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$K(CO)_8^-$ and $Rb(CO)_8^-$: Cube-Like Alkali Octacarbonyls Satisfying the 18-Electron Rule

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Abstract

Inspired by recent discoveries of alkaline-earth octacarbonyls and based on extensive first-principles theory investigations, we predict herein the possibility of perfect cube-like alkali octacarbonyls $M(CO)_8^-$ (O_h , ${}^3A_{1g}$) (1) (M = K, Rb) which satisfy the 18-electron rule in an octacoordinate cubic field with (n - 1)d-orbital participation of alkali metal center playing an important role in M–CO coordination interaction. The slightly elongated neutral $M(CO)_8$ (D_{4h} , ${}^2B_{1g}$) (3) turn out to be similar with the experimentally observed $Ba(CO)_8^+$ monocation in an octacoordinate tetragonal field. Detailed orbital analyses indicate that, similar to neutral alkaline-earth octacarbonyls, $M(CO)_8^-$ monoanions possess the superatomic electronic configuration of $S^2P^6D^8F^2$, with the alkali–CO coordination interaction mainly originating from $M(d_{\pi}) \rightarrow (CO)_8(\pi^*)$ backdonations which result in strong red shifts of the C–O stretching frequencies relative to free CO.

Keywords First-principles theory · Alkali octacarbonyls · Geometrical structures · Electronic structures · Spectral simulations

Introduction

It is well known in chemistry that transition metals with the valence electronic configurations of $[ns^2np^0(n-1)d^{1-10}]$ (n represents the principal quantum number) form stable carbonyl complexes satisfying the 18-electorn rule, as typically exemplified by Fe(CO)₅, Cr(CO)₆, and Ni(CO)₄ [1]. The particular stabilities of such carbonyl complexes originate from their fulfilled *spd* valence shells which facilitate the formation of synergic σ -donation from the carbon lone-pair 5σ orbital (the highest occupied

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molecular orbital (HOMO) of CO) to metal center and π backdonation of electron density from the $(n-1)d_{\pi}$ orbitals of the transition-metal center into the $2\pi^*$ antibonding orbitals of CO ligands [2-5]. The recent discoveries of alkaline-earth octacarbonyls Ca(CO)₈, Sr(CO)₈, and Ba(CO)₈ in low-temperature neon matrix show that alkaline-earth metals with the valence electronic configuration of $[ns^2np^0(n-1)d^0]$ also form stable octacarbonyl complexes matching the 18-electron rule, with (n - 1)dorbital participation of the alkaline earth center playing a dominant role in metal-CO coordination interaction [6]. Detailed first-principles theory analyses indicate that effective $[M(d_{\pi})] \rightarrow (CO)_8(\pi^*)$ backdonations result in the strong red shifts of C-O stretching frequencies relative to free CO in the measured IR spectra of alkaline-earth octacarbonyls [6, 7]. Recent observations of unusual structures and reactivities of calcium and strontium compounds provide further evidence that *d*-orbital participation of the alkaline-earth metals plays an important role [8, 9]. However, to the best of our knowledge, it still remains unknown to date whether other heavy s-block elements beyond alkaline-earth metals in the periodical table can form effective metal-ligand coordination interaction and if the 18-electron rule can be applied to alkali metals with the

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valence electron configuration of $[ns^{1}np^{0}(n-1)d^{0}]$. We speculate that, as the lighter neighbors of alkaline-earth metals, heavy alkali metals could also form alkali octacarbonyls following the 18-electron rule, with *d*-orbital participation from the alkali center playing an important role in alkali–CO coordination bonding.

Based on extensive first-principles theory calculations, we propose herein the possibility of alkali octacarbonyl monoanions $M(CO)_8^-$ (1) $(O_h, {}^3A_{1g})$ (M = K, Rb) which match the 18-electron rule with (n - 1)d-orbital participation of alkali metal center playing a dominant role in M– CO coordination bonding. Neutral $M(CO)_8$ $(D_{4h}, {}^2B_{2g})$ (3) appear to be alkali analogs of the experimentally observed $Ba(CO)_8^+$ monocation. In both $M(CO)_8^-$ monoanions and $M(CO)_8$ neutrals, alkali–CO coordination interactions mainly originate from the $M(d_\pi) \rightarrow (CO)_8(\pi^*)$ backdonations which result in strong red shifts of the C–O stretching frequencies relative to free CO.

