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Gas-Phase Model Studies Relevant to the Decomposition of Transition-Metal Nitrates $M(NO_3)_2$ (M = Co, Ni) into Metal–Oxo Species

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Electrospray ionization (ESI) of aqueous cobalt(II) and nickel(II) nitrate solutions inter alia affords the solvated, mono- and oligonuclear nitrato complexes $[M_m(NO_3)_{2m-1}(H_2O)_n]^+$ (M = Co, Ni; m = 1–5; n = 1–4). The collision-induced dissociation spectra of the mass-selected ions imply that these ions correspond to genuine hydrated metal(II) nitrato complexes in that either cluster degradation through expulsion of neutral $M(NO_3)_2$ or sequential loss of water ligands take place. In the case of the lowest member of the series (m, n = 1), however, loss of water competes with homolytic cleavage of the N–O bond, which leads to the formation of $[M,O_2,H_2]^+$ cations containing formal M^{III}. For $m > 1$, similar activation of the nitrato ligand was observed under harsher ionization conditions in ESI and provides access to cationic transition-metal oxide clusters in the gas phase. In addition to the collision experiments, thermal reactions of the solvated nitrato complexes with nitrogen monoxide reveal bond-activation pathways, which shed some light on the NO-assisted pyrolysis of solid metal nitrates for the preparation of metal oxide catalysts.

Introduction

Metal oxides are among the most widely used catalytic materials in the chemical industry. For the preparation of metal oxide catalysts, often aqueous solutions of suitable metal salts MX_n are used as precursors and an obvious question in this respect is the role of the counterion X. With regard to the formation of metal oxides, nitrates (X = NO_3) deserve particular attention because the counterion can itself serve as an oxidizer. Thus, metal nitrates have indeed been used as precursors for the generation of metal oxides and due to the oxidizing properties of nitrates also high oxidation states may be maintained in the products resulting from thermolysis.[1,2] Recently, controlled pyrolysis of metal nitrates has also been proposed as a new route for the preparation of metal oxide nanoparticles,[3,4] and NiO/SiO_2 catalysts with narrow distributions of particle sizes and particle–particle distances have also been obtained.[5,6] The mechanistic knowledge about the details of the thermal decomposition of nitrates is limited, however, mostly due to the complex radical chain mechanisms that are involved and the partially eruptive character of the degradation processes.[7–12]

With respect to a more detailed understanding at a molecular level, model studies of well-defined metal nitrate species in the idealized gas phase might therefore provide an alternative means to gather additional insight. In the gas phase, nitrato ligands can also be used as donors for oxygen atoms and several reactive metal oxide species have been prepared through this route by using electrospray ionization (ESI) of aqueous solutions of the corresponding nitrates,[13,14] for example, MgO^+,[15] FeO^+,[16] (1,10-phenanthroline)CuO^+,[17] and Ag_2O^+.[18]

ESI is known as a method that allows the gentle transfer of ionic species in solution to the gas phase. In addition to numerous applications of ESI for the mass spectrometric analysis of biomolecules, it finds more and more applications in coordination chemistry, and because ESI can at least to some extent sample the ions present in solution, it has recently found increasing applications in investigations of element speciation[19] and ion hydration.[20] For a bivalent metal salt MX_2 (X = monovalent counterion; e.g., chlorine) in aqueous solution, solvent-driven heterolysis hence leads to hydrated dications $[M(H_2O)_n]^{2+}$ as well as the monocationic contact ion pairs $[MX(H_2O)_n]^+$, where the hydration number n is generally larger for dications than for monocations; note that neutral contact ion pairs, $[MX_2(H_2O)_n]$, can also exist in solution, but these are not sampled by ESI, which only monitors ionic species. In addition to the counterion X, hydroxide ions resulting from autoheterolysis of water can also be bound to the metal dications, which leads to hydrated metal hydroxides $[M(OH)(H_2O)_n]^+$.[21–23]

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Results and Discussion

Under mild source conditions (see Experimental Section), ESI of an aqueous solution of $Co(NO_3)_2$ yields $[Co(H_2O)_n]^{2+}$ dications with n up to 7 and $[Co(NO_3)(H_2O)_n]^+$ as well as $[Co(OH)(H_2O)_n]^+$ monocations with n up to 4 as the leading cationic species. In addition to the cations containing a single cobalt atom, a number of polynuclear clusters of the general formula $[Co_m(NO_3)_{2m-1}(H_2O)_n]^+$ are formed (Table 1). Although these clusters are about an order of magnitude less abundant than the mononuclear ions under the conditions chosen, their formation indicates a pronounced degree of association of the metal cations to form polynuclear ion pairs. Further, the intensities do not decrease in a monotonic manner with the number of cobalt atoms m, in that the pentanuclear species are much more abundant than the cluster with $m = 4$. The latter clusters, $[Co_4(NO_3)_7(H_2O)_n]^+$, also show a significantly lowered average hydration number of $n_{av}(m = 4) = 2.2$, whereas all other clusters have n_{av} of about 3.

