

$K^+[K(CO_8)]^-$: an antipodal crystalline salt of alkalide $[K(C222)]^+ K^-$

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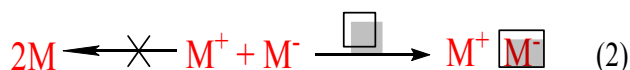
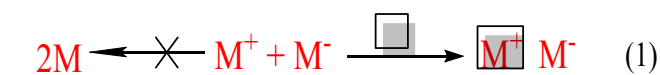
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ABSTRACT: Here we propose an antipodal conjecture, which is based on the synthetic scheme of alkalide $[K(C222)]^+ K^-$, to prepare $K^+[K(CO_8)]^-$. By introducing the concept of antipodal salts of alkalides, $K^+[K(CO_8)]^-$ is defined as antipodal salt of $[K(C222)]^+ K^-$. As Group 1 elements of the Periodic Table, the alkali metal K is conventionally considered to form chemical bonding through its 4s and 4p valence orbitals. Our theoretical results show that the 3d orbitals of K element in $[K(CO_8)]^-$ participate in chemical bonding of $[K(CO_8)]^-$. This makes the alkali metal K shows typical transition metal chemical properties, which also provides the possibility for the synthesis of $K^+[K(CO_8)]^-$. Based on the Born-Haber thermodynamic cycle, the upper-limit stable temperature of $K^+[K(CO_8)]^-$ is estimated to be 24.426 K. Our theoretical results indicate that antipodal salts of alkalides will be a new family of compounds with good synthetic prospects.

1. INTRODUCTION

"Alkali Metals" are located in Group 1 elements of the Periodic Table, have a ns^1 valence-shell configuration, where n is the principal quantum number, and, as such, are exceptionally good electron donors, tending to form monovalent cations by donation of one electron to an acceptor atom or molecule. The resultant cation has a stable inert gas electron configuration with a filled outer p -shell. So it has long been thought that, except for the elemental form and the alloy of these elements, only the oxidation state with a positive valence can be stable. Although some evidence has been presented for the presence of anions in the gas phase^{1,2}, it was not until 1974 that the preparation and characterization of the first crystalline salt which contains an alkali metal anion, $\text{Na}^+\text{C}_{22}\text{Na}^{-3-5}$, established the belief that the negative valence oxidation state of alkali could also exist in the condensed phase. This has opened a new field of research on the properties of these highly-reducing species both in solutions and in solids. Since then, a number of other salts of alkali metal anions (alkalides) have been prepared⁶⁻¹⁰.

Attempts to grow crystals containing alkali metal anion are based on such a scheme 1, as shown in equation 1, whereby alkali metal cations are strongly complexed with appropriate cryptand, potentially preventing M^+ and M^- ($\text{M} = \text{Na}, \text{K}, \text{or Cs}$) from spontaneously recombining to form alkali metals.



Where M stands for alkali metals, [Ligand] stands for appropriate ligands and \times means that this spontaneous chemical reaction path is blocked.

Here, the idea of preventing M^+ and M^- from spontaneously recombining to form alkali metals in scheme 1 is reexamined from the perspective of symmetry. Obviously, the antipodal scheme 2 shown in equation 2, is attractive, that is, whether it is possible to prevent the spontaneous recombination of M^+ and M^- by complexation of alkali metal anions with appropriate ligands.

We define the new species $\text{M}^+ [\text{M}^-]$ as the antipodal crystalline salts of alkalides $\text{[M}^+ \text{M}^-]$.

However, the challenge in synthesizing the new species

$\text{M}^+ [\text{M}^-]$ is that, to date, only a few transition metal anions

with empty $(n-1)d$ AO orbitals, such as iron, can be complexed with ligands with lone pair electrons. Therefore, the complexation between alkali metal anions and ligands seems impossible and the

synthesis of the new species $\text{M}^+ [\text{M}^-]$ seems to be an

aesthetic fantasy. However, the discovery by Zhou and Frenking¹¹ that octacarbonyl complexes $\text{M}(\text{CO})_8$ ($\text{M} = \text{Ca}, \text{Sr}, \text{or Ba}$) can be stabilized in a low temperature neon matrix and that strontium and calcium can effectively use their $(n-1)d$ AOs in chemical bonding has encouraged and strengthened our belief. Because $[\text{k}(\text{CO})_8]^-$ is isoelectronic with $[\text{Ca}(\text{CO})_8]^-$, It is reasonable to suppose that the alkali metal k anions can form stable octacarbonyl complexes $[\text{k}(\text{CO})_8]^-$.

The main work of this paper is as follows:

First of all, the stability and electronic structure of $[\text{k}(\text{CO})_8]^-$ are analyzed qualitatively and quantitatively.

Second, the existence and stability of the antipodal crystalline salt $\text{K}^+[\text{k}(\text{CO})_8]^-$ are studied based on the Born-Haber Cycles method, which is well established and widely used to evaluate the stability of ionic if reliable thermochemical data are available.

2. COMPUTATIONAL METHOD

A variety of initial structures were optimized in search of the ground state structures of $[\text{k}(\text{CO})_8]^-$. Structural optimizations and the Bond Dissociation Energy (D_0) were accomplished at two theoretical levels, DFT-B3LYP-D3¹² and M06-2X-D3^{13,14} using the Gaussian 16 program¹⁵. Ahlrichs def2-TZVPP basis set¹⁶ were used in the calculations.

