometric parameters and energy characteristics of the dodecahedrane endohedral complexes with atoms of the second-row elements $X@C_{20}H_{20}$, where X = C^{4-} (**5a**), N^{3-} (**5b**), O^{2-} (**5c**), F^- (**5d**), Ne (**5e**). We also studied the effect of counterions on the electronic and coordination characteristics of anionic systems.

Calculation Procedure

Quantum chemical calculations were carried out by the density functional theory (DFT)[14] with the B3LYP three-parameter functional and the 6-311G(d,p), 6-311+G(d,p), and 6-311G(df,p) split-valence basis sets using the GAUSSIAN-03 program package.[15] All stationary points were identified by calculating the Hesse matrix. The topological analysis of the total electron density distribution according to Bader[16,17] was carried out using the AIMPAC program package.[18]

Results and Discussion

Structure and stability of complexes 5a—e. According to calculations with all basis sets, systems **5a—e** with I_h symmetry correspond to energy minima ($\lambda^* = 0$) on potential energy surfaces (PES). The geometric parameters of systems **5a—e** are shown in Fig. 1 and their energy characteristics are listed in Table 1.

The calculated distances between the central atoms X and the cage carbon atoms in complexes **5a—e** are much longer than the corresponding lengths of ordinary covalent bonds X—C, being equal to 2.188—2.203 (**5a**), 2.188—2.198 (**5b**), 2.192—2.196 (**5c**), 2.200—2.203 (**5d**), and 2.212—2.214 Å (**5e**) (see Fig. 1). Although the occurrence of a chemical bond between two carbon atoms separated by more than 2 Å is a moot question, the topological analysis according to Bader (see graph **5** in Fig. 1, the graphs of all systems **5** are identical to one another) indicates the formation of twenty bond paths connecting the central atom in systems **5a—e** to the cage carbon atoms. According to Bader´s theory,[16] the bond path connecting two atoms unambiguously indicates the chemical bond between them. Thus, the central atom in systems **5a—e** forms chemical bonds with all cage carbon atoms, thus having a CN of 20. The magnitude and sign of the Laplacian suggest that the X—C bonds in the complexes under study have the donor-acceptor nature. Note that the O—C bonds in complex **5c** are shorter than the axial C—O bonds formed by the bipyramidal pentacoordinate carbon atom in 1,8-dimethoxy-9-dimethoxymethylanthracene (2.192—2.196 Å *vs.* 2.472 Å, respectively).[19,20] Using the relation

$$\chi = \left(\sum_{i=X,Y} R_i - l_{XY}\right) \Big/ \left(\sum_{i=X,Y} R_i - \sum_{i=X,Y} r_i\right) \quad (1)$$

($\sum_{i=X,Y} R_i$ and $\sum_{i=X,Y} r_i$ are the sums of the van der Waals and covalent radii[21] of the atoms X and Y, respectively; l_{XY} is the distance between the atoms X and Y), we calculated the covalency ratios χ[22] of the X—C bonds in systems **5a—e**. They are equal to 0.70 (**5a**), 0.62 (**5b**), 0.58 (**5c**), 0.54 (**5d**), and 0.63 (**5e**) and point to a rather large contribution of the covalent component to the interaction of the central atom with the cage.

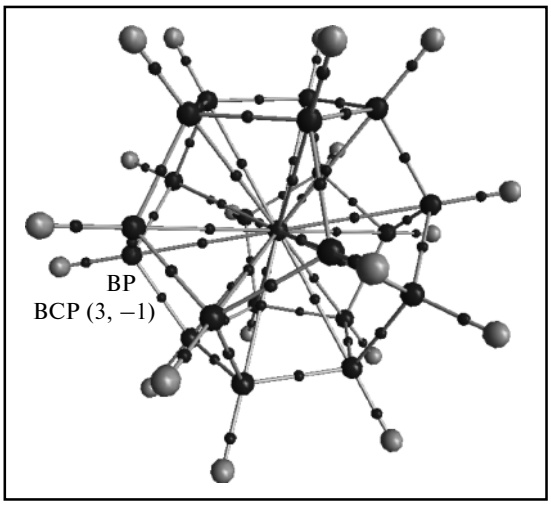
The formation of the donor-acceptor bonds between the central atom and the cage carbon atoms is substantiated by the results of the NBO analysis.[22] Namely, the interaction between the central atom and the hydrocarbon cage in systems **5a—e** occurs by electron density transfer from the filled p-orbitals of the central atom to the vacant antibonding orbitals of C—H bonds (σ^*_{CH}). Our calculations with the three basis sets predict that the energy of this interaction is maximum for complex **5a** (38.7 kcal mol^{-1}), being decreased to 7.2, 4.5, 2.7, and 1.6 kcal mol^{-1} for **5b**, **5c**, **5d**, and **5e**, respectively. This is due to the lowering of the p-orbital energy levels of the central atom (increase in electronegativity), which leads to broadening of the energy gap between the interacting fragment orbitals (Fig. 2).

