

Observation of Structurally Diverse Complexes $\text{OCeNi}(\text{CO})_3^-$ and $\text{CeNi}(\text{CO})_3^-$ with the Shortest Ce–Ni Bond and $\text{Ce}\equiv\text{O}$ Triple Bond

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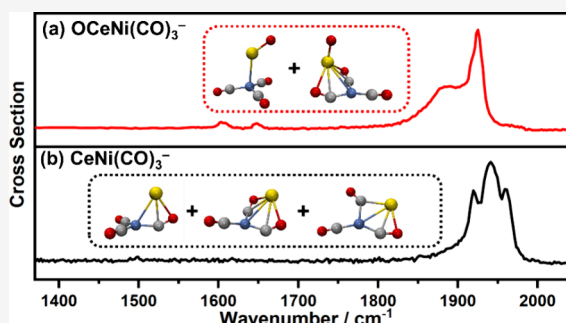


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Supporting Information

ABSTRACT: Gas-phase heteronuclear cerium–nickel carbonyl complexes, $\text{OCeNi}(\text{CO})_3^-$ and $\text{CeNi}(\text{CO})_3^-$, were successfully synthesized and characterized via mass-selected infrared photodissociation spectroscopy in combination with global minimum energy searches. The agreement between experimental and theoretical spectra reveals the coexistence of multiple isomers, different from single-structured iron carbonyl analogues. Besides, these complexes possess the shortest Ce–Ni bond and a relatively higher bond order reported to date, along with a previously unobserved $\text{Ce}\equiv\text{O}$ triple bond. Detailed chemical bonding analyses unravel the formation of multicenter covalent bonds or dative bonds between Ce-based moieties and the $\text{Ni}(\text{CO})_3^-$ fragment, highlighting that the Ni 4p (rather than 3d) orbital plays a key role in bonding with the Ce 6s or 5d orbital. Such diverse bonding modes are found to arise from the singly occupied molecular orbital (SOMO) of the $\text{Ni}(\text{CO})_3^-$ fragment, whose amphiphilic nature and multiple active sites facilitate interactions with Ce-based moieties. These findings advance the scope of metal–metal bond between f-block elements and transition metals, paving a way for exploring novel heterobimetallic interactions.



Elucidating the nature of chemical bonds is a fundamental endeavor in chemistry, providing the basis for rational design and prediction of physicochemical properties of metal complexes. In contrast to the well-characterized transition-metal–metal bonds, the chemical bonding of f-block elements is still in infancy, leaving a significant knowledge gap to be addressed. Since the first documented lanthanide–transition-metal (Ln–TM) bond was reported by Beletskaya and co-workers in 1990,¹ a growing number of analogous complexes involving Ln–TM bonds were observed consecutively.^{2–9} Such heteronuclear complexes have made great advance in frontier fields including single-molecule magnets¹⁰ (SMM) and nitrogen fixation catalysis,¹¹ owing to their unique magnetic properties and potential in small molecule activation. Therefore, the discovery of the complexes with intriguing Ln–TM bonds is of significant scientific value for both fundamental research and practical applications.

Cerium is the most abundant lanthanide element and the synthesis of Ce–TM complexes has received much attention.^{8,12–15} A representative example is the complex $\text{Ce}\{\text{N}[(\text{CH}_2\text{CH}_2\text{N}^+\text{Pr}_2)\text{RhCl}(\text{COD})]_3\}$,⁸ which features multiple Ce–Rh single bonds in its molecular framework. Besides, the complex $[(\text{PyNCH}_2\text{PPh}_2)_3\text{Ce-TM}]$ (TM = Ni, Pd and Pt)¹² represents the first example of species with a Ce–TM bond involving a group 10 metal. In the reported Ce–TM complexes, cerium predominantly exhibits a +3 or near +4 oxidation state, which is attributed to the electronic configuration of $[\text{Xe}]4f^65d^06s^0$.¹⁶ Consequently, Ce–TM

bonds in these systems exhibit predominant ionicity or partial covalency via $\text{TM}\rightarrow\text{Ce}^{3+/4+}$ dative interactions.