Vibrational frequencies were calculated in the harmonic approximation to characterize stationary points and to determine zero-point energies (ZPE). The nature of chemical Bonding was investigated qualitatively and quantitatively by group theory and natural bond orbital method¹⁷. Molecular structure visualization was done using the Multiwfn 3.7 program¹⁸.

Lattice Energies U_{POT} , eq 3¹⁹ was used to estimate the lattice energy, U_{POT} , of the $K^+[K(CO)_8]^-$

$$U_{\text{POT}} = \left| z^+ \right| \left| z^- \right| v \left(\frac{\alpha}{\sqrt[3]{V}} + \beta \right) \text{kJ/mol} = \sum n_k z_k^2 \left(\frac{\alpha}{\sqrt[3]{V}} + \beta \right) \text{kJ/mol} \quad (3)$$

3. RESULTS AND DISCUSSION

The global minimum, low-lying structures of $[K(CO)_8]^-$

Extensive structural searches for the global minimum and low lying isomers of $[K(CO)_8]^-$ were done by starting from the highly symmetric cubic (O_h) configuration at the B3LYP-D3/def2-TZVPP level of theory. By reducing the symmetry of molecular configurations and adjusting the initial configurations along the direction of imaginary frequency vibration, we've traversed and optimized all the possible configurations of $[K(CO)_8]^-$. The results of these calculations that the symmetries, electronic states, relative energies (in bold), minimum vibrational frequencies, and number of imaginary frequencies (in parenthesis) for the optimized structures, are presented in Figure S1 (see Supplementary materials). Figure S1 shows that in the potential energy plane of $[K(CO)_8]^-$, there are many static points with very close energy, which can be considered as degenerate isomers within the accuracy of our

salts, Where Z_k is the respective charges on the cations and anions, n_k is the number of ions of charge Z_k in the formula unit. α (kJ mol⁻¹ nm) and β (kJ mol⁻¹) are coefficients of best fit and α and β take the values 117.3 kJ mol⁻¹ nm and 51.9 kJ mol⁻¹, respectively, for 1:1 salts. V (nm³) is the molecular (formula unit) volume of the salt. The individual ion volumes can be estimated from an ion volume database, inferred in some cases from established crystal structure data.

calculation. And this is not surprising, because high-coordination compounds usually have a lot of isomers that are very close in energy.

The search for the global minimum of $[K(CO)_8]^-$ at the B3LYP-D3/ def2-TZVPP level of theory revealed seven almost degenerate low-lying isomers, I (O_h , ³A_{1g}), II (D_{2h} , ³A_g), III (C_{4v} , ³B₁), IV (D_{4h} , ³B_{2g}), V (D_4 , ³B₂), VI (D_3 , ³A₁) and VII (C_3 , ³A). Due to the presence of competitive isomers for the global minimum of $[K(CO)_8]^-$, we reoptimized the lowest-lying isomers at the m062x-D3/def2-TZVPP level of theory to more accurately assess their relative energies. The results of these calculations are presented in Figure 1. Their Cartesian coordinates at the m062x-D3/def2-TZVPP level are given in Table S1 (see Supplementary materials).

Figure 1 shows that the seven degenerate low-lying isomers are still close in energy (within 0.036 kcal mol⁻¹) at each level of theory. Given that these isomers are very close in energy, they are likely to convert to each other, so it is necessary to discuss them further later.