The geometric parameters and electronic characteristics of systems **5a—e** calculated with all basis sets used in this work are in good agreement with one another. Complexation is accompanied by a slight expansion of the cage compared to the dodecahedrane molecule in which the bond lengths between the cage carbon atoms lie in the range 1.552—1.555 Å (*cf.* 1.562—1.572 (**5a**), 1.562—1.569 (**5b**), 1.564—1.567 (**5c**), 1.570—1.572 (**5d**), and 1.578—1.580 Å (**5e**)). The geometric parameters of complex $Ne@C_{20}H_{20}$ calculated in this work are in agreement with the published theoretical results.[10,11]

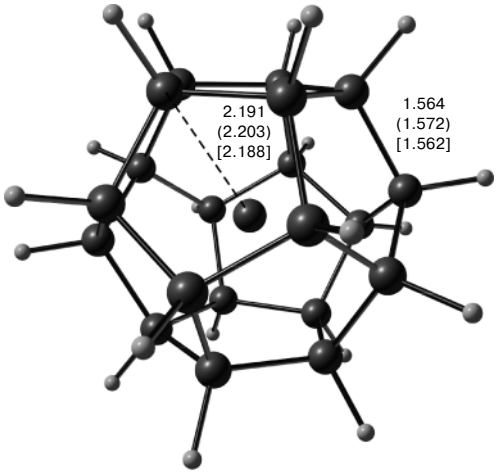
The B3LYP/6-311G(d,p) calculated Mulliken atomic charges of X in the complexes under study are −0.19, −0.60, −0.79, −0.62, and 0.04 e for X = C^{4-}, N^{3-}, O^{2-}, F^- and Ne, respectively. Thus, the degree of charge transfer from the central ion to the cage decreases in the order **5a** (3.81 e) > **5b** (2.40 e) > **5c** (1.21 e) > **5d** (0.38 e) > > **5e** (0.04 e). This is consistent with the decrease in the orbital interaction energies and elongation of the distances between the central atom and the cage atoms and agrees with the tendency of decreasing the degree of charge transfer calculated in the framework of the NBO analysis, namely, 3.38 ($X = C^{4-}$), 1.85 (N^{3-}), 0.92 (O^{2-}), 0.30 (F^-), and 0.08 e (Ne).

It is difficult to calculate the complex formation energies for the multiply charged carbon and nitrogen ions

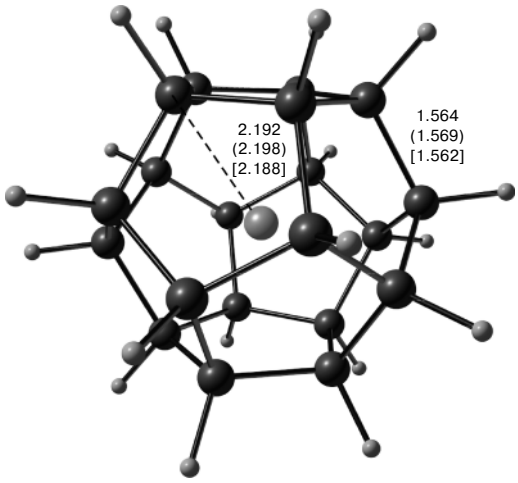
* Stationary point index equal to the number of negative eigenvalues of the Hesse matrix at a given point.