Despite cerium possesses a versatile range of oxidation states among the lanthanides, Ce–TM complexes with low-valent metal centers remain rare in traditional synthetic chemistry due to their high reactivity. To circumvent these synthetic limitations, gas-phase studies using pulsed-laser vaporization have emerged as a powerful platform. Utilizing infrared photodissociation (IRPD) spectroscopic technique, Chi and co-workers recently investigated the $\text{ENi}(\text{CO})_3^-$ (E = Li–Cs) complexes,¹⁷ demonstrating the potential of the $\text{Ni}(\text{CO})_3^-$ fragment to stabilize s-block metals in their zerovalent state. With photoelectron spectroscopic approach, Jiang and co-workers have characterized a series of heteronuclear carbonyl complexes involving zerovalent d-block^{18–22} and f-block metals.²³ In contrast to the previously reported s-block analogues with C_{3v} symmetry,^{21,24–26} these complexes exhibit rich structural diversity with multiple coordination modes of carbonyl ligands (i.e., terminal, bridging, and side-on configurations). Additionally, a combination of experimental

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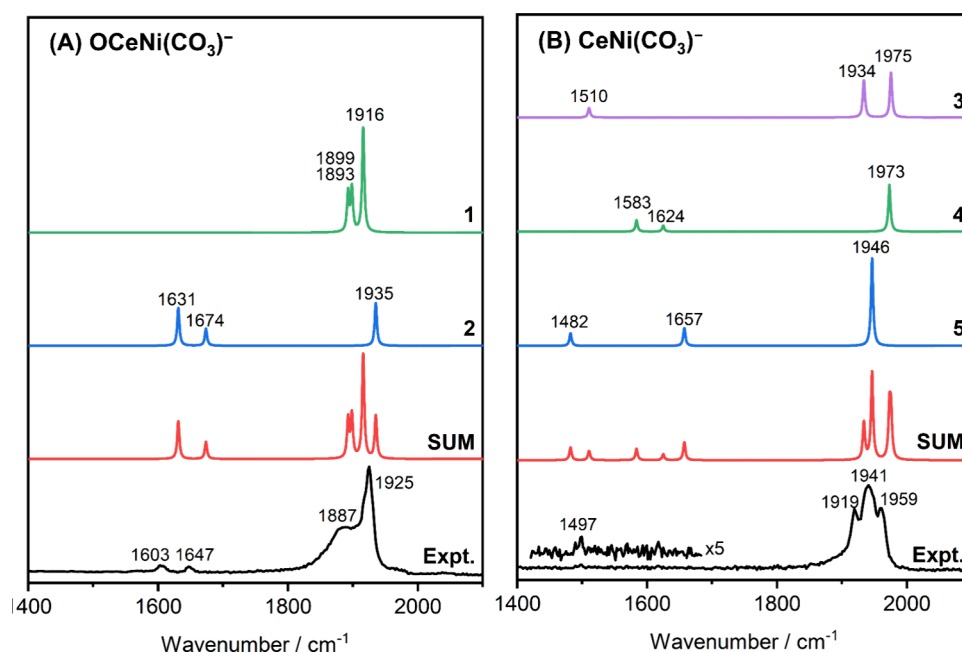


Figure 1. Experimental and simulated vibrational spectra of the (A) $\text{OCeNi}(\text{CO})_3^-$ and (B) $\text{CeNi}(\text{CO})_3^-$ anions in the carbonyl stretching frequency region. The experimental spectrum (Expt.) was recorded by monitoring all fragmentation channels. Simulated spectra (1–5) were generated by applying Lorentzian line shapes ($\text{fwhm} = 5 \text{ cm}^{-1}$) to the harmonic frequencies calculated at the PBE0/def2-TZVPP level. These frequencies were scaled by a factor of 0.956, derived from the ratio of the calculated (2234 cm^{-1}) to experimental (2143 cm^{-1}) wavenumbers of free CO. The sum of simulated spectrum (SUM) represents a 1:1 and 1:1:1 mixture of the corresponding isomers 1–2 and 3–5, respectively.

and theoretical results suggests that several isomers may coexist in these lanthanide–nickel complexes. Nevertheless, the underlying origins of this structural complexity and the nature of the potential Ln–Ni (specifically for Ce–Ni) bonds have not yet been investigated in detail.

Herein, we report a combined experimental and theoretical study on cerium–nickel carbonyl complexes ($\text{OCeNi}(\text{CO})_3^-$ and $\text{CeNi}(\text{CO})_3^-$) in the gas phase. A global search for the minimum-energy structures yielded several low-lying isomers. Frequency calculations revealed that their mixed spectra show excellent agreement with the experimental results. Notably, these complexes are found to possess the shortest Ce–Ni bond identified to date and a distinct $\text{Ce}\equiv\text{O}$ triple bond character. Chemical bonding analysis reveals the critical role of the 4p orbital of Ni in the Ce–Ni bonding, by participating in the delocalized π -orbital of $\text{Ni}(\text{CO})_3^-$, which can stabilize both the ground state and the excited state of Ce and OCe. This work not only expands the bonding limits of f-block elements but also underscores the potential of $\text{Ni}(\text{CO})_3^-$ fragments in tailoring unconventional metal–metal interactions.