Theoretical procedure

We performed extensive calculations on alkali octacarbonyls $M(CO)_8^{-/0}$ (M = K, Rb) employing the density functional theory (DFT) methods to determine their ground-state geometrical and electronic structures and to simulate their electronic and vibrational spectra. Full structural optimizations were achieved using the hybrid M06-2X-D3 approach [10, 11] in conjunction with the def2-QZVPP basis sets [12, 13] implemented in Gaussian09 suite. [14] Scalar-relativistic effective core potential was included for the core electrons of Rb [15]. Frequency analyses were performed to make sure all the optimized structures are true minima of the systems. This approach well reproduced the main results obtained in Ref.6 for alkaline-earth octacarbonyls at M06-2X-D3/def2-TZVPP level and generated consistent high-symmetry geometries for the whole $M(CO)_8^{-/0}$ (M = K, Rb) series, evidencing the reliability of the M06-2X-D3/def2-QZVPP method employed in this work. The photoelectron spectroscopies (PES) of $M(CO)_8^-$ monoanions were simulated using the time-dependent TD-DFT method [16] at M06-2X-D3/def2-QZVPP level. Figure 1 and Fig. 2 depict the optimized geometrical and electronic structures of the most concerned $O_h \operatorname{M}(\operatorname{CO})_8^-(1), D_{4h} \operatorname{M}(\operatorname{CO})_8^-(2)$, and $D_{4h} \operatorname{M}(\operatorname{CO})_8(3)$ and Fig. 3 simulates the IR, Raman, and PES spectra of O_h $K(CO)_8^-$ (1). Table 1 tablets the calculated bond lengths, bond orders, and CO stretching frequencies of $O_h M(CO)_8^-$ (1) and D_{4h} M(CO)₈ (3) (M = K, Rb), in comparison with that of O_h Ca(CO)₈ and Sr(CO)₈ at M06-2X-D3/def2-QZVPP.

Results and discussion

As speculated, similar to the experimentally observed neutral $Ca(CO)_8$ and $Sr(CO)_8$ [6], the isovalent alkali octacarbonyl monoanions $M(CO)_8^-$ (1) $(O_h, {}^3A_{1g})$ (M = K, Rb) possess perfect cube-like geometries with O_h symmetry in a triplet ground state $({}^{3}A_{1g})$ with the electronic configuration of $a_{1g}^2 t_{1u}^6 t_{2g}^6 a_{2u}^2 e_g^2$ (Figs. 1 and 2). M(CO)₈⁻ (1) have the calculated bond lengths of $r_{M-CO} = 2.86$ and 3.04 Å and $r_{C-O} = 1.13$ and 1.13 Å for M = K and Rb, respectively, with r_{M-CO} coordination bond lengths slightly longer than the sums of the single-bond radii of M and C (2.71 and 2.85 Å for M = K and Rb) and r_{C-O} triple bond lengths exactly the same as sum of the triple-bond radii of C and O (1.13 Å) [17]. These values are also well in line with the corresponding calculated bond lengths of $Ca(CO)_8$ and $Sr(CO)_8$ at the same theoretical level (Table 1). The slightly elongated singlet $M(CO)_8^ (D_{4h}, {}^1A_{1g})$ (2) turn out to be the second lowest-lying isomers of the monoanions with the electronic configuration of $a_{1g}^2 a_{2u}^2 e_u^4 e_g^4 b_{1g}^2 b_{2u}^2 a_{1g}^2$ in an octacoordination tetragonal field (Fig. 2). With zeropoint corrections included, D_{4h} M(CO)⁻₈ (2) are 0.30 and 0.16 eV less stable than the corresponding triplet O_h global minima at M06-2X-D3 for M = K and Rb, respectively. The optimized staggered singlet $M(CO)_8^ (D_{4d}, {}^2A_1)$ as the third lowest-lying minima lie 0.32 and 0.17 eV higher in energy than the O_h global minima for M = K and Rb (Figure S1). Ground-state $M(CO)_8^-$ (1) turn out to have the calculated formation energies of $\Delta E_f = -44.5$ and - 36.7 kcal/mol with respect to M + 8CO + $e=M(CO)_8^{-1}$ at M06-2X-D3 for M = K and Rb, respectively. These values occupy about two-thirds of the calculated formation energies of Ca(CO)₈ and Sr(CO)₈ observed in a low-temperature neon matrix [6] at M06-2X-D3 level (Table 1). Similar O_h Cs(CO)⁻₈ and D_{4h} Cs(CO)⁻₈ structures are obtained for $Cs(CO)_8^-$ at the same theoretical level as shown in Figure S2.