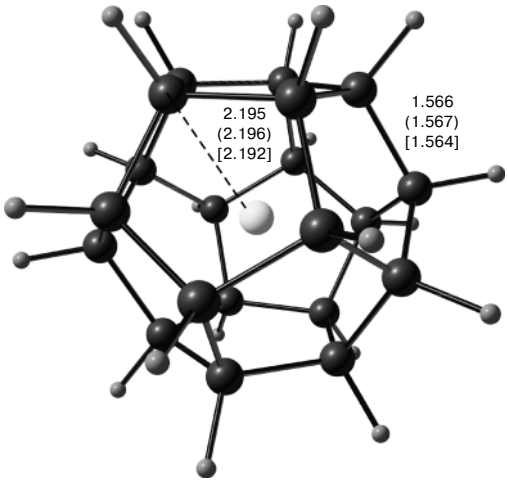
$X@C_{20}H_{20}$ (**5**)



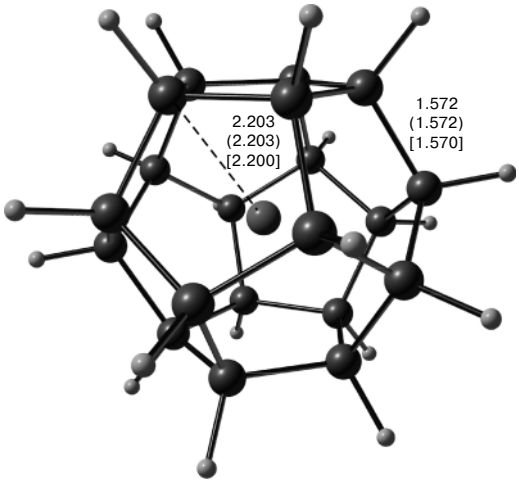
$C@C_{20}H_{20}^{4-}$ (**5a**)



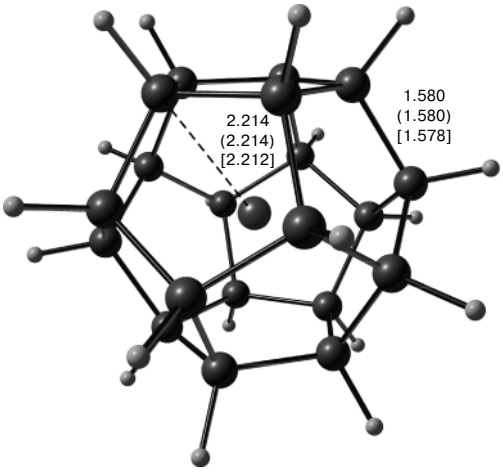
$N@C_{20}H_{20}^{3-}$ (**5b**)



$O@C_{20}H_{20}^{2-}$ (**5c**)



$F@C_{20}H_{20}^{-}$ (**5d**)



$Ne@C_{20}H_{20}$ (**5e**)

Fig. 1. Geometric parameters of complexes **5** obtained from B3LYP calculations with the 6-311G(d,p), 6-311+G(d,p) (figures in parentheses), and 6-311G(df,p) basis sets (figures in brackets); the Bader molecular graphs of structures **5a—e** (inset). Hereafter the bond lengths are given in Ångstrøms, "BP" denotes the Bader bond path; and "BCP" denotes the (3, −1) bond critical point.

Table 1. Energy characteristics[a] of systems **4** and **5** with I_h symmetry obtained from B3LYP calculations with the 6-311G(d,p), 6-311+G(d,p), and 6-311G(df,p) basis sets

Structure	Basis set	$-E_{tot}$	ZPE	E_f[b]	$E_{f,ZPE}$	ω_1
4	6-311G(d,p)	774.356947	0.357383	—	—	480.5
	6-311+G(d,p)	774.359505	0.357098	—	—	480.1
	6-311G(df,p)	774.374958	0.357398	—	—	481.2
5a	6-311G(d,p)	811.217602	0.321609	—	—	513.8
	6-311+G(d,p)	811.446151	0.339797	—	—	462.7
	6-311G(df,p)	811.240068	0.321893	—	—	514.8
5b	6-311G(d,p)	828.377545	0.333388	—	—	515.2
	6-311+G(d,p)	828.458514	0.339540	—	—	508.3
	6-311G(df,p)	828.397792	0.333352	—	—	516.4
5c	6-311G(d,p)	849.262702	0.345640	−167.04	−174.41	514.7
	6-311+G(d,p)	849.280674	0.345380	−24.55	−31.91	510.6
	6-311G(df,p)	849.281314	0.345478	−167.42	−174.90	515.7
5d	6-311G(d,p)	874.140198	0.355117	23.90	22.48	511.7
	6-311+G(d,p)	874.144900	0.354279	64.82	63.05	508.8
	6-311G(df,p)	874.157976	0.354937	24.04	22.50	512.5
5e	6-311G(d,p)	903.153944	0.358853	96.57	97.50	507.7
	6-311+G(d,p)	903.157352	0.358567	102.00	91.49	507.3
	6-311G(df,p)	903.171109	0.358759	97.11	97.96	508.3