Heterometallic carbonyl anion complexes were generated in the gas phase using a pulsed laser vaporization/supersonic-expansion ion source, as described in detail previously.²⁷ The typical mass spectrum in the m/z range 100–400 is shown in Figure S1. The most intense peak in the spectrum corresponds to the 17-electron $\text{Ni}(\text{CO})_3^-$ species, which is commonly observed in our experiments when the carbon monoxide samples containing nickel carbonyl impurity are used. In addition to $\text{Ni}(\text{CO})_3^-$, peaks due to complexes with the chemical formula of $\text{Ce}_x\text{C}_y\text{O}_z^-$, as well as heterobimetallic carbonyl anions $\text{OCeNi}(\text{CO})_3^-$ and $\text{CeNi}(\text{CO})_n^-$ ($n = 2-7$) are also displayed in the spectrum. The peaks corresponding to anions $\text{OCeNi}(\text{CO})_3^-$ and $\text{CeNi}(\text{CO})_3^-$ are presented with high intensities. For both species, the isotopic splitting of

cerium and nickel are well-resolved with the relative intensities, closely matching the natural abundance distributions.

The $\text{OCeNi}(\text{CO})_3^-$ and $\text{CeNi}(\text{CO})_3^-$ anions are respectively mass-selected and subjected to IRPD experiments. When the IR laser is on resonance with the CO stretching fundamentals of the anions, photofragmentation involving the loss of one or more CO ligands is observed. The $\text{OCeNi}(\text{CO})_3^-$ and $\text{CeNi}(\text{CO})_3^-$ anions fragment only under focused IR laser irradiation and were observed to lose up to two CO ligands, indicating that multiphoton absorption is required.

The IRPD spectra of mass-selected $\text{OCeNi}(\text{CO})_3^-$ and $\text{CeNi}(\text{CO})_3^-$ anions in the carbonyl stretching frequency region are shown in Figure 1. The spectrum of $\text{OCeNi}(\text{CO})_3^-$ has three bands centered at 1925, 1647, and 1603 cm^{-1} , as well as a shoulder band at 1887 cm^{-1} on the lower-frequency side of the 1887 cm^{-1} band. The dissociation efficiency reached about 3.9% at 1925 cm^{-1} with a focused laser energy of about 1 mJ/pulse, while the efficiency decreased to about 0.25% at 1603 cm^{-1} . Since one $\text{OCeNi}(\text{CO})_3^-$ structure only contains three CO ligands and would exhibit at most three vibrational fundamentals in the CO stretching region, the observation of four CO stretching bands indicates the coexistence of multiple isomers. The observation of low CO stretching frequencies at 1647 and 1603 cm^{-1} suggests the existence of a structure with side-on CO.²⁸ This finding is distinct from the $\text{OFe}(\text{CO})_3^-$ anion that has a C_{3v} structure with all the CO ligands terminally bonded to the Fe atom.²⁹ The spectrum of $\text{CeNi}(\text{CO})_3^-$ exhibits two narrow bands centered at 1919 and 1959 cm^{-1} , one broad band centered at 1941 cm^{-1} , and one rather weak band centered at 1497 cm^{-1} . Similar to $\text{OCeNi}(\text{CO})_3^-$ anion, the observation of four CO stretching bands implies the presence of multiple isomers. This is quite different from those of nickel carbonyl complexes $\text{ENi}(\text{CO})_3^-$ ($E = \text{Li–Cs}$), which display only two bands and adopt the C_{3v}

geometry.¹⁷ The $\text{CeNi}(\text{CO})_3^-$ anion can be depleted by only about 1.9% at 1941 cm^{-1} with a focused laser energy of about 1 mJ/pulse, while the dissociation efficiency decreased to about 0.08% at 1497 cm^{-1} (This spectral region was validated by repeated scans, as presented in Figure S2(a)). The low frequency of the CO stretching mode at 1497 cm^{-1} also suggests the presence of side-on CO.²⁸

To assign the experimental data and gain deep insight into the structures of the $\text{OCeNi}(\text{CO})_3^-$ and $\text{CeNi}(\text{CO})_3^-$ anion complexes, a comprehensive global minimum structure search was conducted using density functional theory (DFT) (detailed computational methods are available in the Supporting Information). Geometry optimizations and frequency calculations were performed at the PBE0/def2-TZVPP^{30–32} level with the Stuttgart energy-consistent relativistic pseudopotential for Ce,³³ considering the configurations with relative energies below 20 kcal/mol for both complexes (Figures S3 and S4). The global minimum search located two energetically similar isomeric configurations for $\text{OCeNi}(\text{CO})_3^-$ and three nearly identical energy configurations for $\text{CeNi}(\text{CO})_3^-$. These five optimized structures are presented in Figure 2, with corresponding bond lengths and bond orders detailed in Table S1.

