

Communications



Weakly Coordinating Anions Very Important Paper

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Chasing the Mond Cation: Synthesis and Characterization of the Homoleptic Nickel Tetracarbonyl Cation and its Tricarbonyl-Nitrosyl Analogue

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Dedicated to Professor Wolfgang Kaim on the occasion of his 70th birthday



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Abstract: 130 years after Mond discovered the first homoleptic carbonyl complex $Ni(CO)_4$, we report on a $[Ni(CO)_4]^{+}$ salt as the first synthesis of any homoleptic nickel carbonyl cation in the condensed phase. It was prepared by oxidation of nickel metal with the synergistic oxidant $Ag[F{Al(OR^F)_3]_2}]/0.5I_2$ $(R^F = C(CF_3)_3)$ in CO atmosphere. This D_{2d} -symmetric metalloradical represents the last missing entry among the structurally characterized homoleptic carbonyl cations of Groups 6 to 11. Additionally, the nickel tricarbonyl-nitrosyl cation $[Ni(CO)_3(NO)]^+$ was obtained by usage of $NO[F{Al(OR^F)_3}_2]$ and all products were fully characterized by means of IR, Raman, NMR/EPR, single crystal and powder XRD.

he discovery of the first homoleptic carbonyl complex Ni(CO)₄ by Mond in 1890^[1] was the entry to transition metal (TM) carbonyl chemistry, a fascinating area in terms of fundamental bonding with a wide range of applications. The latter include, for instance, the production of base chemicals^[2] or materials^[3] as well as applications in the areas of life science^[4] and catalysis.^[5,6] Anionic TM carbonylates were discovered in 1931,^[7] although the mononuclear nickelate [Ni(CO)₃]²⁻ was not structurally characterized until 2018.^[8] Compared to their anionic counterparts, transition metal carbonyl cations (TMCC) were only discovered about 30 years later, with the first reports published in 1961.^[5,9] Their reduced π -back bonding^[10] leads to greatly blue-shifted COstretching frequencies that may reach values up to 2295 cm⁻¹ in $[Ir(CO)_6]^{3+}$ (cf. CO gas: 2143 cm⁻¹).^[5] These unusual stretching frequencies sparked discussions on the carbonyl bonding in TMCCs.^[9,11] However, according to new analyses,^[10] TMCC as well as TM carbonyl bonding in general is well described by the Dewar-Chatt-Duncanson model.^[12] Yet, it is clear that TMCCs have weaker M-CO bond strengths compared to the long-known neutral or anionic carbonyl complexes.^[9-11,13] Apparently, this lowered stability and increased reactivity of TMCCs accounts for the limited knowledge on homoleptic nickel carbonyl cations. Only investigations by mass spectrometry,^[14,15] at low temperatures in noble gas matrices,^[16,17] and theoretical works^[18] report on the mononuclear $[Ni(CO)_{1-5}]^+$ as well as some clustered cations [Ni₂₋₃₁(CO)₂₋₃₂]^{+/2+}. Most mononuclear carbonyl com-

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plexes are prototypes for the 18-electron rule. Exceptions include the neutral $V(CO)_6$ or the recently reported first examples of mononuclear open-shell TMCCs [M(CO)₆].+ (M = Cr, Mo, W).^[19,20] Here, we present the synthesis and characterization of a 17 valence electron (VE) nickel tetracarbonyl cation salt and its 18 VE tricarbonyl-nitrosyl analogue $[Ni(CO)_3(NO)]^+$. This entry completes the list of structurally characterized homoleptic TMCCs for all elements from group 6 to 11, which were isolated as bulk compounds from superacidic media and/or with a suitable weakly coordinating anion (WCA)^[21] (Table 1).^[5,9,13,22]

