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Infrared photodissociation spectroscopy of trigonal bipyramidal 19-electron $Ni(CO)_5^+$ cation

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ABSTRACT

The 18-electron rule is a fundamental rule in chemistry governing the structure and bonding of transition metal compounds. Here we report the observation of a chemically bound Ni(CO)⁺₅ complex, which was characterized by infrared photodissociation spectroscopy and quantum chemical calculations to be a five-fold coordinated trigonal bipyramidal carbonyl compound having 19 valence electrons with the extra electron residing largely on metal center. This finding provides new insight of ligand interactions and coordination for the transition metals.

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1. Introduction

The well-known 18-electron rule, describing the number of metal and ligands electrons that give the d¹⁰s²p⁶ noble gas configuration lays the foundation of chemistry, governing in general the coordination and structures of transition metal complexes [1-3]. This rule works well in describing the bonding between transition metal and ligands, such as homoleptic metal carbonyl complexes where carbon monoxide serves as a two-electron donor and central metals retain a 18-electron close-shell structure [4-11]. Beyond the close-shell electronic configuration, either electron-withdrawing or electron-adding, would destabilize the complex greatly. Although the electron-deficient open-shell radicals are not unusual under certain synthetic conditions [12-14], over-saturated transition metal complexes with more than 18 electrons are not very common [15,16]. Here we report the production and infrared spectroscopy characterization of a thermodynamically stable 19electron $Ni(CO)_5^+$ complex in the gas phase, a five-fold coordinated trigonal bipyramidal nickel carbonyl complex with the extra electron residing largely on metal center.

2. Experimental and computational methods

The experiment was performed using a collinear tandem timeof-flight mass spectrometer, the details of which have been described recently [17,18]. Nickel carbonyl cations were produced in a Smalley-type laser vaporization supersonic cluster source via laser vaporization of a nickel metal target in expansions of helium gas seeded with 2–4% CO using a pulsed valve [19]. After free expansion, the cations are skimmed and mass analyzed by a time-of-flight mass spectrometer. The cations of interest are mass selected and decelerated into the extraction region of a second collinear time-of-flight mass spectrometer, where they are irradiated by a tunable IR laser generated with an KTP/KTA optical parametric oscillator/amplifier system (OPO/OPA, Laser Vision) pumped by the fundamental output of a Nd: YAG laser (Continuum Powerlite 8000). Infrared photodissociation spectra are obtained by monitoring the fragment ion yield as a function of the dissociation IR laser wavelength.

The density functional theory calculations were performed using the B3LYP and PBE functionals with the 6-311+G(d) basis set for the C, and O atoms, the all-electron basis sets of Wachter and Hay as modified by GAUSSIAN program for the first row transition metal atoms and the SDD pseudo potential and basis set for the second and third row transition metal atoms. The geometries were fully optimized, and the harmonic vibrational frequencies were calculated with analytic second derivatives. The zero-point energies (ZPE) were derived. All calculations were performed using the GAUSSIAN 09 program [20].

3. Results and discussion

The mass spectra of nickel carbonyl cluster cations produced by the laser vaporization supersonic cluster source at different experimental conditions are shown in Figure 1. Spectrum (a) demonstrates the production of mononuclear nickel carbonyl cation complexes containing up to 8 CO's. These cluster ions contain both strongly bound ligands coordinated to metal and weakly bound ligands attached to the external surface of stable complexes (formed only because of the cold supersonic beam conditions). Spectrum (b) is obtained at experimental conditions that only those with relatively strong bonding can survive. Peaks due to Ni(CO)⁺₅, Ni₂(CO)⁺₈



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Figure 1. Mass spectra of the nickel carbonyl cation complexes produced by pulsed laser vaporization of a nickel metal target in an expansion of helium seeded by carbon monoxide. (a) From experiment with short time delay between pulsed valve and vaporization laser, and (b) from experiment with long time delay between pulsed valve and vaporization laser.

and Ni₃(CO)⁺₉ are the most intense peaks in the mass spectrum, indicating that these cation complexes are formed preferentially with high stability. The experiment with ¹³C substituted CO sample adds additional support that the observed peaks in the mass spectra are due to nickel carbonyl clusters (Figure S1 of Supporting information).