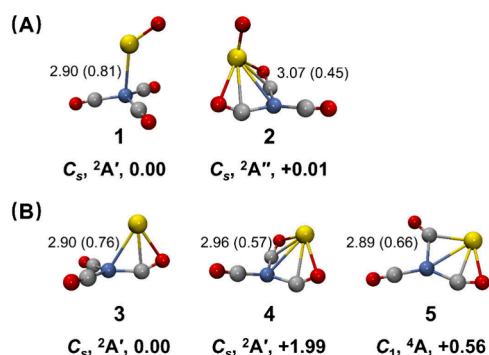


Figure 2. Identified structures of the low-lying isomers for (A) $\text{OCeNi}(\text{CO})_3^-$ and (B) $\text{CeNi}(\text{CO})_3^-$ at the PBE0/def2-TZVPP level of theory (O, red; C, gray; Ni, blue; Ce, yellow). Ce–Ni bond lengths (Å) and Wiberg bond orders are given in regular font and in parentheses, respectively. The point group, electronic state, and relative energy (kcal/mol) of the corresponding isomers are listed below the structures.

In the case of $\text{OCeNi}(\text{CO})_3^-$, isomers 1 and 2 exhibit a C_s symmetry. Notably, isomer 1 displays an O–Ce–Ni bond angle of 131°, instead of a C_{3v} configuration compared to the previously reported $\text{OUFe}(\text{CO})_3^-$.²⁹ The Ce–O bond length in 1 is 1.83 Å, closely matching the sum of Pyykkö covalent triple-bond radii (1.84 Å).³⁴ In contrast, the Ce–Ni bond length (2.90 Å) exceeds the sum of Pyykkö covalent single-bond radii (2.73 Å),³⁵ indicating a weak single bond, which is consistent with the values of Mayer bond order and Wiberg bond order (0.51 and 0.81, respectively; Wiberg bond order is based on Löwdin orthogonalization). However, it still represents the shortest Ce–Ni bond documented to date; only Zhu and co-workers have previously reported a Ce–Ni single bond with a bond length of 3.17 Å.¹² While for isomer 2, both the Ce–O and Ce–Ni bonds are slightly weakened due to the side-on CO. The configurations of 1 and 2 perfectly satisfy the hard–soft–acid–base theory where O atom plays a role as a hard base while CO coordinate with Ni as a soft base.⁹ As for the $\text{CeNi}(\text{CO})_3^-$, the global minimum structure 3 with

one side-on CO and two terminal COs has not been reported yet. Isomer 5 features three different types of CO coordination modes, a configuration first discovered by Jiang and co-workers,²³ which also emerged as a low-lying isomer in our calculations. Imposing a C_s symmetry on 5 results in an imaginary frequency corresponding to a bending mode. The quartet state of 5 is found to be 1.9 kcal/mol more stable than the doublet state (Figure S4). Bond length and bond order analysis reveal several remarkable features of 5: it possesses the shortest Ce–Ni (2.89 Å) and Ce–C (2.40 Å, comparable to the reported Ce=C double bonds^{36,37}) bonding length in the series. Although the Ce–Ni bond in isomer 5 is shorter than that in isomers 1 and 3, it exhibits the weakest bond order among them. This indicates that the side-on and bridging CO ligands form strong bonding interactions with Ce and Ni individually, rather than promoting orbital overlaps between Ce and Ni. Potential energy surface (PES) scan was carried out to explore the structural diversity of the $\text{OCeNi}(\text{CO})_3^-$ and $\text{CeNi}(\text{CO})_3^-$ dimers (Figure S5). For $\text{OCeNi}(\text{CO})_3^-$, the PES reveals three local minima, two of which were assigned as isomers 1 and 2. For $\text{CeNi}(\text{CO})_3^-$, four local minima were found, with three corresponding to isomers 3–5. The remaining structures in both cases, including a C_{3v} -symmetric structure, were excluded from further analysis due to their low energy barriers.