Detaching one electron from a $M(CO)_8^-$ monoanion produces the doublet ground state of eclipsed neutral $M(CO)_8$ (3) $(D_{4h}, {}^2B_{2g})$ which, with the same D_{4h} symmetry as singlet D_{4h} $M(CO)_8^-$ (2), have the calculated formation energies of $\Delta E_f = -29.7$ and -24.0 kcal/mol for M = K and Rb with respect to M + 8CO = $M(CO)_8$, respectively. Neutral $M(CO)_8$ (3) with the electronic configuration of $a_{1g}^2 e_u^4 b_{1g}^2 a_{2u}^2 e_g^4 b_{2u}^2 b_{2g}^1$ turn out to have similar geometries with the sovalent D_{4h} Ba(CO)_8⁺ monocation observed in infrared photodisocciation (IR-PD) measurements [6] due to Jahn–Tellor distortion. $M(CO)_8$ (3) possess slightly longer M–CO coordination distances than $M(CO)_8^-$ (1), with C–O bond lengths remained practically unchanged (Fig. 1). A 45° rotation of four CO ligands on the top of $M(CO)_8$ (3) around the C_4 molecular axis



Fig. 2 Molecular orbital energy levels of **a** triplet $K(CO)_8^-$ (O_h , ${}^3A_{1g}$), **b** singlet $K(CO)_8^-$ (D_{4h} , ${}^1A_{1g}$), and **c** doublet $K(CO)_8$ (D_{4h} , ${}^2B_{2g}$) at M06-2X-D3/def2-QZVPP level

generates the staggered singlet D_{4d} M(CO)₈ which are almost iso-energetic with D_{4h} M(CO)₈ (**3**) (Figure S3). It is noticed that, although M(CO)₈⁻ (**1**) monoanions possess slightly positive singly occupied molecular orbital (SOMO) energies (~+0.10 eV) which can be effectively stabilized by incorporation of a counteraction (like Li⁺) into the system, neutral M(CO)₈ (**3**) have significantly negative SOMO energies of -3.49 and -3.36 eV for M = K and Rb, respectively. These values are well comparable with the corresponding SOMO energies of -4.67 and -4.44 eV calculated for the observed Ca(CO)₈ and Sr(CO)₈ [6] at the same theoretical level.

