

Full Articles

Stabilization of octacoordinate carbon center in metal-containing derivatives of orthocarbonic acid

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The electronic and spatial structures of alkali metal compounds CO_3M_2 , CO_3M_3^+ , and CO_4M_4 ($\text{M} = \text{Li}, \text{Na}, \text{K}$) were investigated by the *ab initio* (MP2(full)/6-311+G**) and density functional (B3LYP/6-311+G**) methods. The calculated energies of formation decrease in the order $E^{\text{Li}} > E^{\text{Na}} > E^{\text{K}}$ for all structural types, being determined by steric and orbital interactions. Stable structures with octacoordinate carbon are formed in the case of CO_4M_4 salts.

Key words: octacoordinate carbon, carbon oxoanions, orthocarbonic acid, alkali metals, quantum-chemical calculations.

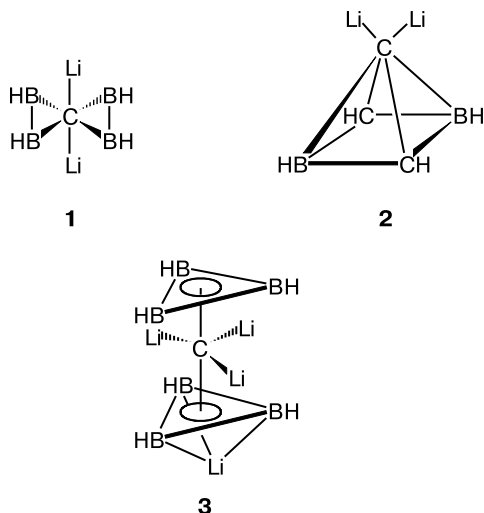
Recently, search for and studies of novel types of non-classical valence systems containing hypercoordinate atoms of main group elements have been the subject of increasing interest.^{1–9} An important problem in chemistry of hypercoordinate compounds, together with the problems of the maximum possible coordination number of an atom of a certain element and corresponding stereochemical conditions for stabilization of such systems,^{1,2,8} is the design of novel systems with unusual stereochemistry or coordination. In this respect, the best developed field is hypercarbon chemistry for which not only a variety of non-classical hypercarbon compounds have been

found but also efficient methods for the design and stabilization of such systems were developed.^{1–9}

One of the most convenient and promising approaches to the design of systems with hypercoordinate centers is based on the "induced aromaticity" effect.¹⁰ This methodology involves the incorporation of counterions (usually, lithium cations) into originally unstable anionic non-classical systems.^{1,10–13} This has been successfully implemented taking various non-classical systems including planar (1),¹¹ pyramidal (2),¹¹ and sandwich (3)¹³ structures with hypercoordinate carbon as examples.

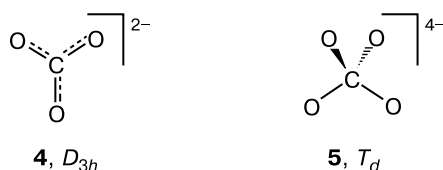
Recent studies^{2,11,13} showed that the role of the lithium counterions is not reduced to the electrostatic stabilization; they are also involved in the charge transfer processes leading to formation of a closed electron shell of

* Dedicated to Academicians A. L. Buchachenko and N. S. Zefirov on the occasions of their 70th birthdays.

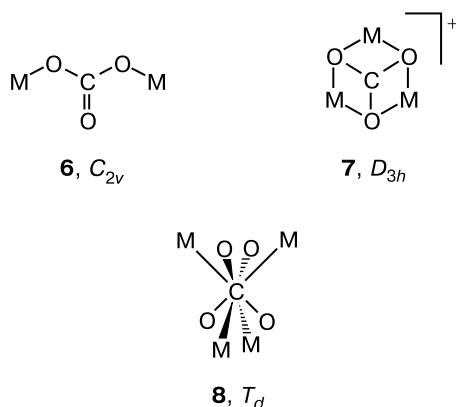


the complex being formed and to stabilization of the hypercoordinate site.

In this work we propose a new method of stabilization of systems with hypercoordinate carbon centers. It involves the interaction of alkali metal counterions with carbon oxoanions, namely, a carbonate anion CO_3^{2-} (**4**) and a CO_4^{4-} tetraanion (**5**) of hypothetical orthocarbonic acid.¹⁴



Systems **6**, **7**, and **8** ($M = \text{Li, Na, K}$) studied in this work are formed by the interaction of anions **4** and **5** with two, three, and four metal cations, respectively. For comparison, we also considered the corresponding protonated systems.



The aim of this work was to study the structural and electronic characteristics of the compounds with hypercoordinate carbon centers thus formed and to analyze the

factors responsible for stabilization of these systems and the efficiency of intramolecular interactions in them.

Calculation Procedure

Quantum-chemical calculations were carried out by the restricted Hartree–Fock (RHF) method with inclusion of correlation of all (valence and core) electrons at the second-order Møller–Plesset level [MP2(full)] of perturbation theory¹⁵ and using the density functional theory (DFT)¹⁵ with the B3LYP three-parameter potential in the 6-311+G** split-valence basis set using the Gaussian-98 program package.¹⁶ All stationary points were identified by calculating the Hessians. The topological analysis of electron density distribution according to Bader (AIM analysis)^{17,18} was performed using the AIMPAC program package.¹⁹ The MO diagrams were constructed using the EHT method²⁰ incorporated into the CACAO program.²¹ Graphic images of the molecular structures shown below were obtained using the PD program (ORTEP mode) incorporated into the PC MODEL program package.²² All calculations were carried out in the gas phase approximation without taking the solvent effect into account.