The simulated spectra of isomers 1 and 2 are compared with the experimental spectrum of $\text{OCeNi}(\text{CO})_3^-$ in Figure 1(A), and those of isomers 3–5 are compared with the experimental spectrum of $\text{CeNi}(\text{CO})_3^-$ in Figure 1(B). Clearly, no individual isomer spectrum can fit the experiment data. In the case of $\text{OCeNi}(\text{CO})_3^-$, isomer 1 exhibits two CO stretching vibrations at 1893 and 1899 cm^{-1} , which correspond well to the shoulder peak observed at 1887 cm^{-1} in the experimental spectrum. Two side-on CO ligands in isomer 2 show a significant red shift in the carbonyl stretching frequencies, exhibiting two small peaks at 1631 and 1674 cm^{-1} , which match well with the two minor experimental bands at 1603 and 1647 cm^{-1} . The 1916 cm^{-1} peak of isomer 1 and the 1935 cm^{-1} peak of isomer 2 are tentatively assigned to contribute to the observed 1925 cm^{-1} peak. Therefore, the coexistence of isomers 1 and 2 can explain the observed spectrum of $\text{OCeNi}(\text{CO})_3^-$. This assignment is also supported by the calculated isomerization barrier (2 → 1), which is predicted to be 11 kcal/mol according to the PES scan. This barrier is sufficiently high to allow both isomers to be kinetically trapped by the soft helium expansion of cold molecular beam, indicative of possible coexistence of isomers 1 and 2.

Regarding $\text{CeNi}(\text{CO})_3^-$, the end-on CO stretching frequencies of all three isomers (3–5) align closely with the experimental bands at 1919, 1941, and 1959 cm^{-1} . However, most of peaks from side-on and bridging COs are obscured in the experimental spectrum due to low dissociation efficiency and background noise. This is attributed to the fact that the side-on and bridging COs in isomers 3–5 are connected with the Ce atom, which reduces the dipole moment of the CO ligands relatively compared to the more polarized OCe in isomer 2 and thus diminishes the intensity of their stretching vibrations. Nevertheless, the calculated peaks at 1510 and 1482 cm^{-1} for the side-on CO stretching modes in isomers 3 and 5 still agree well with the experimental value at 1497 cm^{-1} . Considering that the experimental spectrum has a weak peak at 1615 cm^{-1} and isomer 4 is located at a local minimum on the

PES curve with energy near the global minimum, we still regard isomer **4** to be part of the set of isomers. In the subsequent chemical bonding analysis, we will retain isomer **4** and compare it with isomer **2**, which has a similar structure. Analogously, the coexistence of these isomers is supported by the PES scan, which reveals a calculated barrier of 9 kcal/mol for **3** $\rightarrow$ **4** isomerization. The calculated spectra of the remaining isomers obtained from the global structure search are shown in Figure S2(b). Comparison with experimental spectra confirms the absence of these isomers. Overall, the agreement between the sum of the simulated spectra of isomers **3**–**5** with the experimental spectrum is reasonable to identify these structures.

Figures 3 and 4 present schematic diagrams of frontier canonical Kohn–Sham (KS) valence molecular orbitals (MOs)

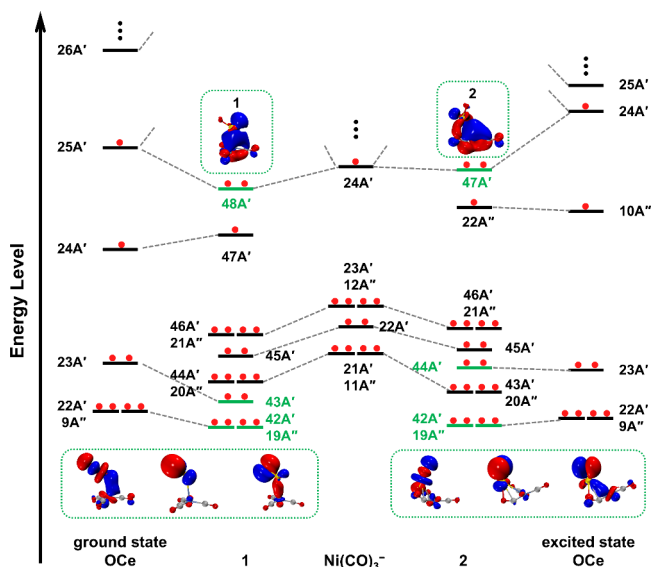


Figure 3. Kohn–Sham energy levels and the contours of the frontier Kohn–Sham canonical valence MOs (isovalue = 0.03 au) of isomers **1** and **2** for OCeNi(CO)₃[−] at the PBE0/def2-TZVPP level.