Since it was expected that the CO-ligands in [Ni(CO)₄]⁺⁺ are rather labile bound, we used the least coordinating WCA $[F{Al(OR^F)_3}_2]^{-[28]}$ in combination with a polar solvent with very low coordinating ability, that is, 1,2,3,4-tetrafluorobenzene (4FB). Note that already ortho-difluorobenzene has the potential to displace CO from the metal in TMCCs.^[26,29] For the oxidation to the target cation we tested Ag⁺ and NO⁺ salts that may react innocent by formation of TMCCs,^[23,26] but also non-innocent by formation of Ag- or NO-complexes.^[20,30,31] Thus, the synergistic $Ag^+/0.5 I_2$ system,^[32,33] reported to be more suitable for the generation of novel TMCCs,^[20] with a high redox potential of about 1.49 V vs. SHE in water was used.^[33] Due to the high toxicity and volatility of neutral $Ni(CO)_4$, we decided to use elemental nickel powder^[34] as the starting material and converted it in CO atmosphere with the selected oxidizers to obtain the target cation $[Ni(CO)_4]^{++}$. Although, it appears that the reaction of the pure silver salt $Ag[F{Al(OR^{F})_{3}}]$ with nickel metal in CO atmosphere is able to generate the target cation $[Ni(CO)_4]^{+}$, only a mixture of compounds that probably also includes the silver complex $[Ag{Ni(CO)_4}_2]^+$ was obtained (see the Supporting Information, Section 4). By contrast, the reactions with NO⁺ [Eq. (1)] and the synergistic $Ag^+/0.5 I_2$ system [Eq. (2)] were conclusive and straightforward. NO⁺ reacts non-innocent with nickel metal in CO atmosphere according to Equation (1). By vapor diffusion of *n*-pentane into the reaction solution red crystals of $[Ni(CO)_3(NO)][F{Al(OR^F)_3}_2]$ 1 (crystalline yield: 55%) were obtained as the first pseudo-ternary mixed nitrosyl/ carbonyl of Ni to be characterized in the condensed phase. Hitherto this compound was only addressed in theoretical investigations.^[35,36,37] Favorably, under the same conditions, the synergistic $Ag^+/0.5 I_2$ system yielded colorless crystals of $[Ni(CO)_4][F{Al(OR^F)_3}_2]$ 2 [Eq. (2); crystalline yield: 66 %].[38]

Ni + NO[F{AI(OR ^F) ₃ } ₂]	CO (3 bar) 4FB, RT, 1 day	[Ni(CO) ₃ (NO)][F{Al(OR ^F) ₃ } ₂] 1	(1)
Ni + Ag[F{Al(OR ^F) ₃ } ₂] + 0.5 l ₂	CO (3 bar) 4FB, RT, 2 days	[Ni(CO) ₄][F{AI(OR ^F) ₃ } ₂] + AgI 2	(2)

However, the formation of light brown solvate crystals of $[Ni(CO)_4][F{Al(OR^F)_3}_2] \cdot 4FB$ 2.4FB was also observed. The solvent molecule in 2-4FB can easily be removed by shortly drying in vacuo or by leaving the light brown crystals of 2-4FB in the crystallization solution for a few days to yield colorless and solvent-free 2 (Supporting Information, Figure S7). Both

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Table 1: Hitherto structurally characterized mononuclear homoleptic transition metal carbonyl cations.^[a]

			,							
	3	4	5	6	7	8	9	10	11	12
3 d 4 d 5 d	Sc* Y* La*	Ti* Zr* Hf*	V* [Nb(CO) ₇] ^{+[26]} [Ta(CO) ₇] ^{+[26]}	$[Cr(CO)_6]^{+[23]}$ $[Mo(CO)_6]^{+[20]}$ $[W(CO)_6]^{+[20]}$	[Mn(CO) ₆] ^{+[24]} [Tc(CO) ₆] ⁺ [Re(CO) ₆] ⁺	$[Fe(CO)_6]^{2+}$ $[Ru(CO)_6]^{2+[27]}$ $[Os(CO)_6]^{2+[27]}$	$[Co(CO)_5]^+$ $[Rh(CO)_4]^{+[b]}$ $[Ir(CO)_4]^{+[b]}$ $[Ir(CO)_6]^{3+}$	Ni^{*} [Pd(CO) ₄] ^{2+[b]} [Pt(CO) ₄] ^{2+[b]}	[Cu(CO) ₁₋₄] ^{+[25]} [Ag(CO) ₁₋₂] ⁺ [Au(CO) ₂] ⁺	Zn Cd [Hg(CO) ₂] ²⁺

[a] TMCCs were only cited when the reference to the crystal structure is not included with the reviews.^[5,9,13,22] [b] 16 VE species. Note: TMCCs of metals indicated by * were only spectroscopically characterized in the gas phase by mass-selected infrared laser photodissociation spectroscopy or in noble gas matrices. To the best of our knowledge, none of them were hitherto isolated in the condensed phase.

products **1** and **2** were fully characterized by means of IR, Raman, NMR/EPR and single crystal XRD and bulk purity was proven with powder XRD and EDX.

In the crystal structure of **1**, the NO ligand is disordered over multiple positions (Supporting Information, Section 6)^[54] and the cation $[Ni(CO)_3(NO)]^+$ almost appears T_d symmetric, like the isoelectronic Ni(CO)₄. The expected difference in the mean Ni-C/N bond lengths between the products **1** (1.847(9) Å) and **2** (1.931(5) Å) agrees with the calculated values for $[Ni(CO)_3(NO)]^+$ (1.872 Å) and [Ni- $(CO)_4]^{+}$ (1.975 Å) (@B3LYP(D3BJ)/def2-TZVPP). The NO stretch in **1** resonates at 1953 cm⁻¹, while the CO frequencies are significantly blue-shifted (2202 cm⁻¹ (A_1), 2182 cm⁻¹ (E); Figure 1 a).^[36,37] The NO ligand is visible in the ¹⁴N NMR spectrum at 4.9 ppm (Supporting Information, Figure S4). Product **1** is isomorphous and isoelectronic to earlier reported [Mn(NO)₄]^{+[39]} and [Fe(CO)(NO)₃]⁺ salts.^[31] Their almost linear M-C-O/M-N-O units (176 to 179°) are described in terms of the Enemark–Feltham notation^[40] as {MNO}¹⁰.