Results and Discussion

Structure and stability of CO_3^{2-} and CO_4^{4-} anions and their protonated derivatives. Structure **4** (D_{3h} symmetry) of the stable form of carbonate anion, CO_3^{2-} , corresponds to an energy minimum ($\lambda = 0$, λ is the number of negative eigenvalues of the Hesse matrix at a given point) on the potential energy surface (PES). According to both types of calculations, a hypothetical tetrahedral anion CO_4^{4-} (**5**) corresponds to an energy minimum on the PES; this is consistent with the results of earlier quantum-chemical studies.^{14,23} The structural and electronic characteristics of anions **4** and **5** are shown in Fig. 1 and their energy characteristics are listed in Table 1.

Transition from tricoordinate to tetracoordinate carbon is followed by appreciable weakening of the bonds between the carbon atom and the oxygen centers in anion **5** compared to anion **4** (C–O bonds are lengthened by ~ 0.15 Å). The first harmonic frequencies of anion **5** are lower than those of the carbonate anion, thus indirectly indicating a lower kinetic stability of the former.

Protonated forms of the carbonate anion, *i.e.*, the molecule of carbonic acid **6a** (C_{2v} symmetry) and a triquater-shaped cationic system **7a** with C_{3h} symmetry (see Fig. 1, Table 1) also correspond to an energy minima ($\lambda = 0$) on the PES. The energies of formation of compounds **6a** and **7a** were calculated as the differences between the total energies of the systems in question and the sums of the total energies of the anions and cations. According to MP2 calculations, they are 790.3 and 978.3 kcal mol^{−1}, respectively. Somewhat higher values, namely, 832.0 and 1020.7 kcal mol^{−1}, respectively, were obtained from the

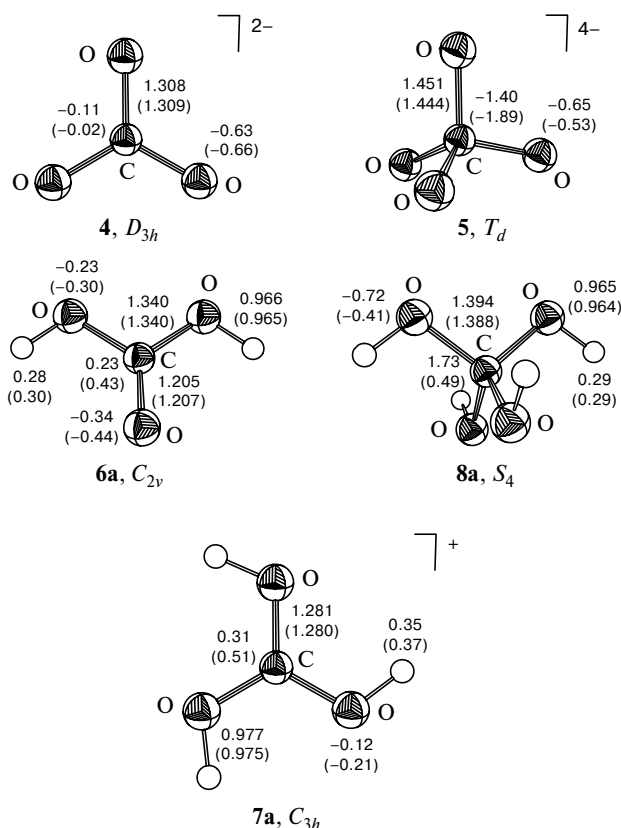


Fig. 1. Geometric characteristics and the Mulliken atomic charges for structures **4**, **5**, and **6a–8a** corresponding to energy minima ($\lambda = 0$) on the PES obtained from B3LYP/6-311+G** (DFT) and MP2(full)/6-311+G** calculations (MP2, figures in parentheses). Here and in Figs. 2–7 the bond lengths are given in Å.

density functional calculations. The calculated geometric parameters of molecule **4** ($l_{\text{CO}} = 1.308$ Å) are in good

agreement with the experimental data (1.294 Å in the CaCO_3 crystal).²⁴ Protonation of the carbonic acid molecule **6a** leads to considerable shortening of all C–O bonds in the central site, CO_3 , of system **7a** compared to the initial anion **4**.

The molecule of orthocarbonic acid **8a** has an S_4 symmetry (see Fig. 1, Table 1) and corresponds to an energy minimum ($\lambda = 0$) on the PES, which is consistent with the results of earlier studies.²⁵ The calculated energy of formation of system **8a** is 2176.9 (MP2) and 2171.7 kcal mol^{−1} (DFT).

Structure and stability of CO_3M_2 ($\text{M} = \text{Li}, \text{Na}, \text{K}$) salts. The interaction of CO_3^{2-} anion with Li^+ , Na^+ , and K^+ cations results in two types of metal derivatives similar to **6a** and **7a**. An increase in the cation size on going from acids to the alkali metal salts leads to formation of more symmetric systems in which each alkali metal cation is coordinated to two oxygen centers simultaneously.

According to calculations, the interaction of CO_3^{2-} anion with two M^+ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) cations leads to formation of salts **6b–d** with C_{2v} symmetry, which correspond to energy minima ($\lambda = 0$) on the PES. The structural and electronic characteristics of carbonates **6b–d** are shown in Fig. 2 and their energy characteristics are listed in Table 2.

The MP2 calculated energies of formation of salts **6b–d** decrease in the order $\text{Li} > \text{Na} > \text{K}$, being equal to 473.5, 410.8, and 373.2 kcal mol^{−1}, respectively. The corresponding values obtained from DFT calculations are slightly different, namely, 473.0, 413.1, and 373.4 kcal mol^{−1}. Thus, replacement of protons by alkali metal cations causes the energies of formation to be nearly halved. The formation of the metal derivatives **6b–d** is accompanied by changes in the structural characteristics of the initial dianion **4**, namely, lengthening of the C–O

Table 1. Results of DFT (B3LYP/6-311+G**) and MP2 (MP2(full)/6-311+G**) calculations of structures **4**, **5**, and **6a–8a**

Structure	Method	E_{total}	ZPE	E_{f}	ω_1
		a.u.		/kcal mol ^{−1}	/cm ^{−1}
4 , D_{3h}	DFT	−263.771044	0.013189	—	643
	MP2	−263.207662	0.013268	—	646
5 , T_d	DFT	−338.075609	0.010367	—	303
	MP2	−337.354585	0.009303	—	329
6a , C_{2v}	DFT	−265.096891	0.039605	831.98	516
	MP2	−264.467035	0.039985	790.27	490
7a , D_{3h}	DFT	−265.397693	0.051637	1020.74	524
	MP2	−264.766736	0.052362	978.33	512
8a , S_4	DFT	−341.536408	0.065744	2171.68	96
	MP2	−340.728527	0.067028	2117.18	101

Note. $\lambda = 0$ is the number of negative eigenvalues of the Hessian; ZPE is the zero-point vibrational energy; E_{f} is the energy of formation of the complex; 1 a.u. = 627.5095 kcal mol^{−1}; and ω_1 is the lowest harmonic vibrational frequency.