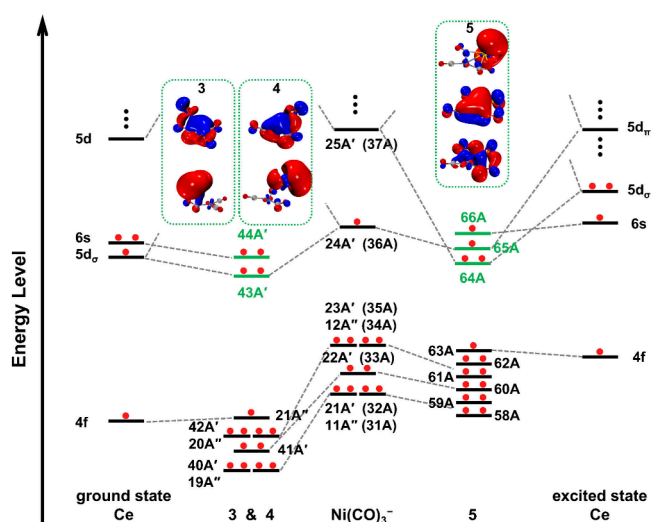


Figure 4. Kohn–Sham energy levels and the contours of the frontier Kohn–Sham canonical valence MOs (isovalue = 0.03 au) of isomers **3**–**5** for CeNi(CO)₃[−] at the PBE0/def2-TZVPP level.

for OCeNi(CO)₃[−] and CeNi(CO)₃[−], respectively. The KS MOs of the OCe, Ce, and Ni(CO)₃[−] fragments are shown in Figures S6 and S7, respectively. Only the highest occupied molecular orbital (HOMO) in **1** and **2** shows a multicenter bonding interaction between OCe and Ni(CO)₃[−]. Figure S6 shows that in the ground state of OCe, the singly occupied molecular orbital (SOMO, 25A') is primarily composed of the Ce 6s orbital, which can interact with the SOMO (24A') of Ni(CO)₃[−] to form a σ -covalent multicenter bond (48A'), similar to the previous reports.¹⁷ On the other hand, the HOMO of **2** (47A') shows a σ -dominant interaction with minor π -characters between the Ce 5d orbital and the SOMO of Ni(CO)₃[−]. An examination of frontier MOs of ground state OCe reveals that the lowest unoccupied molecular orbital (LUMO, 26A') contributes to the formation of the HOMO of **2**. This suggests that the unpaired electron in the SOMO (25A') of OCe is excited to the LUMO, forming an excited state OCe (Figure S6). This excited species can be effectively stabilized by Ni(CO)₃[−] owing to favorable symmetry matching and strong orbital overlap between the Ce 5d orbital and the SOMO of Ni(CO)₃[−]. Beyond the HOMOs of **1** and **2**, we also identified a Ce $\equiv$ O triple bond, consisting of one σ - and two π -bonds, which is consistent with the aforementioned analyses of bond length and bond order.

The bonding orbitals in **3** and **4** are similar to that in **2** but are located at the HOMO–1 (43A'). Instead, the HOMOs of **3** and **4** (44A') are nonbonding and predominantly consist of the lone pair of the Ce 6s orbital. Simple electron counting rules indicate that isomers **1**–**4** perfectly satisfy the 18-electron rule, because Ce (whether from the OCe moiety or the lone Ce atom) acts solely as a one-electron donor. While for **5** with a quartet electronic state, Ce donates only one unpaired 6s electron residing at the SOMO (66A). The HOMO (64A) and SOMO–1 (65A), both of which involve the Ce 5d orbital, show the multicenter bonding interactions between Ce and Ni(CO)₃[−]. Isomer **5** can be well described by the Dewar–Chatt–Duncanson (DCD) model:^{38,39} the Ce atom acts as a metallic ligand donating two d_σ electrons to the LUMO (37A) of the Ni(CO)₃[−] fragment, while Ni(CO)₃[−] donates the unpaired electron from its SOMO (36A) to the vacant d_π orbital of Ce which forms a back-donation π -half-bond (65A) (Figure 4 and Figure S7). We note that the main components of both the SOMO and LUMO of Ni(CO)₃[−] are the π^* orbitals of COs. The HOMO of **5** (64A) is hard to classify the bonding types specifically as the 5d orbital of Ce mainly forms a σ -interaction with the bridging CO and a π -interaction with the side-on CO.