The infrared induced fragmentation mass spectra for Ni(CO)⁺_n (n = 4-6) obtained by taking the difference between the mass spectra recorded with the photodissociation laser on versus off are shown in Figure S2 of Supporting information. It was found that both Ni(CO)⁺₄ and Ni(CO)⁺₅ dissociate by losing one CO ligand by focused IR laser with low efficiency. This is consistent with the stronger binding of these systems. The dissociation energy of the last CO from Ni(CO)⁺₄ was measured previously to be 0.75 ± 0.03 eV (17.3 kcal/mol) [21]. In contrast, the complexes larger than n = 5 are observed to dissociate very efficiently even using unfocused laser beam, revealing that the pentacarbonyl of Ni⁺ is the strongly bound fully-coordinated ion.

The vibrational spectra in the CO stretching frequency region for the n = 4-7 complexes are shown in Figure 2. The spectrum of Ni(CO)⁴₄ has one band centered at 2179 cm⁻¹, about 3 cm⁻¹ higher than that measured in solid neon matrix [22]. The spectrum of Ni(CO)⁵₅ cation has two broad bands centered at 2169 and 2183 cm⁻¹. The spectra of Ni(CO)⁶₆ and Ni(CO)⁷₇ are essentially the same exhibiting two well-resolved bands at 2168 and 2183 cm⁻¹. As discussed previously [10,11], the external CO ligand(s) have a negligible effect on the spectrum of the core ions. The complexes larger than n = 5 can be regarded as CO 'tagged' Ni(CO)⁵₅. The external CO ligand(s) is expected to have weak CO stretching vibration(s) in the range of 2160–2170 cm⁻¹ [11,23], which is overlapped by the strong band of the core ion in the spectra of the n = 6 and 7 complexes.

To support the experimental assignment and to gain insight into the geometric and electronic structures of Ni(CO)₅⁺, density functional theory (DFT) calculations were performed. The Ni(CO)₅⁺ cation is predicted to have a trigonal bipyramidal structure with D_{3h} symmetry (Figure 3). From DFT calculations, the removal of the fifth CO from Ni(CO)₅⁺ (to Ni(CO)₄⁺) is energetically unfavorable, requiring 24.2 kJ/mol (B3LYP) or 53.5 kJ/mol (PBE). This is in line with the observed stronger Ni(CO)₅⁺ signal in mass spectrum with respect to Ni(CO)₄⁺. All CO molecules are found to



Figure 2. The experimental vibrational spectra of the Ni(CO) $_n^+$ (n = 4-7) cations and the simulated spectrum of Ni(CO) $_5^+$ in the carbonyl stretching frequency region. Computed frequencies were scaled by 0.971 (B3LYP, trace a) and 1.017 (PBE, trace b), and bands were given a 5 cm⁻¹ fwhm Lorentzian line shape.

bond chemically with Ni cation. At the B3LYP level, the two Ni–C bonds along the principal C₃ axis are slightly longer (by 0.16 Å) and consequently the two axial C–O bonds are slightly shorter (by 0.002 Å). Consistent with the structural information, the computed spectrum (also shown in Figure 2) agrees well with the experiment. The cation has three IR active CO stretching modes. The peak at 2169 cm⁻¹ is assigned to the antisymmetric CO stretching of the three equatorial CO ligands, which is doubly degenerate. The 2183 cm⁻¹ band is attributed to the antisymmetric CO stretching of the two axial CO ligands. Both bands are blue-shifted with respect to the gas phase CO frequency (2143 cm⁻¹), implying a weak backdonation from metal cation to CO $2\pi^*$ [24,25].