With eight equivalent CO ligands at the eight corners of a perfect cube and one alkali metal coordinated at the center, $O_h M(CO)_8^-$ (1) (M = K, Rb) behave like a superatom in both electronic structures and bonding patterns. According to the energetic sequence and the nodal shape of the molecular orbitals (MOs), a series of superatomic orbitals in the sequence of S², P⁶, D⁸, and F² can be clearly identified in $M(CO)_8^-$ (1), that is S², P²_x, P²_y, P²_z, D²_{xy}, D²_{xz}, D²_{yz}, F²_{xyz}, D¹_{x2-y2}, and D¹_{z2} in specific orbital occupations (Fig. 2) [18–21]. These superatomic MOs can be classified into two groups, a σ group including S², P_x², P_y², P_z², D_{xy}², D_{xz}^2 , D_{yz}^2 , and F_{xyz}^2 and a π group encompassing D_{x2-y2}^1 and D_{z2}^{1} (Fig. 2). Such a superatomic description can also be applied to the isovalent $Ca(CO)_8$, $Sr(CO)_8$, and $Ba(CO)_8$ in which the metal-carbon monoxide coordination interaction mainly arises from $M(d_{\pi}) \rightarrow (CO)_8(\pi^*) \pi$ backdonations $(D_{x^2-v^2}^1)$ and $D_{z^2}^1$, with the σ -group containing basically ligand-only MOs [6]. We address the following concerns to interpret the electronic structures and bonding motifs of the concerned alkali octacarbonyl complexes. First, similar to $Ca(CO)_8$ and $Sr(CO)_8$, the two degenerate SOMOs D_{x2-v2} and D_{z2} (e_g) of M(CO)₈⁻ (1) are occupied by two electrons in the same spin in an octacoordinate cubic (O_h) field, resulting in two singly occupied SOMOs $(D_{x2-y2}^1 \text{ and } D_{z2}^1)$ in Hund's rule which define the ${}^{3}A_{1g}$ triplet electronic ground state of the system. Detailed natural bonding orbital (NBO) [22] analyses indicate that the d atomic orbitals (d_{z2}) and d_{x2-v2}) of K and Rb contribute 11.9% and 13.6% to the singly occupied degenerate superatomic MOs (D_{z2}^1) and D_{x2-y2}^1 of $M(CO)_8^-$ (1), respectively (Table 1). The



Fig. 3 Simulated **a** IR, **b** Raman, and **c** PES spectra of $O_h \text{ K}(\text{CO})_8^-$ (1) at M06-2X-D3/def2-QZVPP. The IR and Raman spectra are scaled by a factor of 0.941. The little red bars stand for the calculated peak positions (Color figure online)

Table 1 Calculated bond lengths r_{M-CO}/r_{C-O} , formation energies $\Delta E_{\rm f}$, *d*-orbital contribution to π -backdonations, total Wiberg bond indexes WBI_M, Wiberg coordination bond orders WBI_{M-CO}, C–O asymmetrical stretching vibrational frequencies v_{C-O} , and red shifts

observed Ca(CO)₈ and Sr(CO)₈ in which the metal-CO coordination bonds have proven to mainly arise from $[M(d_{\pi})] \rightarrow (CO)_8(\pi^*)$ backdonation [6], evidencing the important role the *d*-orbital participation of the alkali centers play in M-CO coordination in $M(CO)_8^-$ (1) and $M(CO)_8$ (3). Second, 2 of the 18 valence electrons occupy the non-degenerate superatomic MO F_{xyz} (a_{2u}) in M(CO)₈⁻ (1) which is ligand-only without contribution from the alkali metal center. There have therefore 18 - 2 = 16electrons in the *spd* valence shells of the system, with the two degenerate π -HOMOs (D_{x2-v2} and D_{z2}) involving dparticipation of the metal center singly occupied. Thus, although both alkali octacarbonyls $M(CO)_8^-$ (1) and alkaline-earth octacarbonyls $Ca(CO)_8$ and $Sr(CO)_8$ [6] formally possess 18 valence electrons related with M-CO coordination interactions (including 16 electrons in the partially filled superatomic $S^2P^6D^8$ valence shells and 2 electrons in the fulfilled ligand-only F_{xyz}^2), they are different in electronic structures from classic 18-electron transition metal carbonyls like $Fe(CO)_5$, $Cr(CO)_6$, and $Ni(CO)_4$ which possess 18 electrons to fulfil the $s^2p^6d^{10}$ valence shells of the metal center. Third, slight elongation in either x, y, or z direction effectively eliminates the eg degeneracy in triplet $O_h \operatorname{M}(\operatorname{CO})_8^-$ (1) to produce the singlet $D_{4h} \operatorname{M}(\operatorname{CO})_8^-$ (2) in an octacoordinate tetragonal field (Fig. 1). As shown in Fig. 2, D_{4h} M(CO) $_8^-$ (2) possess the superatomic electronic configuration of $S^2 P_x^2 P_y^2 P_z^2 D_{xy}^2 D_{xz}^2 D_{yz}^2 F_{xyz}^2 D_{z2}^2$ with the doubly occupied D_{z2}^{2} as its HOMO (a_{1g}), while the D_{x2-y2} MO in a cubic O_h field has been squeezed out of the occupied valence shells to become the lowest unoccupied molecular orbital (LUMO, b_{2g}) of the system. Finally, in comparison with $O_h M(CO)_8^-$ (1) which possess two singly occupied