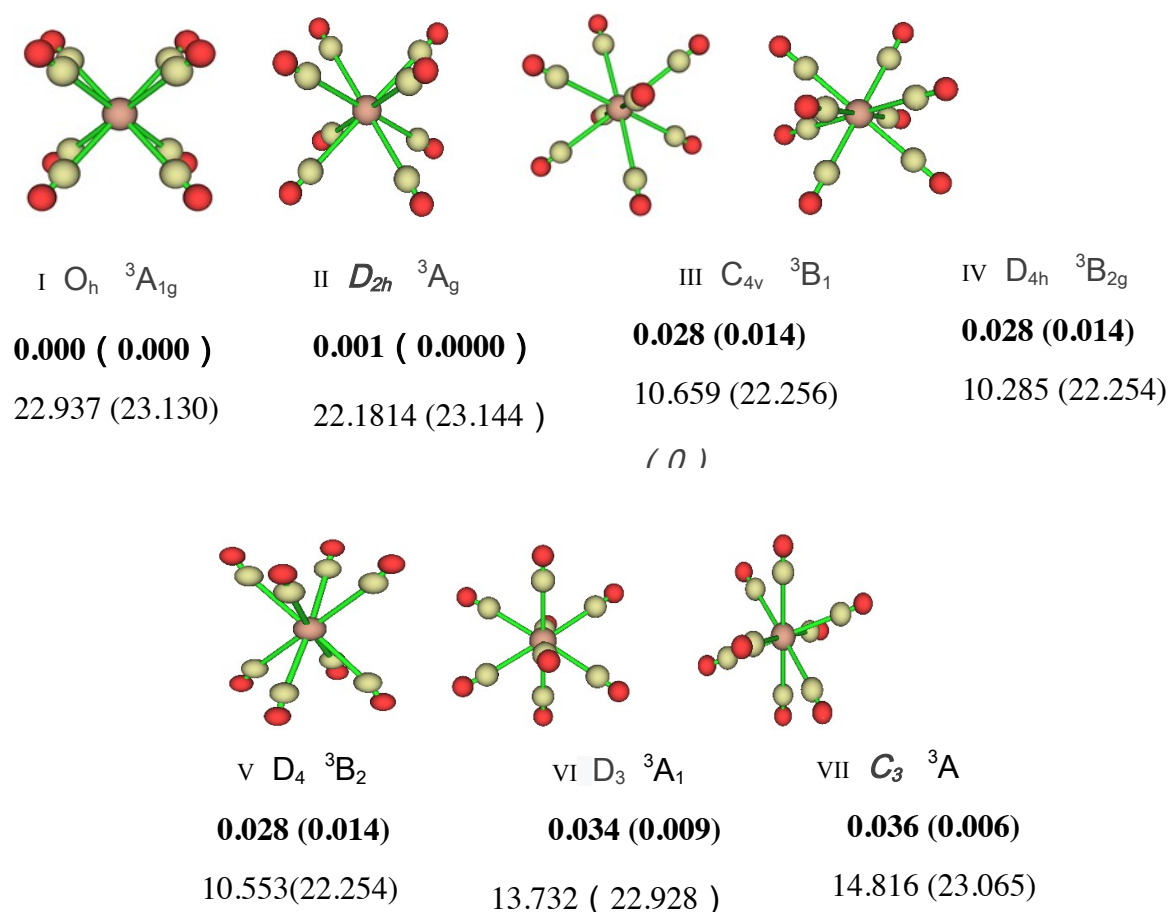


Figure. 1. The global minimum structure and low-lying structures of $[K(CO)_8]^-$. Labeled below each structure are the symmetries and electronic states, relative energies in kcal mol⁻¹ (bold), and the lowest vibrational frequencies (in cm⁻¹). The relative energies values and the lowest vibrational frequency values without parentheses are from M06-2X-D3/def2-TZVPP calculations; The relative energies values and the lowest vibrational frequency values in parentheses are from B3LYP-D3/def2-TZVPP.

Bond dissociation energies of $[K(CO)_8]^-$,

The calculated zero-point energy-corrected bond dissociation energies D_0 of $[K(CO)_8]^-$ for loss of eight CO ligands are exhibited in Chart 1. At the M06-2X-D3/def2-

TZVPP+ ZPE level, the calculated D_0 values was 36.213 kcal mol⁻¹. The calculated values at the B3lyp-D3/def2-TZVPP + ZPE level was 41.682 kcal mol⁻¹. All the $[K(CO)_8]^-$ species proved to be thermodynamically stable with respect to dissociation into K^- and CO.

Chart 1. Calculated Energies (hartrees) and Reaction Energies D_0 (kcal mol⁻¹) for Dissociation reactions of Structures I ^(a). The values without parentheses are from M06-2X-D3/def2-TZVPP + ZPE calculations; the values in parentheses are from B3lyp-D3/def2-TZVPP + ZPE calculations.

^(a) Because the seven low-lying isomers, I (O_h , $^3A_{1g}$), II (D_{2h} , 3A_g), III (C_{4v} , 3B_1), IV (D_{4h} , $^3B_{2g}$), V (D_4 , 3B_2), VI (D_3 , 3A_I) and VII (C_3 , 3A) are almost degenerate, their dissociation energies are also very close.

4. Analysis of Molecular Orbitals for σ and π BONDING

What is the nature of the chemical bonding in $[K(CO)_8]^-$? We answer these questions in a two-pronged approach, qualitative and quantitative perspectives.

4.1 Treating the σ and π molecular orbitals of $[K(CO)_8]^-$ with the group theory^{20,21}

Group theory is a powerful tool for qualitative analysis of molecular orbitals. Without any quantitative calculations whatever, from symmetry considerations alone, we can always tell what the qualitative features of a problem must be.

The global minimum searches for $[K(CO)_8]^-$ have revealed seven nearly degenerate isomers, I (O_h , $^3A_{1g}$), II (D_{2h} , 3A_g), III (C_{4v} , 3B_1), IV (D_{4h} , $^3B_{2g}$), V (D_4 , 3B_2), VI (D_3 , 3A_I) and VII (C_3 , 3A). Now we use Group theory to investigate the σ and π molecular orbitals of these isomers in turn.

(Additional notes: In order to make the discussion easy to understand and avoid repetition, we will take structure I as an example to illustrate how to describe the molecular orbital of complex based on the group theory. For structure II- VII, we will only give the most important basic elements involved in the group theory and the most important conclusions about these structures from these basic elements.)

4.1.1 structure I (O_h point group)

The O_h configuration structure I turns out to be the global minimum according to two theoretical levels, B3LYP-D3 and M06-2X-D3, which has an electronic configuration of $a_{1g}^2 t_{1u}^6 t_{2g}^6 a_{2u}^2 e_g^2$, where the degenerate e_g HOMO is half-filled, resulting in a triplet ground state. By using group elements to

operate on σ and π orbitals of $[K(CO)_8]^-$, we get

reducible representations Γ^{red} and their component irreducible

representations Γ^{irred} of these orbitals (see Table 1). Table 1

shows that the irreducible representations to which the σ bonding MOs must belong: are $A_{1g} \oplus T_{2g} \oplus A_{2u} \oplus T_{1u}$. But, in the valence shell, consisting of s, p and d orbitals, we cannot find all the AOs on the central K atom needed to form a complete set of σ bonding MOs, because there are no atom orbitals of A_{2u} symmetry on central k atom (assuming, as always, that we