The striking observation in this work is the structural diversity of cerium–nickel carbonyl complexes, which is distinctly different from the exclusive C_{3v} configuration exhibited by other previously reported carbonyl complexes.^{17,24,25,29,40,41} The origin of such structural variability is explored through electronic structure characterizations. Compared with the previously reported iron carbonyl complexes,^{29,40,41} Ni has two more valence electrons than Fe (3d⁸4s² vs 3d⁶4s²). An analysis of the molecular orbitals of the M(CO)₃[−] (M = Fe and Ni) fragments clearly shows that the 3d orbitals of Fe(CO)₃[−] are incompletely filled, which accounts for the tendency of iron carbonyl complexes to form multiple metal–metal bonds. Turning to nickel carbonyl complexes, the 3d orbitals of Ni are fully occupied (blue dashed lines in Figures S6 and S7), indicating that it is rather difficult for these d-orbitals to participate in bonding. Instead,

Table 1. EDA Results of Isomers 1 and 2 at the PBE0/TZ2P//PBE0/def2-TZVPP Level with Different Interacting Fragments Shown Below

Fragments:	Isomer 1			Isomer 2		
	OCe ⁺ + Ni(CO) ₃ ²⁻	OCe + Ni(CO) ₃ ⁻	OCe ⁻ + Ni(CO) ₃	OCe ⁺ + Ni(CO) ₃ ²⁻	OCe + Ni(CO) ₃ ⁻	OCe ⁻ + Ni(CO) ₃
ΔE_{int}	-265.3	-39.2	-48.6	-140.4	-72.0	-276.0
ΔE_{Pauli}	89.4	87.4	126.7	178.1	98.9	78.2
ΔE_{elstat}	-284.2	-90.0	-101.6	-117.4	-82.1	-268.3
ΔE_{orb}	-70.5	-36.6	-73.8	-201.1	-88.8 ^a	-85.9

^aConsidering that ΔE_{int} should be comparable with isomer 1, the second partitioning scheme is adopted though ΔE_{orb} is slightly higher than the third one.

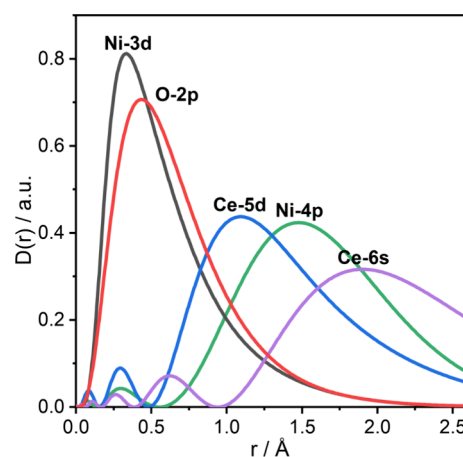
its valence orbital is featured as a delocalized π -orbital involving the 4p orbitals of Ni. Such a large planar active region offers sufficient spatial capacity for the bonding of Ce's valence electrons, at sites above (1), laterally above (2–4), or directly adjacent to the Ni center (5). In addition to its electrophilicity, Ni(CO)₃⁻ carries a negative charge, endowing it with prominent nucleophilicity, which allows the OCe moiety to bind to it favorably. From the perspective of Ce, both its 5d and 6s orbitals serve as valence orbitals with close energy levels, and thus the energy required for the transition from the ground state to the excited state is relatively low. The combined effects of the aforementioned factors give rise to the formation of multiple isomers with comparable energies for cerium–nickel carbonyl complexes.

The Adaptive Natural Density Partitioning (AdNDP) analysis further supports the presence of multicenter bonding identified in MOs for isomers 1–5 (Figures S8–S12).⁴² In both 1 and 2, an 8 center-2 electron (8c-2e) bond was found, respectively. Consistent with the visual representation of the KS MOs, the delocalized π -orbital of Ni(CO)₃⁻ is one of the dominant contributions to the multicenter bond. It is worth noting that the Ce≡O triple bond observed in MOs was also confirmed by the AdNDP results. The composition contributions of the three orbitals were analyzed and compared with free CO, isolated OCe and the previously reported Ce=O double bond⁴³ (Table S2). The contributions from the Ce 5d orbital are about 15% and 10% for the σ -bond and π -bonds, respectively, higher than the reported Ce=O double bond. On the other hand, the Ce 4f and 6s electrons remain nonbonding in 3–5, with only the 5d orbitals engaging in bonding interactions. An 8c-2e bond was identified in 3 and 4 between the Ce 5d orbital and the delocalized π -orbital of Ni(CO)₃⁻. In contrast, 5 exhibits a different bonding scheme, featuring a 6c-2e σ - π -bond and an 8c-1e back-donation π -bond. The orbital compositions of these multicenter bonds are summarized in Table S3, with Ni 4p and Ce 6s or 5d accounting for approximately 9%–15% and 22%–49%, respectively. Specially, the 6c-2e σ - π -bond of 5 contains the component of Ni 3d orbital instead of 4p orbital, with a small proportion of 5.7%.