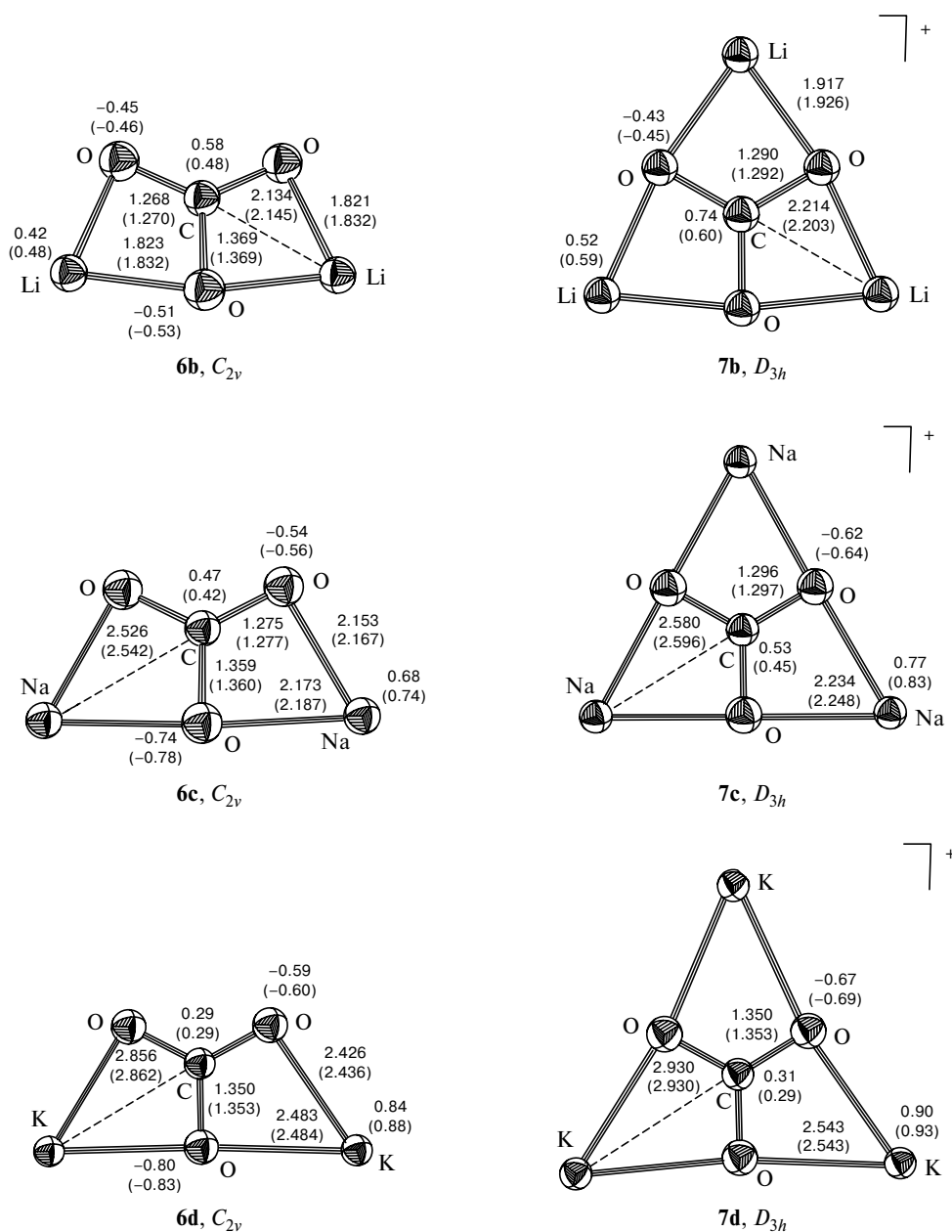


Fig. 2. Geometric characteristics and the Mulliken atomic charges for structures **6b–d** and **7b–d** corresponding to energy minima ($\lambda = 0$) on the PES obtained from B3LYP/6-311+G** (DFT) and MP2(full)/6-311+G** calculations (MP2, figures in parentheses).

bonds aligned with the symmetry axes and shortening of two other C—O bonds. These structural changes are most pronounced in the case of the lithium derivative where the central C—O bond is lengthened by ~ 0.06 Å and the other two C—O bonds are shortened by ~ 0.04 Å (see Fig. 2). According to MP2 calculations, the interatomic distances C—M in salts **6b–d** are ~ 2.145 , 2.542 , and 2.862 Å for M = Li, Na, and K, respectively, being slightly longer than the corresponding ordinary bonds C—M. The results of the DFT calculations of the interatomic distances C—M are consistent with those obtained at the MP2 level of theory.