Next, we have analyzed the electronic structure of $Ni(CO)_5^+$ and the bonding picture is summarized in Figure 4. It shows that $Ni(CO)_5^+$ has a large HOMO–LUMO gap and the dominant bonding between Ni and CO ligands is mainly via CO 5 σ donation to Ni empty 4s and 4p orbitals with little participation of CO empty



Pd(CO)5⁺, D_{3h}, ²A₁'

Figure 3. Optimized structures of the $Ni(CO)_5^+$, $Pd(CO)_5^+$ and $Cu(CO)_5^{2+}$ cations (bond lengths in angstrom) at the B3LYP level.

 $2\pi^*$ orbitals. The five 5σ orbitals evolves into five molecular orbitals, namely, a'_1 (+Ni 4s), a_1' (+Ni $3d_2^2$), e' (doubly degenerate, +Ni $4p_x$, $4p_y$) and a''_2 (+Ni $4p_z$). The HOMO orbitals originate primarily from nonbonding 3d orbitals of Ni. Most importantly, the singly occupied MO (SOMO, a'_1) has a rather low eigenvalue (-0.47 a.u.), being only 0.016 a.u. above HOMO-1, but 0.219 a.u. lower than LUMO. The SOMO is mainly of Ni $3d_z^2$ origin, having antibonding features with two axial CO 5σ orbitals. Obviously, the presence of the low-lying SOMO can be attributed to the weak coupling between the axial CO 5σ and Ni $3d_z^2$ orbital. In fact, considering that CO 5σ and Ni d orbitals are fully or nearly fully occupied, only a weak 5σ -3d interaction is expected to contribute positively to the overall stability of the complex.

From its electronic structure, the formal valence electron of $Ni(CO)_{5}^{+}$ can therefore be counted as 19, 10 from five CO 5 σ orbitals and 9 from 3d of Ni⁺. Based upon the generally-regarded 18electron noble gas rule, one would expect that the nickel cation with an odd number of electrons should form 17-electron $Ni(CO)_4^+$ complex instead of the over-saturated 19-electron $Ni(CO)_5^+.$ The thermodynamic stability of the 19-electron $Ni(CO)_5^+.$ complex can be attributed to the weak 5σ -3d coupling but strong 5σ donation to metal empty s/p orbitals. By comparing a series of isovalence M(CO)₅ complexes, including Co, Ni, Cu, Pd and Pt using DFT/B3LYP, we found that 19-electron homoleptic metal carbonyl complex should not be unique to Ni: they can be stable also for Cu and Pd $(Pd(CO)_5^+$ signal in mass spectrum has appreciable intensity, Figure S3). We notice that $Cu(CO)_5^{2+}$ is very stable with the fifth CO binding energy predicted to be 71.9 kJ/mol. On the contrary, the $D_{3h} Pt(CO)_5^+$ and $Co(CO)_5$ are not minimum structures with imaginary frequencies. The stable structures are optimized to be very weak $Pt(CO)_4^+$ -CO and $Co(CO)_4$ -CO complexes. Instead, tetra-coordinated $Pt(CO)_4^+$ cation is characterized to be the strongly



Figure 4. The bonding picture for $D_{3h} Ni(CO)_5^+$ as revealed from DFT calculations. The contour plots of the key molecular orbitals are shown in Figure S4 of Supporting information.

bound fully-coordinated ion [26]. The stability order of the $M(CO)_5$ complexes identified above are in accordance with the 5σ -3d coupling strength: the coupling strength (as quantified by the coupling matrix element V_{3d}^2) decreases from left to right, but increases from top to bottom in periodic table [27].