consider only s, p, and d type orbitals. Even though the f_{xyz} -type orbitals has this A_{2u} symmetry, energy criteria makes it unlikely be important.). So the A_{2u} symmetry MO is a ligand-only, nonbonding MO. Then we now examine the right side of the Table 1 to see what AOs on central K atom are available to match $A_{1g} \oplus T_{2g} \oplus T_{1u}$ MOs. Within an s, p, d manifold, to match $A_{1g} \oplus T_{2g} \oplus T_{1u}$ MOs, the only possible AOs combination on the central k atom is $S, (d_{xz}, d_{yz}, d_{xy})$ and (p_x, p_y, p_z) . This is usually designated briefly as d^3sp^3 hybridization.

For structure I, table 1 also shows that the irreducible representations to which the π bonding MOs must belong: are $E_g + T_{1g} + T_{2g} + E_u + T_{1u} + T_{2u}$ and within an s, p, d manifold, we cannot find all the AOs on the central k atom to match these requirements, because there are none for T_{1g} , E_u or T_{2u} . For

E_g, T_{2g} and T_{1u} we have, respectively, $(d_{z^2}, d_{x^2-y^2})$, (d_{xz}, d_{yz}, d_{xy}) , and (p_x, p_y, p_z) . If we look back at

our previous treatment of σ bonding, we find that the T_{2g} and T_{1u} set was also needed there. In view of the need for strong

σ bonds. We are then left with only the E_g type of π bonding.

The overall results of the foregoing analysis are as follows:

(a) The $[K(CO)_8]^-$ has the following bonding MOs: a ligand-only, nonbonding A_{2u} MOs, a $A_{1g} + T_{1u} + T_{2g}$ set of σ bonding MOs and the two degenerate E_g symmetry π bonding MO. Since these can hold 2, 2, 6, 6 and 4 electrons, respectively, a total of 20 electrons are required to occupy the bonding orbitals completely. But only 18 electrons are available in $[K(CO)_8]^-$ with O_h point group, so the degenerate E_g MO is occupied by two electrons with the same spin (according to the Hund's rule). This explains our previous calculation that the triplet state of $[K(CO)_8]^-$ with O_h point group is more stable than the singlet state. (See figure S1)

(b) The analysis with the group theory also show that the E_g type of π bonding are linear combinations of the empty antibonding $2\pi^*$ orbitals of ligands CO and $(d_{z^2}, d_{x^2-y^2})$ AOs of the K atom (Symmetry matching rule). So the electronic reference state of the K atom in $[K(CO)_8]^-$ with O_h point group is a triplet state with $4s(0)3d_z(1)3d_{x^2-y^2}(1)$ electron configuration and These ligands CO can stabilize the E_g type orbitals of K atom and receive some π density from K atom. The two E_g type MOs are the $[K(d)] \rightarrow (CO)_8 \pi$ backdonation MOs . .

Table 1: Results for the σ and π molecular orbitals of structure I with O_h Symmetry treated with group theory. The reducible representations Γ^{red} in σ and π orbitals basis, their component irreducible representations Γ^{irred} and the AOs on the central K atom matching corresponding irreducible representation .

O_h	E ₀	8 C ₃	3 C ₂	6 C ₄	6 C ₂ '	i ₀	8 S ₆	3 σ_h	6 S ₄	6 σ_d	AOs on central K atom
A _{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	S
A _{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	
E _g	+2	-1	+2	+0	+0	+2	-1	+2	+0	+0	($d_{z^2}, d_{x^2-y^2}$)
T _{1g}	+3	+0	-1	+1	-1	+3	+0	-1	+1	-1	(d_{xz}, d_{yz}, d_{xy})
T _{2g}	+3	+0	-1	-1	+1	+3	+0	-1	-1	+1	
A _{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	f_{xyz}
A _{2u}	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	
E _u	+2	-1	+2	+0	+0	-2	+1	-2	+0	+0	(p_x, p_y, p_z), ($f_{z^3}, f_{x^3}, f_{y^3}$)
T _{1u}	+3	+0	-1	+1	-1	-3	+0	+1	-1	+1	
T _{2u}	+3	+0	-1	-1	+1	-3	+0	+1	+1	-1	($f_{x^2-y^2}, f_{y^2-x^2}, f_{z^2-y^2}$)
$\Gamma_{\sigma}^{\text{red}}$	8	2	0	0	0	0	0	0	0	4	= $\sum \Gamma_{\sigma}^{\text{irred}}$ = A _{1g} + T _{2g} + A _{2u} + T _{1u}

$$\Gamma_{\pi}^{\text{red}} \quad 16 \quad -2 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad = \sum \Gamma_{\pi}^{\text{irred}} = E_g + T_{1g} + T_{2g} + E_u + T_{1u} + T_{2u}$$

note: The symbol $\Gamma_{\sigma}^{\text{red}}$ and $\Gamma_{\pi}^{\text{red}}$ denote a reducible representation of σ and π molecular orbitals, respectively. The symbol $\Gamma_{\sigma}^{\text{irred}}$ and $\Gamma_{\pi}^{\text{irred}}$ denote irreducible representations components of $\Gamma_{\sigma}^{\text{red}}$ and $\Gamma_{\pi}^{\text{red}}$.