Salts **6b–d** are characterized by a considerable degree of electron density transfer from anions to the alkali metal cations. Electron-density donation is most pronounced in the case of lithium carbonate ($\sim 1.2e$), which indicates a marked contribution of the covalent component to stabilization of this system. The degree of electron density transfer in the sodium and potassium carbonates is much lower ($\sim 0.6e$ and $\sim 0.3e$, respectively). The results of the AIM analysis¹⁹ of the electronic structures of salts **6** (Fig. 3) show that in spite of rather short interatomic distances C—M the alkali metal counterions are bonded to the oxygen centers only and that valence bonding be-

Table 2. Results of DFT (B3LYP/6-311+G**) and MP2 (MP2(full)/6-311+G**) calculations of structures **6b–d**, **7b–d**, **8b–d**, **9**, and **10b–d**^a

Structure, symmetry	Method	E_{total}	ZPE	E_{form}	λ	ω_1^b
		a.u.		/kcal mol ⁻¹		/cm ⁻¹
6b , C_{2v}	DFT	-279.094608	0.019952	472.97	0	181
	MP2	-278.458916	0.020135	473.49	0	174
6c , C_{2v}	DFT	-588.604447	0.017335	413.07	0	114
	MP2	-587.450584	0.017505	410.79	0	105
6d , C_{2v}	DFT	-1463.888231	0.016430	373.42	0	79
	MP2	-1462.337570	0.016599	373.18	0	61
7b , D_{3h}	DFT	-286.504536	0.021780	551.42	0	181
	MP2	-285.833594	0.022076	552.76	0	186
7c , D_{3h}	DFT	-750.814571	0.018718	489.97	0	107
	MP2	-749.368604	0.018948	488.52	0	101
7d , D_{3h}	DFT	-2063.759424	0.017524	442.53	0	77
	MP2	-2061.719163	0.017726	444.71	0	75
8b , T_d	DFT	-369.485311	0.025952	1424.47	0	213
	MP2	-368.616976	0.026550	1423.82	0	240
8c , T_d	DFT	-988.506525	0.021966	1305.62	0	134
	MP2	-986.600785	0.022437	1298.70	0	141
8d , T_d	DFT	-2739.057266	0.020089	1215.76	0	92
	MP2	-2736.363423	0.020516	1216.38	0	99
9 , T_d	DFT	-369.329668	0.026298	1326.80	0	100
	MP2	-368.443714	0.026185	1315.09	0	89
10b , D_{2d}	DFT	-369.490747	0.028416	1427.90	0	86
	MP2	-368.615442	0.028880	1422.85	0	93
10c , D_{2d}	DFT	-988.461895	0.021862	1277.64	1	i38
	MP2	-986.547206	0.022192	1265.08	1	i44
10d , D_{2d}	DFT	-2739.003920	0.019877	1182.31	1	i37
	MP2	-2736.296783	0.020305	1174.56	1	i42

^a See notes to Table 1.^b The lowest or imaginary harmonic vibrational frequency.

tween the central carbon atom and counterions in systems **6** does not occur.

Structure and stability of complexes CO_3M_3^+ ($\text{M} = \text{Li}, \text{Na}, \text{K}$). The interaction of CO_3^{2-} anion with three M^+ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) cations leads to formation of charged complexes CO_3M_3^+ (**7b–d**) with D_{3h} symmetry, which correspond to energy minima ($\lambda = 0$) on the PES. Similarly to the preceding case, the calculated energies of formation of complexes **7b–d** (see Fig. 2, Table 2) decrease in the order Li, Na, K, being respectively equal to 552.8, 488.5, and 444.7 kcal mol⁻¹ (MP2) and 551.4, 490.0, and 442.5 kcal mol⁻¹ (DFT).

As for cation **7a**, the formation of the lithium and sodium complexes **7b** and **7c** causes the C–O bonds to be slightly shortened (by ~0.02 and ~0.01 Å, respectively) compared to the initial dianion. Contrary to this, the formation of the potassium complex **7d** is accompanied by a marked elongation of the C–O bond (~0.04 Å). The calculated lengths of the bonds between counterions and oxygen centers increase in the order Li, Na, K, being somewhat longer than in corresponding complexes **6**. The

C–M interatomic distances in complexes **7b–d** are also appreciably longer (by ~0.1 Å) than in complexes **6b–d**.

The MO analysis of the structure of complexes **7b–d** showed that electron-density donation from the filled C–O bond orbitals, σ_{CO} , and p-orbitals of the oxygen centers to the vacant s-orbitals of the alkali metal cations (Fig. 4) is the key attractive component in the formation of these systems.

An increase in the energies of the valence s-orbitals in the order Li^+ , Na^+ , K^+ leads to broadening of the energy gap between the interacting fragment orbitals and to weakening of the orbital interaction in the same order; this is consistent with the trend to a decrease in the energies of formation of the corresponding complexes. Yet another reason for weakening of the orbital interaction in the order Li^+ , Na^+ , K^+ is the increase in the cation size, which makes the planar systems more sterically strained and precludes efficient orbital overlap. Thus, the lithium complex **7b** provides the most favorable structural and orbital conditions for the interaction between anions and cations, which is substantiated by the highest energy of