of C–O stretching Δ^* relative to free CO (2143 cm⁻¹) in $O_h M(CO)_8^-$ (M = K, Rb) and $D_{4h} M(CO)_8^-$ (M = K, Rb) compared with the corresponding values of $O_h M(CO)_8$ (M = Ca, Sr) at M06-2X-D3/ def2-QZVPP level

	$r_{M-CO}/r_{C-O}/\text{\AA}$	$\Delta E_{\rm f}/\rm kcal/mol$	<i>d</i> -contribution (%)	WBI _M	WBI _{M-CO}	$\nu_{C-O/cm}^{-1}$	$\Delta * /_{\rm cm}^{-1}$
$O_h \operatorname{K}(\operatorname{CO})_8^-$	2.86/1.13	- 44.5	11.9	1.16	0.12	1954 (t _{1u})	- 189
$O_h \operatorname{Rb}(\operatorname{CO})_8^-$	3.04/1.13	- 36.7	13.6	1.11	0.11	1964 (t _{1u})	- 179
D _{4h} K(CO) ₈	2.94/1.12	- 29.7	15.6	0.93	0.10	2044 (e _u)	- 99
$D_{4h} \operatorname{Rb}(\operatorname{CO})_8$	3.11/1.12	- 24.0	13.7	0.84	0.09	2043 (e _u)	- 100
O_h Ca(CO) ₈	2.60/1.13	- 66.0	14.9	1.38	0.14	2015 (t _{1u})	- 128
$O_h \operatorname{Sr}(\operatorname{CO})_8$	2.75/1.13	- 62.3	18.8	1.39	0.14	2027 (t _{1u})	- 116

corresponding *d*-orbital participations are 15.6% and 13.7% in neutral K(CO)₈ (**3**) and Rb(CO)₈ (**3**). These values are comparable with the calculated *d*-orbital contributions of 14.9% and 18.8% in the experimentally

degenerate SOMOs (D_{z2} and D_{x2-y2}) to form the $M(d_{\pi}) \rightarrow (CO)_8(\pi^*)$ backdonations evenly distributed in x, y, and z three directions, $D_{4h} M(CO)_8^-$ (2) has only one doubly occupied HOMO (D_{z2}) to form the $M(d_{\pi}) \rightarrow (CO)_8(\pi^*)$

backdonation in z direction. This qualitatively explains why $M(CO)_8^-$ (2) are slightly less stable than the global minima $M(CO)_8^-$ (1). Interestingly, singlet $D_{4d} M(CO)_8^$ with the superatomic configuration of $S^2P^6D^{10}$ and doublet D_{4d} M(CO)₈ (3) with the superatomic configuration of $S^{2}P^{6}D^{9}$ have one doubly occupied MO (D_{z2}^{2}) and one singly occupied MO (D_{z2}^1) to form the $M(d_{\pi}) \to (CO)_8(\pi^*)$ backdonation, respectively (Figure S4). The superatomic MO F_{xvz} is absent in a D_{4d} octacoordinate field due to symmetry restriction. NBO analyses indicate that metal centers in $M(CO)_8^-$ (1) have the total Wiberg bond indexes of $WBI_M = 1.16$ and 1.10 and the corresponding M-CO interactions possess the Wiberg coordination bond orders of $WBI_{M-CO} = 0.12$ and 0.11 for M = K and Rb, respectively. These values are comparable with the corresponding bond orders of $WBI_M = 1.38$ and 1.39 and WBI_{M-CO-} = 0.14 and 0.14 calculated for $Ca(CO)_8$ and $Sr(CO)_8$ [6] at the same theoretical level, indicating that, similar to the situation in alkaline-earth octacarbonyls, effective M-CO coordination interactions are formed in $M(CO)_8^-$ (1) alkali octacarbonyl complexes. Neutral $M(CO)_8$ (3) without the extra negative charge appear to have lower \ensuremath{WBI}_M and WBI_{M-CO} bond orders than $M(CO)_8^-$ (1) monoanions (Table 1).