4.1.2 structure II - VII

For structure II (D_{2h} , 3A_g), III (C_{4v} , 3B_1), IV (D_{4h} , $^3B_{2g}$), V (D_4 , 3B_2), VI (D_3 , 3A_1) and VII (C_3 , 3A), molecular orbitals can be analyzed in the same way as above. The analysis results were shown in Table S2, S3, S4, S5, S6 and S7 (see Supplementary materials).

The analysis results in Table S2, S3, S4, S5, S6 and S7 show that, like the structure 1, these structures also have one non-bonding MOs, seven σ bonding MOs and the two single-occupying π backdonation MOs.

The two π backdonation MOs in structure II (D_{2h} , 3A_g), III (C_{4v} , 3B_1), and IV (D_{4h} , $^3B_{2g}$) are linear combinations of the empty antibonding $2\pi^*$ orbitals of ligands CO and (d_{z^2} , $d_{x^2-y^2}$) AOs

of the K atom. But the two π backdonation MOs in structure V (D_4 , 3B_2) arise from linear combinations of the empty antibonding $2\pi^*$ orbitals of ligands CO and (d_{z^2} , d_{xy}) AOs of the K atom. For structure VI (D_3 , 3A_1) and VII (C_3 , 3A), the two π backdonation MOs arise from linear combinations of the empty antibonding $2\pi^*$ orbitals of ligands CO and (d_{xz} , d_{yz}) AOs of the K atom. So the electronic reference state of the K atom in $[K(CO)_8]^-$ is a triplet state with

$$4S(0)3d_{z^2}(1)3d_{x^2-y^2}(1)$$

electron configuration for structure II (D_{2h} , 3A_g), III (C_{4v} , 3B_1), and IV (D_{4h} , $^3B_{2g}$),

$$4S(0)3d_{z^2}(1)3d_{xy}(1)$$

electron configuration for structure V (D_4 , 3B_2) and

$$4S(0)3d_{xz}(1)3d_{yz}(1)$$

electron configuration for structure VI (D_3 , 3A_1) and VII (C_3 , 3A), respectively.

The most important insight from our treatment of σ and π bonds above for $[K(CO)_8]^-$ is

that the 3d atom orbitals of the K atom in $[K(CO)_8]^-$ are activated to form bonds. The σ contributions in $[K(CO)_8]^-$ to the total orbital

interactions arise from 4s, $3d_{xz}$, $3d_{yz}$, $3d_{xy}$ and 4p orbitals of the K atom for structure I (O_h , $^3A_{1g}$), II (D_{2h} , 3A_g), III (C_{4v} , 3B_1), IV (D_{4h} , $^3B_{2g}$), from 4s, $3d_{xz}$, $3d_{yz}$, $3d_{x^2-y^2}$ and 4p orbitals of the K atom for structure V (D_4 , 3B_2) and from 4s, $3d_{z^2}$, $3d_{x^2-y^2}$, $3d_{xy}$ and 4p orbitals of the K atom for structure VI (D_3 , 3A_1) and VII (C_3 , 3A), respectively. $[K(CO)_8]^-$ have two π backdonation MOs. They all come from linear combinations of the empty antibonding $2\pi^*$ orbitals of ligands CO and d AOs of the K atom. ($(3d_{z^2}, 3d_{x^2-y^2})$ for structure I (O_h , $^3A_{1g}$), II (D_{2h} , 3A_g), III (C_{4v} , 3B_1), IV (D_{4h} , $^3B_{2g}$), ($3d_{z^2}, 3d_{xy}$) for structure V (D_4 , 3B_2) and ($3d_{xz}, 3d_{yz}$) for structure VI (D_3 , 3A_1) and VII (C_3 , 3A)).

4.2 Analysis of natural bond orbital and calculated wave numbers

Above, we carried out a qualitative analysis of $[K(CO)_8]^-$ molecular orbitals, and now we further confirm the above conclusions from a quantitative perspective.

we first investigated the metal-ligand interactions ($K-(CO)_8$) using the NBO methods in order to evaluate the contribution of $[K(d)] \leftarrow (CO)_8$ σ donation and $[K(d)] \rightarrow (CO)_8$ π back

donation. Table 2 gives the results of the NBO methods for structure I - VII.

The analysis of the electron configuration shows that the charge of the $4S$ orbital on the central K atom decreases while that of the $3d$ orbital increases, which is consistent with the results of our previous qualitative analysis, that is, the electron reference state of the K metal atom is a triplet state with $4S(0)3d(2)$ electron configuration.

For structure I ($O_h, {}^3A_{1g}$), II ($D_{2h}, {}^3A_g$), III ($C_{4v}, {}^3B_1$) and IV ($D_{4h}, {}^3B_{2g}$), because the σ contributions in $[K(CO)_8]^-$ to the total orbital

interactions arise from $4S, 3d_{xz}, 3d_{yz}, 3d_{xy}$ and $4p$ orbitals of the K atom and the π contributions from $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals, the total $[K(d)] \leftarrow (CO)_8$ σ donation, $\Delta q_\sigma(K)$, is equal to $q(4S) + q(3d_{xz}) + q(3d_{yz}) + q($

$3d_{xy}) + q(4P)$ and the total $[K(d)] \rightarrow (CO)_8$ π back donation, $\Delta q_\pi(K)$, is $2 - q(3d_{z^2}) - q($

$3d_{x^2-y^2})$ (where 2 is the sum of the charges in the $3d_{z^2}(1)$ and $3d_{x^2-y^2}(1)$

orbitals of the electronic reference state K atom in $[K(CO)_8]^-$). So the ratio of the calculated π -

back donation and σ donation (b:d) is 0.696, 0.696, 0.716 and 0.716 for structure I ($O_h, {}^3A_{1g}$), II ($D_{2h}, {}^3A_g$), III ($C_{4v}, {}^3B_1$) and IV ($D_{4h}, {}^3B_{2g}$), respectively.