[a] E_{tot} (a.u.) is the total energy (1 a.u. = 627.5095 kcal mol^{-1}); ZPE (a.u.) is the zero-point vibration energy; E_f (kcal mol^{-1}) is the complex formation energy; $E_{f,ZPE}$ (kcal mol^{-1}) is the complex formation energy with inclusion of ZPE; and ω_1 (cm^{-1}) is the lowest harmonic vibrational frequency.
[b] Calculated using Eq. (2).

that are intrinsically unstable. As to systems **5c—e**, these energies can formally be estimated for the reaction

$$X^{n-} + C_{20}H_{20} \longrightarrow X@C_{20}H_{20}^{n-}. \qquad (2)$$

The B3LYP/6-311G(d,p) calculated energies are −167.0 (**5c**), 23.9 (**5d**), and 96.6 kcal mol^{-1} (**5e**), *i.e.*, the formation energies of the complexes decrease as the electronegativity of the central atom increases; this correlates

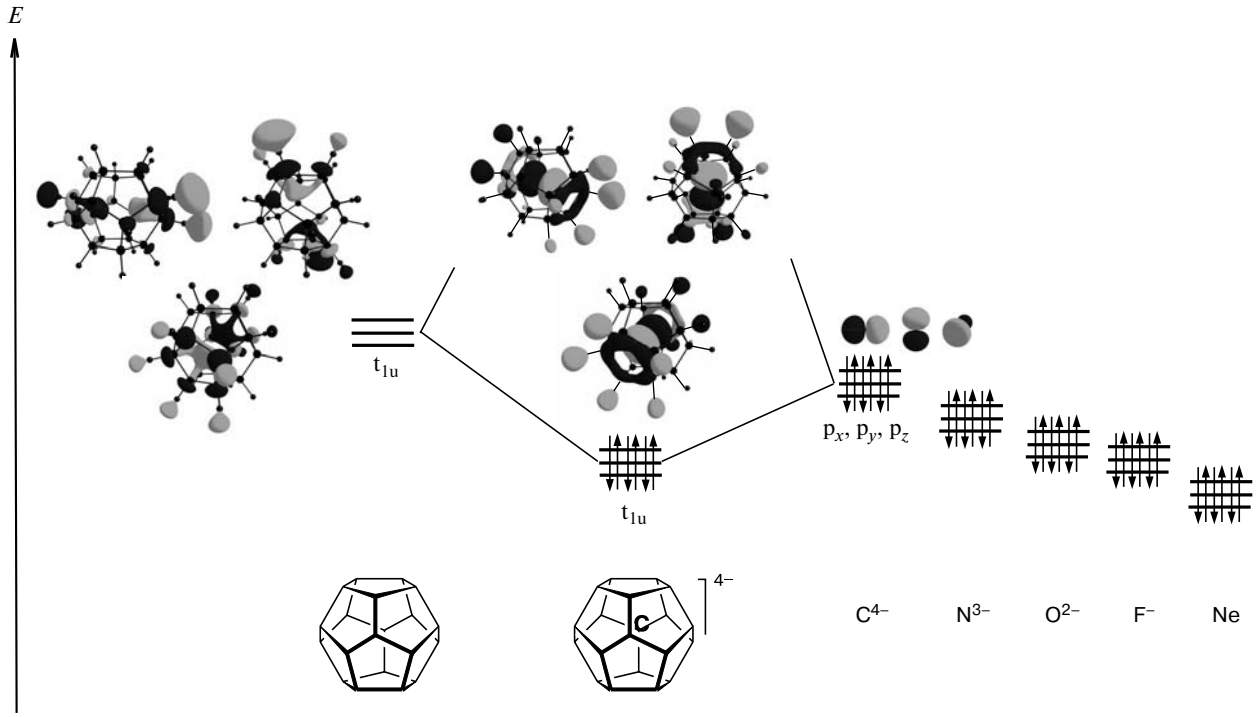


Fig. 2. Schematic diagram of formation of the main bonding MOs in systems **5** from fragment orbitals.

with the decrease in the orbital interaction energies. Thus, complexation is exothermic only for system **5c**, whereas the formation of endohedral complexes with fluorine and neon is energetically unfavorable.