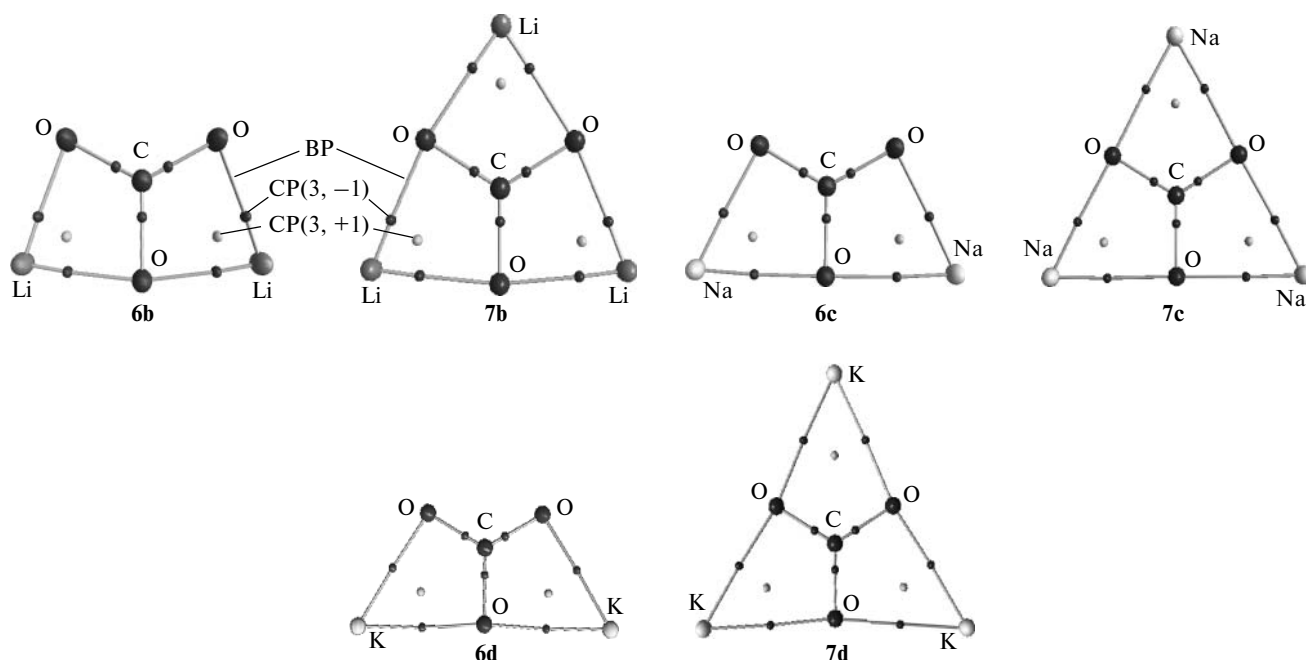


Fig. 3. Bader molecular graphs of structures **6b–d** and **7b–d** (BP denotes the bond path according to Bader, CP (3; –1) is the bond path stationary point, and CP (3, +1) is the ring stationary point).

formation of the lithium derivative. On the contrary, the potassium counterion has the smallest stabilizing effect.

Conclusions drawn based on the results of the MO analysis are confirmed by the electron density distribution in complexes **7b–d**. According to calculations, the de-

gree of electron density transfer from the dianion to cations in complexes **7b–d** decreases in the order Li, Na, K, being lower than in the carbonates **6**. As in the salts **6**, only the lithium derivative **7b** is characterized by a high degree of electron density donation from the anion to

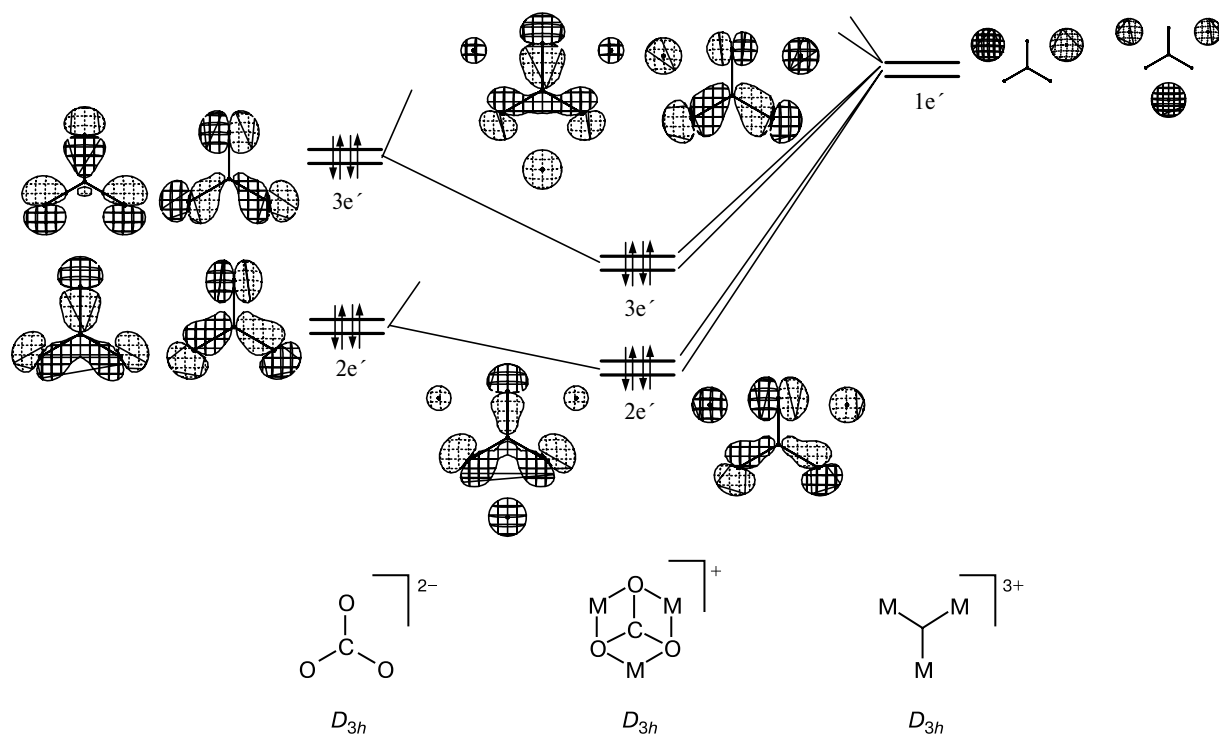


Fig. 4. Scheme of formation of the main stabilized MOs of system **7** from the fragment MOs of CO_3^{2-} anion and M_3^{3+} group orbitals.

counterions ($\sim 1.2e$), which indicates a rather large contribution of covalent bonding in this system. On the contrary, the degree of electron density transfer in the potassium complex **7d** is very low, which allows this complex to be treated as an ionic compound.

In spite of rather short interatomic distances C—M, the AIM analysis of complexes **7b–d** revealed no valence interaction between the central carbon atom and counterions (see Fig. 3).