Obviously, the total $[K(d)] \leftarrow (CO)_8$ σ donation, $\Delta q_\sigma(K)$, is $q(4S) + q(3d_{xz}) + q(3d_{yz}) + q($

$3d_{x^2-y^2}) + q(4P)$ for Structure V and $q($

$4S) + q(3d_{x^2-y^2}) + q(3d_{z^2}) + q(3d_{xy}) + q($

$4P)$ for Structure VI and Structure VII. And the total $[K(d)] \rightarrow (CO)_8$ π back donation, $\Delta q_\pi(K)$, is

$q(3d_{z^2}) + q(3d_{xy})$ for Structure V and $q($

$3d_{xz}) + q(3d_{yz})$ for Structure VI and Structure

VII. So the ratio of the calculated π back donation and σ donation (b:d) is 0.697, 0.709 and 0.709 for Structure V, VI and VII, respectively.

The ratios b:d for structure I - VII indicate that the σ contributions are larger than the π contributions. But the π contributions are also considerable, accounting for at least 41.058%. The NBO results for structure I - VII are agree nicely with the previous conclusion of group theory analysis that the $3d$ atom orbitals of the K atom in

$[K(CO)_8]^-$ are activated to form σ and π

back bonds and metal-ligand interactions come from the synergistic effects of σ - π backbonding in

$[K(CO)_8]^-$.

Table 2 Results of the NBO analysis of $[K(CO)_8]^-$ at the M06-2X-D3/def2-TZVPP level, taking K^{-1} with a $4s(0)3d(2)$ valence electronic configuration as the electronic reference state of the K atom in $[K(CO)_8]^-$

$[K(CO)_8]^-$	electron configuration on the central K atom	$[K(d)] \rightarrow (CO)_8$ π backdonation	$[K(d)] \leftarrow (CO)_8$ σ donation	$q(K)^a$	$\Delta q(K)^b$	$\Delta q_\pi(K)^c$	$\Delta q_\sigma(K)^d$	$b:d^e$
Structure I	[core]4S(0.32) 3d(1.55)4p(0.67)	$3d_{z^2}$ (0.382) $3d_{x^2-y^2}$ (0.382)	4S(0.32) $3d_{xz}$ (0.262) $3d_{yz}$ (0.262) $3d_{xy}$ (0.262) 4P(0.67)	-1.522	0.522	1.236	1.776	0.696
Structure II	[core]4S(0.32) 3d(1.55)4p(0.67)	$3d_{z^2}$ (0.382) $3d_{x^2-y^2}$ (0.382)	4S(0.32) $3d_{xz}$ (0.262) $3d_{yz}$ (0.261) $3d_{xy}$ (0.262) 4P(0.67)	-1.523	0.523	1.236	1.775	0.696
Structure III	[core]4S(0.32) 3d(1.55)4p(0.67)	$3d_{z^2}$ (0.382) $3d_{x^2-y^2}$ (0.261)	4S(0.32) $3d_{xz}$ (0.262) $3d_{yz}$ (0.262) $3d_{xy}$ (0.381) 4P(0.67)	-1.522	0.522	1.357	1.895	0.716
Structure IV	[core]4S(0.32) 3d(1.55)4p(0.67)	$3d_{z^2}$ (0.382) $3d_{x^2-y^2}$ (0.261)	4S(0.32) $3d_{xz}$ (0.262) $3d_{yz}$ (0.262) $3d_{xy}$ (0.381) 4P(0.67)	-1.522	0.522	1.357	1.895	0.716
Structure V	[core]4S(0.32) 3d(1.55)4p(0.67)	$3d_{z^2}$ (0.382) $3d_{xy}$ (0.381)	4S(0.32) $3d_{xz}$ (0.262) $3d_{yz}$ (0.262) $3d_{x^2-y^2}$ (0.261) 4P(0.67)	-1.522	0.522	1.237	1.775	0.697
Structure VI	[core]4S(0.32) 3d(1.55)4p(0.67)	$3d_{xz}$ (0.342) $3d_{yz}$ (0.342)	4S(0.32) $3d_{x^2-y^2}$ (0.302) $3d_{z^2}$ (0.262) $3d_{xy}$ (0.302) 4P(0.67)	-1.522	0.522	1.316	1.856	0.709
Structure VII	[core]4S(0.32) 3d(1.55)4p(0.67)	$3d_{xz}$ (0.342) $3d_{yz}$ (0.342)	4S(0.32) $3d_{x^2-y^2}$ (0.302) $3d_{z^2}$ (0.262) $3d_{xy}$ (0.302) 4P(0.67)	-1.522	0.522	1.316	1.856	0.709