Effect of counterions on characteristics of anionic endohedral complexes 5a—d. Attachment of lithium counterions to systems **5a—d** results in neutral complexes **6a—d** with the general formula $X@C_{20}H_{20}\cdot n$Li. The geometric parameters of systems **6a—d** are shown in Fig. 3 and their energy characteristics are listed in Table 2.

According to the results of topological analysis of the electron density distribution, the central atoms in the lithium complexes **6a—d** have CN = 20, which is similar to systems **5**. Thus, the attachment of counterions does not change the coordination features of the starting anionic systems. The distances between the central atom X and the cage carbon atoms in complexes **6a**, **6b**, **6c**, and **6d** lie in the ranges 2.161—2.236, 2.161—2.254, 2.180—2.213, and 2.169—2.234 Å, respectively. The carbon—carbon bond lengths in the cage are

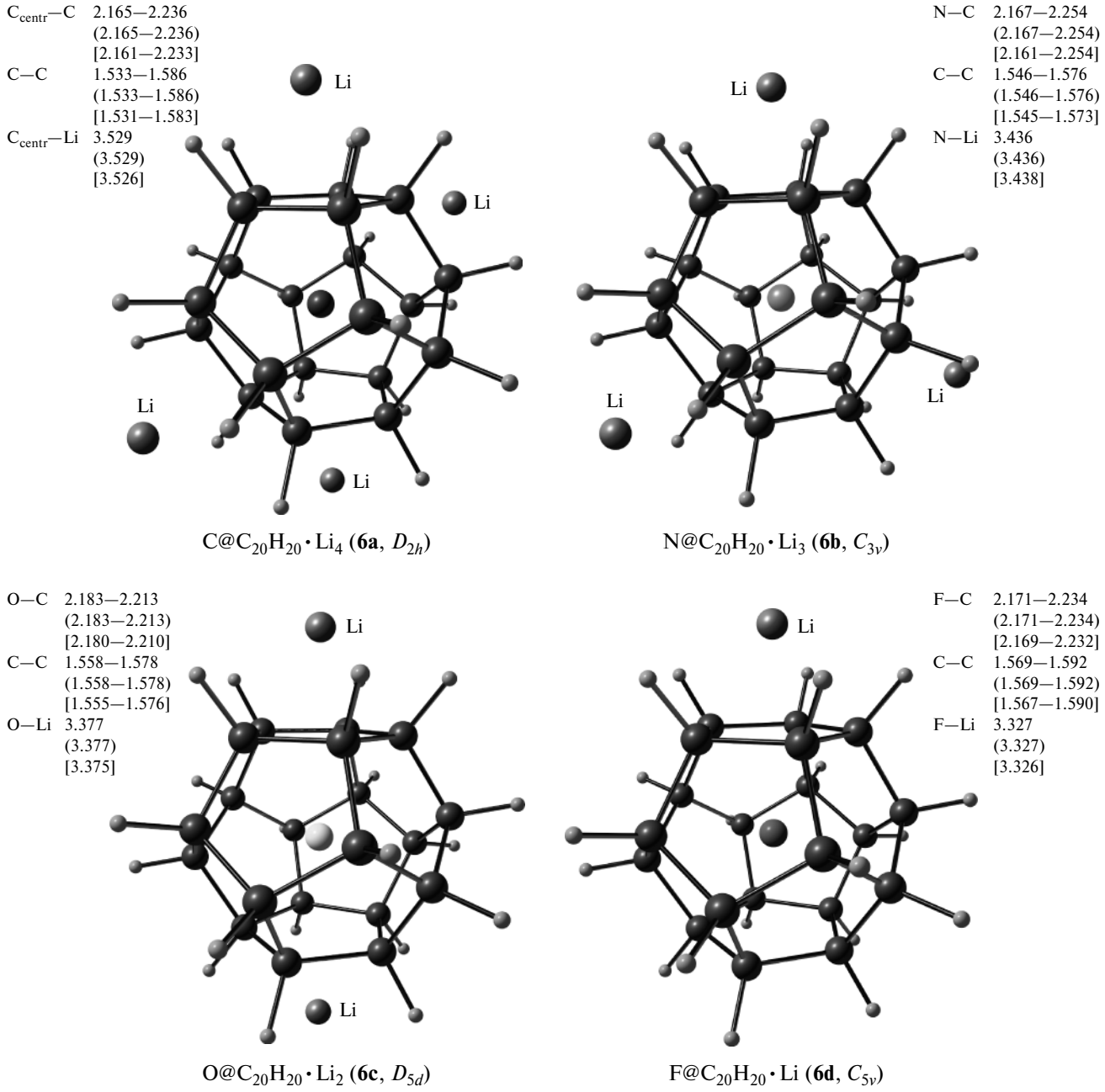
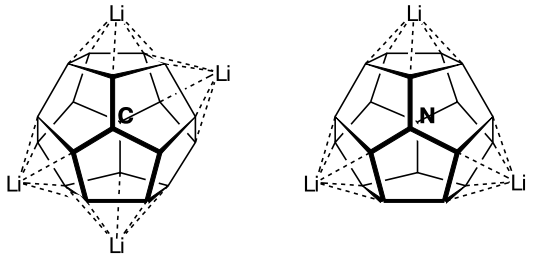