Structure and stability of salts CO_4M_4 ($\text{M} = \text{Li}, \text{Na}, \text{K}$). The orthocarbonic acid salts **8b–d** have a T_d symmetry and correspond to energy minima ($\lambda = 0$) on the PES.

Similarly to carbonates, an increase in the cation size on going to alkali metals leads to formation of more symmetric (compared to the acid) systems with increased coordination numbers of the counterions. However, unlike the derivatives **6b–d** and **7b–d** with dicoordinate alkali metals, the more favorable stereochemical conditions in salts **8b–d** allow each counterion to be coordinated to three oxygen centers simultaneously.

As in the preceding cases, the calculated energies of formation of complexes **8b–d** (Fig. 5, Table 2) decrease in the order Li, Na, K, being respectively equal to 1423.8, 1298.7, and 1216.4 kcal mol $^{-1}$ (MP2) and to 1424.5,

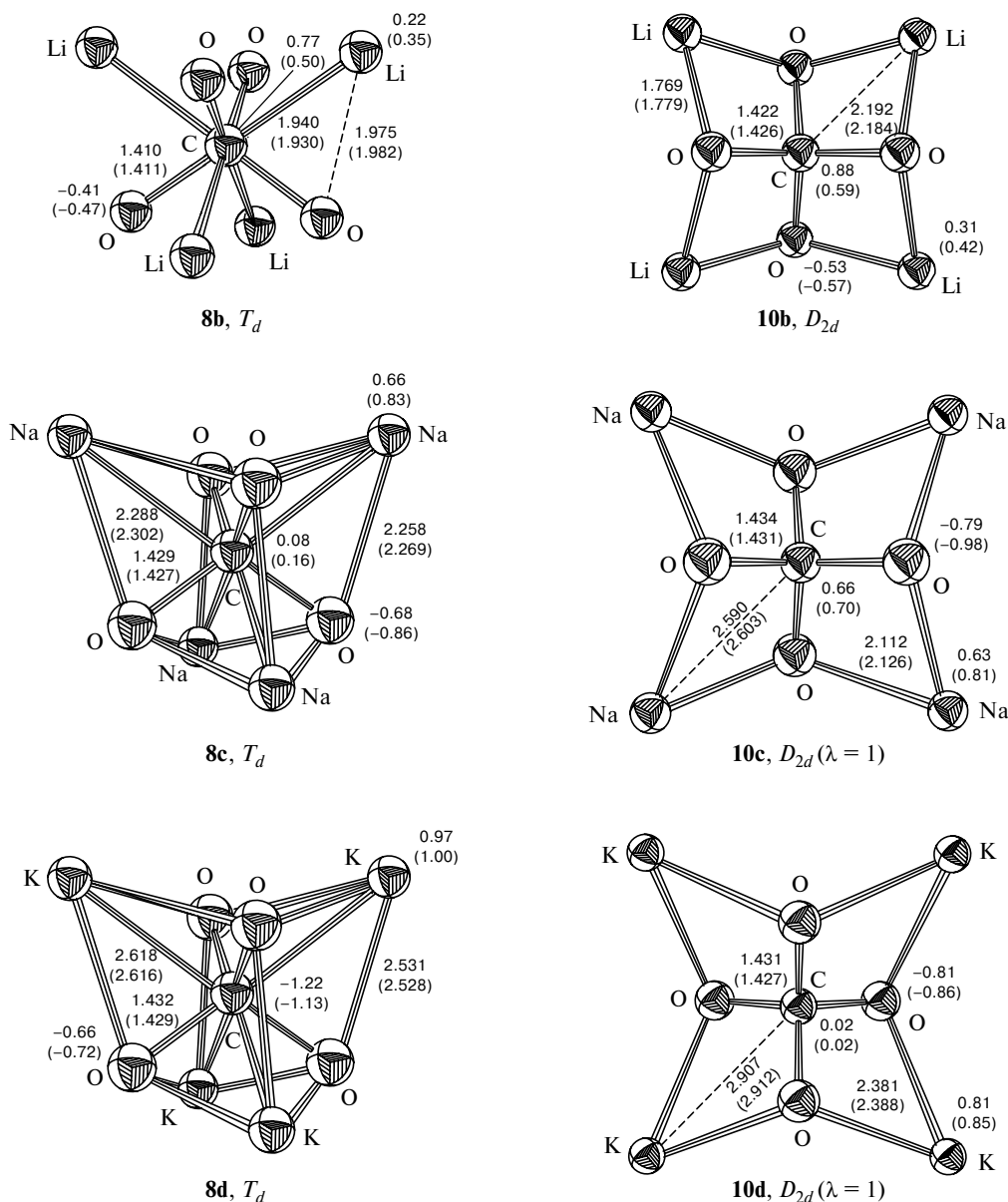


Fig. 5. Geometric characteristics and the Mulliken atomic charges for structures **8b–d** and **10b** corresponding to energy minima ($\lambda = 0$) on the corresponding PESs and for structures **10c–d** corresponding to the first-order saddle points ($\lambda = 1$) obtained from B3LYP/6-311+G** (DFT) and MP2(full)/6-311+G** (MP2, figures in parentheses) calculations.

1305.6, and 1215.8 kcal mol⁻¹ (DFT). The C—O bonds in complexes **8b–d** are shorter than those in the free CO₄⁴⁻ anion. The shortening is maximum for the lithium complex (~0.04 Å, *cf.* ~0.02 Å for the sodium and potassium complexes). As in the free anions **4** and **5**, the C—O bonds in tetrahedral systems **8** are much weaker than in **6**. Namely, the C—O bonds in the lithium and sodium derivatives are ~0.15 and ~0.13 Å longer, respectively, while for the potassium derivative weakening of the bonds between the carbon atom and oxygen centers is less pronounced (~0.08 Å).