The quantum theory of atoms-in-molecules (QTAIM) analysis⁴⁴ offers a topological view of the bonding interactions between Ce and Ni or O (Tables S4 and S5). Several QTAIM metrics at the bond critical point (BCP) are presented, including electron density (ρ), energy density (H), electron density Laplacian ($\nabla^2\rho$), etc. For 1, the low ρ , positive $\nabla^2\rho$ and negative H values at the Ce–Ni BCP indicate a weak polar covalent Ce–Ni bond, consistent with the bond order analysis. The BCP ellipticity ϵ of Ce≡O in both 1 and 2 is 0.00, reflecting the characteristics of a triple bond Ce≡O, similar to the bonding scheme of C≡O. In comparison to the previously

reported Ce=C and Ce≡C bonds,^{36,37,45} the oxygen atom can additionally contribute a dative bond (O→Ce) due to the presence of two extra 2p electrons. As reported in previous studies,^{43,46} Ce⁴⁺ dominates the Ce=O bond via its 4f orbital component due to strong polarization, which seriously affects the determination of bond order. In contrast, Ce exists in the +2 valence state in isomers 1 and 2, where the 5d orbital is the major contributor to bond formation (Table S2). This conclusion is also supported by the EDA^{47,48} analysis (Table 1), as the smallest ΔE_{orb} represents the best fragments for describing the bonding situation.⁴⁹ Detailed ETS-NOCV and PIO⁵⁰ analyses are provided in the Bonding Analysis part of the Supporting Information.

The atomic valence-orbital radial distribution functions were further analyzed to assess the possibility of bonding between the Ni 3d or 4p orbitals and the Ce 5d or 6s orbitals at a distance of approximately 3.0 Å (Figure 5). The Ni 3d orbital

**Figure 5.** Atomic valence-orbital radial distribution functions of O, Ni, and Ce.

is relatively more contracted ($r_{\text{max}} \sim 0.4$ Å) compared to the 4p orbital ($r_{\text{max}} \sim 1.5$ Å), suggesting that the Ni 4p could achieve better orbital overlap with Ce 5d/6s ($r_{\text{max}} \sim 1.1/1.9$ Å) at 3.0 Å. Generally, the fully occupied Ni 3d orbital and poor orbital overlap hinder effective bonding interactions. This helps to explain the low Ce–Ni bond order in 5 despite the shortest Ce–Ni distance, as only the SOMO-1 (65A) can describe the bonding interaction between Ce and Ni. In contrast, the HOMO (64A) contributes almost nothing to the Ce–Ni bond order. It is worth mentioning that the Ce 5d orbital have significant orbital overlaps with the O 2p ($r_{\text{max}} \sim 0.5$ Å) at a distance of around 1.8 Å, which further corroborates the dominant role of the Ce 5d orbital in the formation and stabilization of the Ce–O bond.

To confirm the results of the single-configuration DFT results, the multiconfiguration complete active space self-consistent field (CASSCF) method was performed (computational details are provided in the [Supporting Information](#)).^{51–53} The calculations reveal that the ground state of 1–5 is dominated by one single configuration, with configuration interaction (CI) weights of 77.4%, 83.4%, 75.7%, 84.5%, and 79.2% (Figures S20–S24). The strong single-reference character indicates that DFT is appropriate for describing these molecules.

In summary, the heteronuclear cerium–nickel carbonyl anion complexes $\text{OCeNi}(\text{CO})_3^-$ and $\text{CeNi}(\text{CO})_3^-$ were synthesized in the gas phase. Global minimum searches using DFT methods found several low-lying isomers (1–5), whose simulated IR spectra agree well with mass-selected IR photodissociation experimental spectra. This study highlights the observation of structural diversity, which stands in sharp contrast to the C_{3v} symmetry typically found in previously reported iron carbonyl analogues. Notably, these complexes feature the shortest Ce–Ni bond and a $\text{Ce}\equiv\text{O}$ triple bond. The $\text{Ni}(\text{CO})_3^-$ fragment plays a crucial role in stabilizing the Ce center (in its 0 or II oxidation state) by forming multicenter bonds through its SOMO orbital. This study highlights the crucial role of the Ni 4p orbital in forming a s-p or p-d σ -type multicenter metal–metal bond, which differs from traditional transition metals primarily using d orbitals. These findings offer a promising direction for the rational design and synthesis of novel heterometallic bonds with d- and f-block metals.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.6c01315>.

Experimental and theoretical methods; bonding analysis; structural parameters, orbital composition, QTAIM analyses, EDA-NOCV results, and comparison of the bonding orbital energy proportion (Tables S1–S8); spectra, structures, PES results, MO contours, AdNDP analyses, plots of the deformation densities, PIO analyses, and NOs and NOONs (Figures S1–S24) (PDF)

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■ DEDICATION

Dedicated to Professor Fang-Yu Xue on the occasion of his 80th birthday.

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