To facilitate future experimental characterization of these alkali octacarbonyls, we simulate the IR, Raman, and PES spectra of $O_h \text{ K(CO)}_8^-$ (1) in Fig. 3 at TD-M06-2X-D3 level. IR and Raman spectra are scaled by a factor of 0.941 [6] which is the ratio of the calculated stretching frequency of free CO (2277 cm^{-1}) to the corresponding experimental value of 2143 cm⁻¹ [23]. $M(CO)_8^{-1}$ (1) appear to have highly simplified vibrational spectra due to the unusually high geometrical symmetry (O_h) of the systems, with the IR active C-O asymmetrical stretching frequencies of $v_{C-O} = 1954 (t_{1u})$ and 1964 $(t_{1u}) \text{ cm}^{-1}$ and Raman active symmetrical stretching frequencies of $v_{C-O} = 1961(t_{2g})$ and 1966(t_{2g}) for M = K and Rb, respectively. Similar IR and Raman spectra are simulated for $O_h \operatorname{Rb}(\operatorname{CO})_8^-$ (1) (Fig.S4). Interestingly, $O_h M(CO)_8^-$ (1) (M = K, Rb) appear to have stronger C–O stretching even red shifts of $\Delta^* = -189$ to -179 cm⁻¹ relative to free CO than the corresponding red shifts of $\Delta^* = -125$ to -116 cm⁻¹ calculated for Oh Ca(CO)8 and Ca(CO)8 at M06-2X-D3/ def2-TZVPP level 6 (almost the same Δ^{\ast} values of -128 to -116 cm⁻¹ are obtained at M06-2X-D3/def2-QZVPP in Table 1), suggesting that strong $M(d_{\pi})$ \rightarrow (CO)₈(π^*) backdonations exist in M(CO)₈⁻ (1). Neutral D_{4h} M(CO)₈ (3) also appear to have strong calculated red shifts ($\Delta^* = -99$ to -100 cm⁻¹) (Table 1) in comparison with the corresponding values of $\Delta^* = -30$ to -24 cm⁻¹ reported for the isovalent D_{4d} $Ca(CO)_8^+$ and $D_{4d} Sr(CO)_8^+$ monocations [6].

The simulated PES spectrum of $K(CO)_8^-(1)$ features an extremely low first vertical detachment energy of $VDE_1 = 0.75 \text{ eV}$ followed by a huge energy gap of 7.27 eV, with the second vertical detachment energy of $VDE_2 = 8.02 \text{ eV}$. These excitation processes correspond to detaching one electron from the degenerate π -SOMOs (eg) and second highest-lying ligand-only σ -MO (a_{2u}), respectively. Rb(CO)₈ possesses a similar simulated PES spectrum with a big energy gap (Figure S5).

Conclusions

In summary, extensive first-principles theory investigations performed in this work support the speculation that alkali octacarbonyl complexes $M(CO)_8^{-/0}$ (M = K, Rb) may exist in low-temperature experiments with important (n – 1)*d*orbital participation in M–CO coordination bonding. The metal-non-metal transition may therefore start at the very beginning of the periodical table in group IA. IR spectra in inert-gas matrixes and IR-PD [6, 7] and PES [24, 25] measurements in gas phases may serve as powerful means to characterize such novel clusters experimentally. Further joint experimental and theoretical investigations on alkali carbonyl complexes with new bonding motifs are well worth trying to achieve the limit of the 18-electron rule.

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Compliance with Ethical Standards

Conflict of interest All the authors of this paper have no conflict of interest.

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