The atomic partial charge of K in $[K(CO)_8]^-$. ^b Difference between $q(K^{-1}) = -1$ and $q(K)$, $\Delta q(K) = -1 - q(K)$. ^c The total $[K(d)] \rightarrow (CO)_8$ π backdonation. ^d The total $[(K(d)) \leftarrow (CO)_8$ σ donation. ^e Given by $\Delta q_\pi(K) / \Delta q_\sigma(K)$

In fact, the synergistic effect of $\sigma - \pi$ backbonding in $[K(CO)_8]^-$ can also be verified by calculating the vibration frequency of $C\equiv O$ stretching mode. The theoretical wave numbers for the $C\equiv O$ stretching modes of $[K(CO)_8]^-$ are shown in Table 3 along with the experimental

values. Theory results indicate a considerable red shift of the $C\equiv O$ stretching vibration frequencies for the $[K(CO)_8]^-$ systems. This is a clear evidence for the existence of the synergistic effects of $\sigma-\pi$ backbonding in $[K(CO)_8]^-$. These interactions reduce the CO triple bond character.

Table 3. Calculated (M06-2X-D3/def2-TZVPP) vibrational frequencies (cm^{-1}) of the $C\equiv O$ stretching mode and frequency shifts of $[K(CO)_8]^-$

$[K(CO)_8]^-$	Point group	symm	Calculated numbers ^a ν (C-O)	wave Δ^b	Experimental wave numbers	^a The
Structure 1	O_h	T1u	1,953.404	-189.596	2143	
Structure II	D_{2h}	B3U	1,954.713	-188.287		
		B2U	1,954.747	-188.253		
		B1U	1954.821	-188.179		
Structure III	C_{4v}	A1	1,952.178	-190.822		
		E	1,952.637	-190.363		
Structure IV	D_{4h}	A2U	1,952.151	-190.849		
		EU	1,952.717	-190.283		
Structure V	D_4	A2	1,952.185	-190.815		
		E	1,952.651	-190.349		
Structure VI	D_3	A2	1,951.721	-191.279		
		E	1,951.874	-191.126		
Structure VII	C_3	A2	1,951.756	-191.244		
		E	1,951.764	-191.236		

calculated values are scaled by a factor of 0.940, which comes from the ratio of the calculated stretching mode of free CO (2280.818cm^{-1}) to the experimental value (2143 cm^{-1})²². ^b Frequency shift relative to free CO.

5. Existence and stability prediction of

$K^+[K(CO)_9]^-$ Based on Born-Haber Cycles

A synthetic route according to reaction 1 could be adopted to prepare $K^+[K(CO)_9]^-$ salt compound.

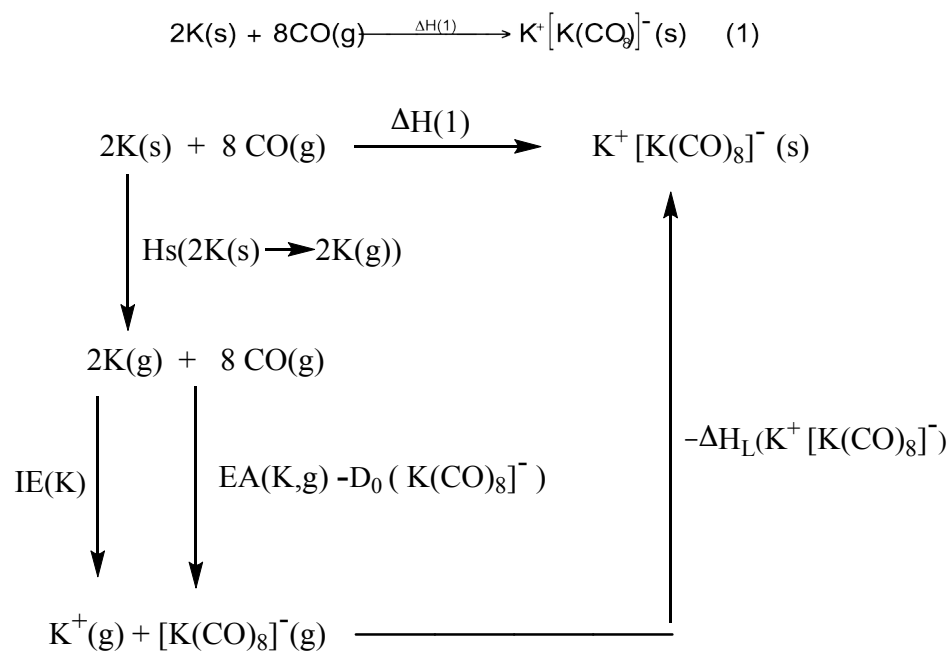


Figure 2. Born–Haber cycle for the preparation of $\text{K}^+ [\text{K}(\text{CO})_8]^-$ via preparative route (1).