The results of the MO analysis show that, similarly to systems **7b–d**, stabilization of systems **8b–d** is due to electron density donation from the filled orbitals of the C—O σ-bonds and the orbitals of the lone electron pairs of the oxygen centers to vacant s-orbitals of the alkali metal cations (Fig. 6).

A trend to lowering the relative stability of salts **8** in the order Li, Na, K is due to factors similar to those considered above for the systems **7**. At the same time the

orbital interaction in the tetrahedral derivatives **8** is much more efficient than in the planar complexes **7** as a result of a more favorable spatial structure of salts **8**. Enhancement of the orbital interaction effects is accompanied by an increase in the degree of electron density transfer from anion to cation on going from systems **7** to systems **8**. The degree of charge transfer in salts **8** decreases in the order Li, Na, K. The lithium derivative is characterized by the highest degree of electron density donation and the potassium salt is characterized by a very small degree of electron density transfer (see Fig. 5). This situation is similar to that found in the systems discussed above.

Among all alkali metal derivatives, salts **8b–d** have the highest energies of formation and the shortest bonds between the central carbon atom and counterions, namely, ~1.9 (Li), 2.3 (Na), and 2.6 Å (K). These values fall in the range of covalent bond lengths. The results of the AIM analysis (Fig. 7) confirm the occurrence of a valence bonding C—M in systems **8b–d**. Thus, the carbon atoms in salts **8b–d** are octacoordinate. It is noteworthy that al-

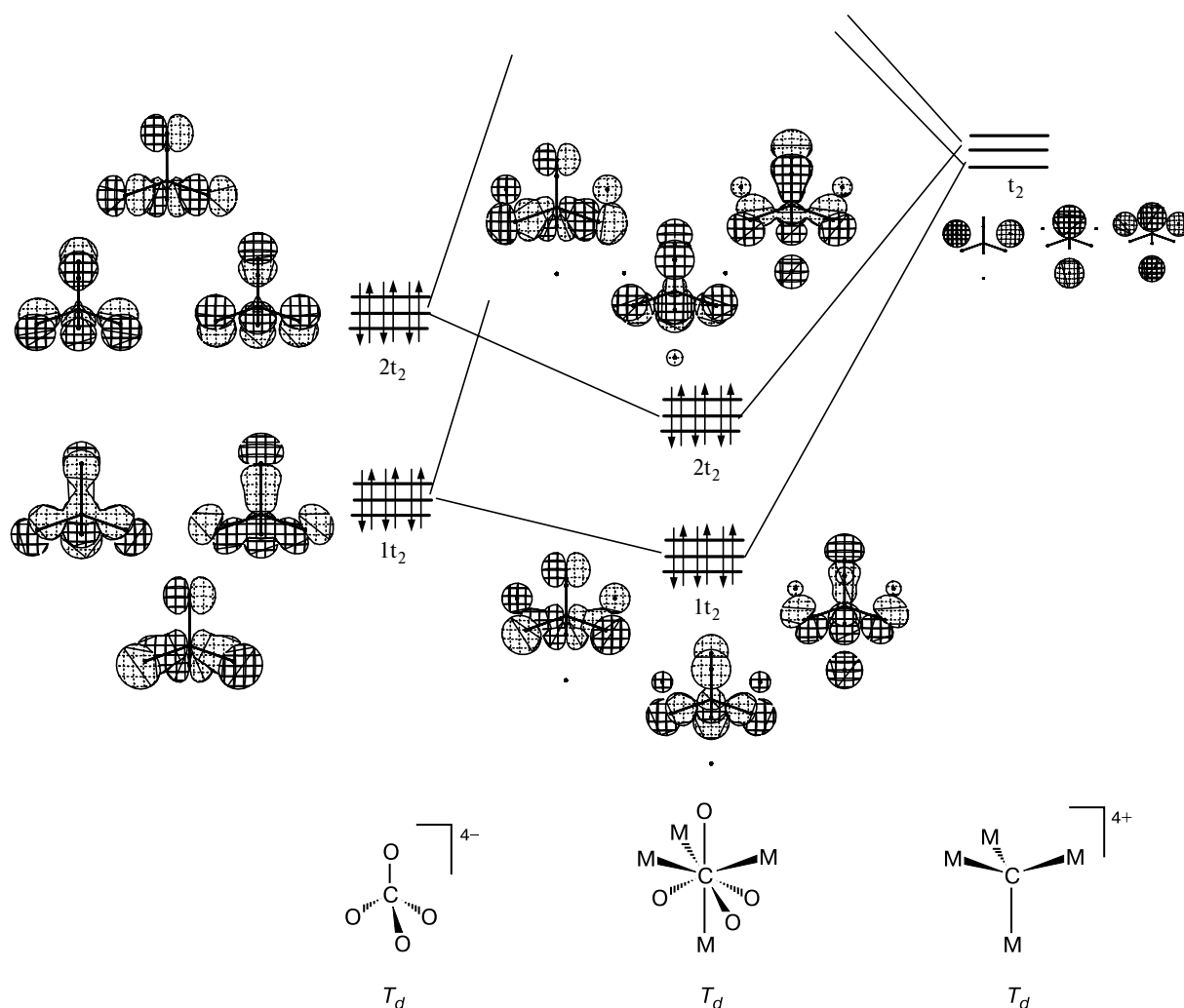


Fig. 6. Scheme of formation of the main stabilized MOs of system **8** from the fragment MOs of CO₄⁴⁻ and M⁴⁺ group orbitals.