The 19-electron complexes were reported previously with the stable complexes involving generally the ring ligands, e.g. Cp_2M . The extra (19th) electron resides majorly in the ring to afford a high stability [15,16]. Although some over saturated transition metal carbonyl cations have been theoretically considered [28], no experimental isolation of 19-electron homoleptic carbonyl complexes have been reported. The Ni(CO)⁺₅ cation is the first example of chemically bound fully-coordinated homoleptic carbonyl demonstrating that the 19-electron metal carbonyl complex with the extra electron residing largely on metal center can be stable. The results demonstrate new chemistry in transition-metal-based organometallic complexes.

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Appendix A. Supplementary data

Supplementary data associated with this Letter can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2012.06. 006.

References

- F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, Wiley, New York, 1999.
- [2] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry Principles of Structure and Reactivity, Harper Collins, New York, 1993.
- [3] R. Hoffmann, Angew. Chem. Int. Ed. Eng. 21 (1982) 711.
- [4] M. Elian, R. Hoffmann, Inorg. Chem. 14 (1975) 1058.
- [5] G. Frenking, N. Frohlich, Chem. Rev. 100 (2000) 717.
- [6] K.M. Ervin, Int. Rev. Phys. Chem. 20 (2001) 127.
- [7] F. Aubke, C. Wang, Coord. Chem. Rev. 137 (1994) 483.
 [8] Y.M. Xie, H.F. Schaefer III, R.B. King, J. Am. Chem. Soc. 122 (2000) 8746.
- [9] H.Y. Wang, Y.M. Xie, R.B. King, H.F. Schaefer III, J. Am. Chem. Soc. 128 (2006) 11376.
- [10] A.M. Ricks, Z.D. Reed, M.A. Duncan, J. Am. Chem. Soc. 131 (2009) 9176.
- [11] A.M. Ricks, Z.D. Reed, M.A. Duncan, J. Mol. Spectrosc. 266 (2011) 63.
- [12] H. Willner, F. Aubke, Angew. Chem. Int. Ed. Eng. 36 (1997) 2402.
- M.F. Zhou, L. Andrews, C.W. Bauschlicher Jr., Chem. Rev. 101 (2001) 1931.
 E. Bernhardt, H. Willner, A. Kornath, J. Breidung, M. Buhl, V. Jonas, W. Thiel, J. Phys. Chem. A 107 (2003) 859.
- [15] D. Astruc, Chem. Rev. 88 (1988) 1189.
- [16] D.R. Tyler, Acc. Chem. Res. 24 (1991) 325.
- [17] G.J. Wang, C.X. Chi, J.M. Cui, X.P. Xing, M.F. Zhou, J. Phys. Chem. A 116 (2012) 2484.
- [18] C.X. Chi, J.M. Cui, X.P. Xing, G.J. Wang, M.F. Zhou, Chem. Sci. 3 (2012) 1698.
- [19] T.G. Dietz, M.A. Duncan, D.E. Powers, R.E. Smalley, J. Chem. Phys. 74 (1981) 6511
- [20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, et al., GAUSSIAN 09, Revision A.02, GAUSSIAN Inc., Wallingford CT, 2009.
- [21] F.A. Khan, D.L. Steele, P.B. Armentrout, J. Phys. Chem. 99 (1995) 7819.
- [22] B.Y. Liang, M.F. Zhou, L. Andrews, J. Phys. Chem. A 104 (2000) 3905.
- [23] A.D. Brathwaite, Z.D. Reed, M.A. Duncan, J. Phys. Chem. A 115 (2011) 10461.
- [24] A.J. Lupinetti, G. Frenking, S.J. Strauss, Angew. Chem. Int. Ed. 37 (1998) 2113.
- [25] A.J. Lupinetti, S.J. Strauss, G. Frenking, Prog. Inorg. Chem. 49 (2001) 1.
- [26] J. Velasquez III, M.A. Duncan, Chem. Phys. Lett. 461 (2008) 28.
- [27] B. Hammer, J.K. Norskov, Nature 376 (1995) 238.
- [28] A.J. Lupinetti, V. Jonas, W. Thiel, S.H. Strauss, G. Frenking, Chem. Eur. J. 5 (1999) 2573.