An estimation of the enthalpy change for reaction 1, $\Delta H(1)$, can be acquired via a thermochemical cycle such as that in Figure 2. The cycle requires us to estimate the lattice potential energy of $K^+[K(CO_9)]^-$. Prediction of lattice energies, U_{POT} , based on eq 3 requires an estimate of the volumes of $[K(CO_9)]^-$ and K^+ ions. The volume of $[K(CO_9)]^-$ is not known. But $V([K(CO_9)]^-)$ can be estimated from consideration of $V([Co(CO_4)]^-)$. $V([Co(CO_4)]^-)$ is estimated to be 0.16858 nm^3 based on the reported crystal structure volume for $K^+[Co(CO_4)]^-$ ($V(K^+[Co(CO_4)]^-) = 0.17844 \text{ nm}^3$)²³ by subtraction of $V(K^+) = 0.00986 \text{ nm}^3$ (Table 4, ref 19). An upper limit for $V([K(CO_9)]^-)$ is estimated to be $2V[Co(CO_4)]^- = 2 \times 0.16858 \text{ nm}^3 = 0.33716 \text{ nm}^3$. Thus we obtain: $V(K^+[K(CO_9)]^-) = V(K^+) + V([K(CO_9)]^-) = 0.00986 \text{ nm}^3 + 0.33716 \text{ nm}^3 = 0.34702 \text{ nm}^3$ ($V^{1/3} = 0.70272 \text{ nm}$). Substituting the value of $V(K^+[K(CO_9)]^-)$ into eq 3 leads to a value of $U_{POT}(K^+[K(CO_9)]^-) = 104.699 \text{ kcal mol}^{-1}$.

The necessary ancillary thermochemical data are as follow: sublimation enthalpy of solid phase $K(s)$ ²⁴, $\Delta H_s(2K(s) \rightarrow 2K(g)) = 2 \times 89.0 \text{ kJ mol}^{-1} = 42.584 \text{ kcal mol}^{-1}$, ionization potential of gaseous K^{24} , $IE(K, g) = 0.419 \text{ MJ mol}^{-1} = 100.239 \text{ kcal mol}^{-1}$, dissociation Energy of $[K(CO_9)]^-$, $D_0 = 36.213 \text{ kcal mol}^{-1}$ and electron affinity of gaseous K^{24} , $EA(K, g) = -0.662 \text{ eV} = -11.575 \text{ kcal mol}^{-1}$. So the corresponding enthalpy change $\Delta H(1)$ is estimated to be $< -9.996 \text{ kcal mol}^{-1}$.

The compound stability depends on free energy changes ΔG and not on enthalpy ones. Hence, the entropy contributions from the $T\Delta S$ term to the free energy must be included. The entropy change of reaction 1, ΔS , will be negative (i.e., the products are more ordered than the reactants) and equal to $S^\circ(K^+[K(CO_9)]^-)$, s , $-2S^\circ(K, s)$, $-8S^\circ(CO, g)$. The entropy of $K^+[K(CO_9)]^-$ (s) is not known. The well-established entropies of $K(s)$ and $CO(g)$ are 64.68 and $197.660 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively²⁴. Based on these values, we obtain a lower limit for the entropy of reaction 1, $\Delta S = -409.244 \text{ cal mol}^{-1} \text{ K}^{-1}$.

For a chemical reaction to be thermodynamically favorable, its free energy change must be negative. Hence, substituting the estimations of the entropy change ΔS^* and enthalpy change $\Delta H(1)$ above into $\Delta G = \Delta H - T\Delta S < 0$ allows us to predict that the upper-limit stable temperatures of $K^+[K(CO_9)]^-$ salt compounds is 24.426 K .

To assess the reliability of our theoretical prediction on existence and stability of $K^+[K(CO_9)]^-$, we carried out a benchmark calculations on $K^+[Co(CO_4)]^-$ salt (see Supplementary materials). $K^+[Co(CO_4)]^-$ is a particularly appropriate molecule for a benchmark calculations because it has been studied in great detail experimentally. The success in existence and stability prediction of $K^+[Co(CO_4)]^-$ ensure that our calculation results on $K^+[K(CO_9)]^-$ are reliable.

6. Summary

6.1 The theoretical study shows that the 3d orbitals of K element in $[K(CO_8)]^-$ participate in the chemical bonding of $[K(CO_8)]^-$. The alkali metal K shows typical transition metal bonding characteristics.

6.2 The theoretical results predict that the synthesis of the new concept compound $K^+[K(CO_8)]^-$ is feasible, and the upper limit stable temperature of $K^+[K(CO_8)]^-$ is estimated to be 24.426 K .

7. Chemical Significance

7.1 Alkalides are a large family of compounds with the strongly reducing nature. In this paper, we present the concept of the antipodal salts of alkalides based on the antipodal conjecture. Our theoretical results indicate that antipodal salts of alkalides will be a new family of compounds with good synthetic prospects.

7.2 Although Zhou and Frenking have found that the alkaline earth metal elements of the main group could form stable octacarbonyl complexes $M(CO)_8$ ($M = \text{Ca, Sr, or Ba}$), showing typical transition metal bonding characteristics, the octacarbonyl complexes $M(CO)_8$ ($M = \text{Ca, Sr, or Ba}$) are stable only in a low-temperature solid neon matrix. So these compounds are not genuine accessible as chemical reagent.

We believe that the synthesis of $K^+[K(CO_8)]^-$ will be a very promising and meaningful thing, because this will be the first crystalline salt of the main group simulating transition metals to be actually isolated (ie, as a chemical reagent), as distinct from just spectroscopically detected species.

7.3 Our theoretical results indicate that alkali metal elements have more abundant chemical properties than the general cognition, which will help to design and synthesize more alkali metal compounds with special bonding and reaction characteristics in the future.

ASSOCIATED CONTENT

Supplementary Materials .

Figure.S1, Tables S1 to S8 , Benchmark calculations: the existence and stability predictions of $\text{K}^+[\text{Co}(\text{CQ}_4)]^-$

NOTES

The authors declare no competing financial interests.

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