The assignment of oxidation states in nitrosyl complexes is not trivial due the covalent character of the metal nitrosyl bond as published by Klüfers et al.^[41] With CASSCF calculations and the effective-oxidation-state method^[42] they assigned the π -bonding M-NO electrons. Yet, due to the



Figure 1. a),b) One formula unit of the crystal structure of 1 ($P\bar{1}$, $R_1 = 6.1\%$, $wR_2 = 12.4\%$)^[54] and 2 ($P\bar{1}$, $R_1 = 6.5\%$, $wR_2 = 16.1\%$)^[54] together with the corresponding experimental and simulated IR spectra (calculated at BP86(D3BJ)/def2-TZVPP level without scaling factor). c) Measured and simulated X-band continuous wave EPR spectrum of solid 2 at 100 K. The *g*-values obtained by numerical simulation of the experimental spectrum are shown together with calculated values and the calculated spin density (cutoff: 0.005 a.u., B3LYP/EPR-II(6-31G* for Ni)). d) Cyclic voltammogram (100 mVs⁻¹) of 2 (10 mM) in **4FB** with Fc[Al(OR^F)₄] (10 mM) as internal reference and [NBu₄][Al(OR^F)₄] (100 mM) as conducting salt together with the calculated half wave potential (@B3LYP(D3BJ)/def2-TZVPP, solvent correction with the COSMO-RS^[45] model, see the Supporting Information, Section 11).

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	Table 2:	Comparison	of the ex	perimental	data of	1 and 2	with N	i(CO)₄	and the	correspo	onding	calculated	value
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	1	calcd $[Ni(CO)_3(NO)]^+ (C_3v)^{[a]}$	2	calcd [Ni(CO) ₄] ^{•+} (D ₂ d) ^[a]	Exp. Ni(CO) ₄	calcd Ni(CO) ₄ (<i>T</i> _d) ^[a]
IR \tilde{v} (CO/NO) [cm ⁻¹]	1953 (w) 2182 (w) 2202 (vw)	1993 (100), v(NO), A ₁ 2147 (88), v _{as} (CO), <i>E</i> 2179 (8), v _s (CO), A ₁	2170 (w)	2137 (100), ν _{as} (CO), <i>E</i> 2139 (24), ν _{as} (CO), <i>B</i> ₂	2057 (vs.) ^[46]	2038 (100), v _{as} (CO), T ₂
Raman $ ilde{ u}$ (CO/NO) [cm $^{-1}$]	1955 (w) 2184 (vs.) 2202 (s)	1993 (3), v(NO), A ₁ 2147 (19), v _{as} (CO), <i>E</i> 2179 (20), v _s (CO), A ₁	2174 ^[b] 2201 ^[b]	2137 (38), v _{as} (CO), <i>E</i> 2139 (54), v _{as} (CO), <i>B</i> ₂ 2175 (37), v _s (CO), <i>A</i> ₁	2037 (m) ^[48] 2128 (vw) ^[48]	2038 (31), v _{as} (CO), <i>T</i> ₂ 2105 (6), v _s (CO), <i>A</i> ₁
avg. d(Ni-CO/Ni-NO) [Å] avg. d(C-O/N-O) [Å] avg. α(Ni-C-O/Ni-N-O)[°]	1.847(9) 1.124(6) 177.3(3)	1.872 1.191 179.4	1.931(5) 1.110(4) 177.8(5)	1.975 1.119 176.3	1.827(3) ^[47] 1.138(1) ^[47] 179.57(15) ^[47]	1.842 1.135 180
$\delta^{ m 14}$ N NMR [ppm]	4.9	12.6	-	-	-	-
QTAIM charges q(Ni), q(CO), q(NO) [e]	-	0.72, 0.06, 0.10	-	0.77, 0.06, -	-	0.52, -0.13, -

[a] IR and Raman spectra were calculated at the BP86(D3BJ)/def2-TZVPP level of theory without scaling factor. All other calculated values in this table were determined using B3LYP(D3BJ)/def2-TZVPP. [b] Due to the low quality of the obtained Raman spectrum of **2**, only the frequencies of the carbonyl stretching modes without intensities are reported.