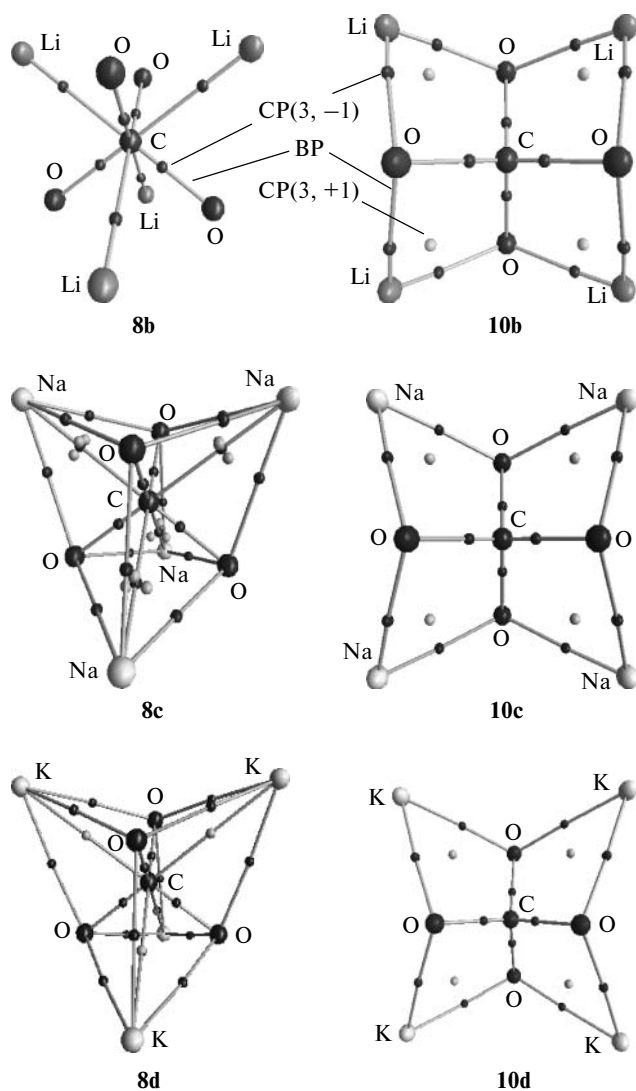
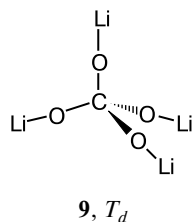


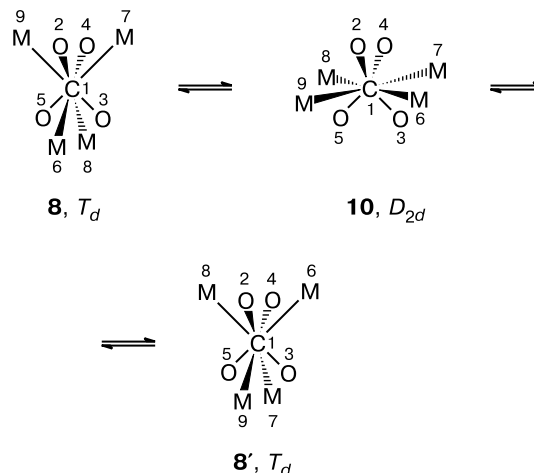
Fig. 7. Bader molecular graphs for structures **8b–d** and **10b–d** (for notations, see caption to Fig. 3).

though the counterions in complexes **8b–d** are formally coordinated to three oxygen centers, the AIM analysis of the lithium derivative **8b** revealed no valence interactions O–M. An increase in the cation size on going to sodium and potassium enhances the coordination capabilities of the counterions and the cations in systems **8c** and **8d** are tetracoordinate (see Fig. 7).

According to calculations, there is yet another energy minimum ($\lambda = 0$) on the PES of the CO_4Li_4 system, corresponding to isomer **9** with T_d symmetry and monocoordinate lithium atoms that interact with oxygen centers only. But system **9** is more than $100 \text{ kcal mol}^{-1}$ destabilized relative to isomer **8b**.



A polytopic rearrangement $\mathbf{8} \rightleftharpoons \mathbf{10} \rightleftharpoons \mathbf{8}'$ can occur in complexes **8**. It involves inversion and simultaneous rotation of the tetrahedral site, CM_4 , about the twofold axis and proceeds *via* an intermediate structure **10** with D_{2d} symmetry (see Fig. 5, Table 2).



If $M = \text{Li}$, structure **10** corresponds to a minimum ($\lambda = 0$) on the PES. The energies of the isomers **8b** and **10b** differ only slightly, namely, the former is $\sim 1 \text{ kcal mol}^{-1}$ more stable than the latter according to MP2 calculations. The reverse is predicted by the DFT calculations, *viz.*, isomer **10b** is $3.4 \text{ kcal mol}^{-1}$ more stable than isomer **8b**. An increase in the radius of the metal atom on going to sodium and potassium makes the planar CM_4 site in structure **10** more strained and leads to destabilization of this structure; unlike the lithium compound, structures **10** of the sodium and potassium derivatives correspond to transition states ($\lambda = 1$) on the PES. The barrier to rearrangement $\mathbf{8} \rightleftharpoons \mathbf{10} \rightleftharpoons \mathbf{8}'$ is 28.0 (DFT) and $33.6 \text{ kcal mol}^{-1}$ (MP2) for the sodium complex, being even higher, *viz.*, 33.5 (DFT) and $41.8 \text{ kcal mol}^{-1}$ (MP2) for the potassium complex.

The calculated interatomic distances O–M in structures **10b–d** are appreciably shorter (by $\sim 0.15\text{--}0.21 \text{ \AA}$), whereas the C–M distances are considerably longer, by $\sim 0.25\text{--}0.30 \text{ \AA}$, than those in complexes **8b–d**. These changes in the structural parameters on going from complexes **8b–d** to complexes **10b–d** are also substantiated by the results of the AIM analysis (see Fig. 7), according to which the metal atoms in all systems **10b–d** are dicoordinate and involved in valence bonding only with the nearest oxygen atoms, whereas the carbon atoms are tetracoordinate as usually.

Thus, structures **8** considered in this work are representatives of a novel type of stable neutral non-classical compounds with octacoordinate carbon center. According to our calculations, carbon oxoanions provide a convenient structural framework for the formation of hypercoordinate sites involving counterions. The lithium de-

rivatives are characterized by the most efficient stabilization due to the mutual effect of steric and orbital factors.

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