Fig. 3. Geometric parameters of complexes **6a—d** obtained from B3LYP calculations with the 6-311G(d,p), 6-311+G(d,p) (figures in parentheses), and 6-311G(df,p) basis sets (figures in brackets).

Table 2. Energy characteritics[a] of systems **6** obtained from B3LYP calculations with the 6-311G(d,p), 6-311+G(d,p), and 6-311G(df,p) basis sets

Structure (symmetry)	Basis set	$-E_{tot}$	ZPE	$-E_f$[b]	$-E_{f,ZPE}$	ω_1
6a (D_{2h})	6-311G(d,p)	841.979221	0.340322	1017.82	1006.07	33.8
	6-311+G(d,p)	841.984736	0.340345	877.83	877.49	42.2
	6-311G(df,p)	842.000943	0.340286	1017.35	1005.81	39.8
6b (C_{3v})	6-311G(d,p)	851.258868	0.347402	644.20	635.41	122.3
	6-311+G(d,p)	851.263645	0.347283	596.37	591.51	123.5
	6-311G(df,p)	851.279795	0.347201	644.63	635.94	128.3
6c (D_{5d})	6-311G(d,p)	864.372173	0.352942	338.64	334.06	155.6
	6-311+G(d,p)	864.376339	0.352749	329.96	325.34	155.9
	6-311G(df,p)	864.391778	0.352806	339.26	334.66	159.2
6d (C_{5v})	6-311G(d,p)	881.613990	0.357635	118.53	116.95	202.3
	6-311+G(d,p)	881.617485	0.357362	117.76	115.83	202.0
	6-311G(df,p)	881.632358	0.357426	118.90	117.34	205.5

[a] See note[a] to Table 1.
[b] Calculated using Eq. (3).



6a (D_{2h}) **6b** (C_{3v})

6c (D_{5d}) **6d** (C_{5v})

1.531—1.586 (**6a**), 1.545—1.576 (**6b**), 1.555—578 (**6c**), and 1.567—1.592 Å (**6d**).

In all cases the addition of Li^+ counterions to anionic complexes **5a—d** resulting in complexes **6a—d** is exothermic. The formation energies of complexes **6** calculated from the equation

$$n\,Li^+ + X@C_{20}H_{20}{}^{n-} \longrightarrow X@C_{20}H_{20}\cdot nLi, \qquad (3)$$

decrease in the order X = C > N > O > F (see Table 2). Changes in the complexation energies are independent of the number of interacting cations, namely, the interaction between the endohedral complexes and counterions becomes less efficient as the electronegativity of the central atom increases.

The degree of charge transfer from the anionic endohedral complex to lithium cations is maximum for complex **6a** (0.46 e according to NBO analysis; obtained from B3LYP/6-311G(d,p) calculations) and decreases to 0.32, 0.14, and 0.06 e for X = N, O, and F, respectively. The results of analysis of the electron density distribution according to Mulliken are consistent with this trend, but the degree of charge transfer to the lithium cations is some higher, being equal to 0.83, 0.78, 0.68 and 0.60 e for X = C, N, O, and F, respectively. These results also characterize the efficiency of the interaction between the endohedral anions **5a—d** and the lithium cations and are consistent with the changes in the formation energies of systems **6a—d**.

Thus, the results of calculations suggest the possibility of hypercoordination in polyhedral cage systems if the central atom has the closed eight-electron shell and the molecular cage is large enough. Systems **5a—d** and **6a—d** studied in this work are the first theoretically predicted stable compounds containing the atoms of the second-row elements with CN = 20.

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