covalency of the M-NO back bonds, small changes in the charge distribution are sufficient to either assign both degenerate π -MOs to the metal, resulting in a formal NO⁺ ligand, or to allocate all four electrons to the ligand, resulting in a formal NO^{3-.[41]} Furthermore, complex **1** could be described as Ni^{II} (*S*=1) antiferromagnetically coupled to a NO⁻ (*S*=1).^[43] Due to the rather formal assignment, we decided to omit these expensive calculations, and thus we make no statement about the formal oxidation states in [Ni(CO)₃(NO)]⁺ and only refer to the NO stretching frequency at 1953 cm⁻¹ (compared to $\tilde{\nu}(NO^+) = 2376 \text{ cm}^{-1}$, $\tilde{\nu}(NO^0) = 1904 \text{ cm}^{-1}$, $\tilde{\nu}(NO^-) = 1363 \text{ cm}^{-1}$]^[44] and the QTAIM charges (Table 2). The results indicate that the positive charge is mainly located on the metal atom.

Compared to the T_d symmetric Ni(CO)₄, the d⁹ complex [Ni(CO)₄]⁺ exhibits Jahn-Teller distortion and DFT calculations support a D_{2d} symmetric ground state. In the IR spectrum of crystalline 2 (Figure 1b, Table 2) one CO stretch is visible at 2170 cm⁻¹. Also $[Ni(CO)_4]^{+}$ in the gas phase $(2179 \text{ cm}^{-1})^{[14]}$ and in solid neon matrix $(2176.2 \text{ cm}^{-1})^{[16]}$ only revealed one band, blue-shifted relative to neutral gaseous $Ni(CO)_4$ at 2057 cm⁻¹ (T₂).^[46] The expected splitting of the IR-active T_2 CO stretching mode in neutral Ni(CO)₄ appears to be small in $[Ni(CO)_4]^{++}$, which is supported by DFT calculations (2139 cm⁻¹ (B_2), 2137 cm⁻¹ (E), @BP86(D3BJ)/ def2-TZVPP). The blue-shift results from the reduced π -back bonding in $[Ni(CO)_4]^{+}$, which is also responsible for the elongated average Ni-C bond length (1.931(5) Å) and reduced average C-O distance (1.110(4) Å) in the crystal structure of **2**, compared to 1.827(3) $Å^{[47]}$ and 1.138(1) $Å^{[47]}$ in crystalline Ni(CO)₄ (see Table 2 for comparison). Two crystallographically independent [Ni(CO)₄]+ cations are present in the crystal structure of 2. One of them shows an almost undistorted D_{2d} symmetry, just like the cation in **2-4FB**, whereas the other cation in 2 displays a slightly stronger distortion from the gas phase structure (Supporting Information, Table S6).^[54] The X-band cw-EPR spectrum of solid microcrystalline **2** at 100 K includes an anisotropic signal with two principle *g*-values, which agree with DFT calculations of the 17 VE complex $[Ni(CO)_4]^{++}$. The calculated spin density of $[Ni(CO)_4]^{++}$ is mainly located on the metal atom (Figure 1c).

With Evans NMR method^[49] a value of 2.35 μ_B (1.88 μ_B without diamagnetic correction) was obtained for the effective magnetic moment of 2 in 4FB, which roughly corresponds to the doublet expectation value of $1.73 \,\mu_B$ (Supporting Information, Section 8). The cyclic voltammogram of 2 in 4FB (Figure 1 d) reveals a reversible redox process at 1.21 V against Fc⁺/Fc. This agrees well with the calculated potential of the couple [Ni(CO)₄]⁺/[Ni(CO)₄]⁰ in 4FB of 1.18 V against Fc⁺/Fc (see the Supporting Information, Section 11 for details). This Ni⁺/Ni⁰ potential is remarkably high compared to other Ni⁺/Ni⁰ couples (for example, [Ni(bis(5H-dibenzo-[a,d]cyclohepten-5-yl)amine)(PPh₃)] (-1.28 V),^[50] $[Ni(P^{Ph}_{2}N^{p-Tol}_{2})_{2}]^{+}$ (-1.08 V), [51] $[Ni(PPh_{3})_{3}]^{+}$ (-1.06 V)[52]and $[Ni(cod)_2]^+$ (-0.68 V)^[52]). The π -back bonding and electron-withdrawing ability of CO compared to the other ligands with mostly σ -donating character might cause this high potential value, explaining why a strong oxidant like $Ag^+/0.5 I_2$ is necessary for the clean synthesis of 2.

The herein reported compounds **1** and **2** are novel textbook entries. Furthermore, they can be prepared in organic solvent in up to 1 g batches and are stable at room temperature. Preliminary work suggests that they can be used as starting material to expand the coordination chemistry of ionic nickel compounds in the rare oxidation state of +1.^[52,53]

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Conflict of interest

The authors declare no conflict of interest.

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