Table 1. Relative abundances (A_{rel})[a] of the hydrated cobalt–nitrato cluster ions upon ESI of an aqueous solution of cobalt(II) nitrate under mild ionization conditions.[b]

Formula	m/z	A_{rel}	n_{av}[c,d]
$[Co(NO_3)(H_2O)_2]^+$	157	405	
$[Co(NO_3)(H_2O)_3]^+$	175	2100	2.8
$[Co_2(NO_3)(H_2O)_4]^+$	193	8	
$[Co_2(NO_3)_3(H_2O)_2]^+$	340	35	
$[Co_2(NO_3)_3(H_2O)_3]^+$	358	100[a]	2.9
$[Co_2(NO_3)_3(H_2O)_4]^+$	376	15	
$[Co_3(NO_3)_5(H_2O)_2]^+$	523	2	
$[Co_3(NO_3)_5(H_2O)_3]^+$	541	20	3.1
$[Co_3(NO_3)_5(H_2O)_4]^+$	559	5	
$[Co_4(NO_3)_7(H_2O)]^+$	688	1	
$[Co_4(NO_3)_7(H_2O)_2]^+$	706	4	2.2
$[Co_4(NO_3)_7(H_2O)_3]^+$	724	2	
$[Co_5(NO_3)_9(H_2O)_2]^+$	889	1	
$[Co_5(NO_3)_5(H_2O)_3]^+$	907	14	3.2
$[Co_5(NO_3)_5(H_2O)_4]^+$	925	6	

[a] Given relative to the most abundant binuclear cluster $[Co_2(NO_3)_3(H_2O)_3]^+$ ($A_{rel} = 100$). [b] The spectra were only scanned up to $m/z = 1000$; thus, larger clusters are not monitored in the present experiments. [c] This parameter describes the average hydration number for a given number of cobalt atoms in the cluster. Although the actual value depends on the ionization conditions, comparison among the different clusters indicates their tendency to form microhydrates in the gas phase. For a given cluster size m, the value is calculated as $n_{av}(m) = \Sigma\{A_{rel,n_i}([Co_m(NO_3)_{2m-1}(H_2O)_{n_i}]^+)n_i\}/\Sigma\{A_{rel,n_i}([Co_m(NO_3)_{2m-1}(H_2O)_{n_i}]^+)\}$. [d] For the mononuclear hydroxo complexes $[Co(OH)(H_2O)_n]^+$ formed under the same conditions, a value of $n_{av} = 2.9$ is found.

For further characterization, the ions were mass selected by using the first quadrupole, then collided with xenon as a collision gas in the hexapole collision cell, and the fragments were monitored by using the second quadrupole. In these collision-induced dissociation (CID) experiments, the cluster ions either lose water ligands [Reaction (1)] or undergo cluster degradation to the corresponding lower members of the series concomitant with release of cobalt(II) nitrate as a neutral fragment [Reaction (2)]; the mononuclear complexes are accordingly formed as the quasiterminal fragments of the series. To a limited extent, also N–O bond cleavage of the nitrato ligands is observed, for example, Reaction (3), a process to which we return in more detail further below.

$$[Co_m(NO_3)_{2m-1}(H_2O)_n]^+ \rightarrow [Co_m(NO_3)_{2m-1}(H_2O)_{n-1}]^+ + H_2O \quad (1)$$

$$[Co_m(NO_3)_{2m-1}(H_2O)_n]^+ \rightarrow [Co_{m-1}(NO_3)_{2m-3}(H_2O)_n]^+ + Co(NO_3)_2 \quad (2)$$

$$[Co_2(NO_3)_3(H_2O)]^+ \rightarrow [Co_2O(NO_3)_2(H_2O)]^+ + NO_2 \quad (3)$$

An important feature of ESI is that the ionization process can be changed gradually from a very soft regime to an increasingly harsher one[24] by appropriate adjustment of the potentials in the medium pressure regions of the differential pumping system from the ESI operating at atmospheric pressure to the high-vacuum manifold, which effects multicollisional activation of the ions formed initially upon ESI.[25] Under very hard conditions, ESI might in fact be more energetic than electron ionization.[26] When the ionization conditions are accordingly enforced gradually upon ESI of aqueous cobalt(II) nitrate, the larger clusters first lose their water ligands [Reaction (1)], then degrade to smaller clusters [Reaction (2)], and then to the mononuclear ions, which continue to lose water molecules. In the following discussion, we focus on one of the final members of this fragmentation series, that is, the mononuclear, monohydrated species $[(H_2O)Co(NO_3)]^+$ ($m/z = 139$), because for this ion, the further decrease in solvation by losing the final water ligand is so demanding that other bond-activation processes begin to compete.

CID of mass-selected $[(H_2O)Co(NO_3)]^+$ ($m/z = 139$) affords two fragmentations at low collision energies [Reactions (4) and (5)], in which the ionic products are assigned as $Co(NO_3)^+$ and $[CoO_2H_2]^+$, respectively. With regard to the latter fragment ion, recent density functional calculations predict that, of the conceivable isomeric structures, the cobalt dihydroxide cation $Co(OH)_2^+$ is 0.2 eV more stable than the hydrated cobalt oxide cation $(H_2O)CoO^+$.[27] At collision energies of 10 eV, a few additional fragment ions are observed in small amounts, that is, CoO^+ ($m/z = 75$; 6% relative to the largest fragment ion $[CoO_2H_2]^+$), NO_2^+ ($m/z = 46$; 4%), and NO^+ ($m/z = 30$; 12%), which are attributed to the consecutive fragmentation Reactions (6), (7), (8), and (9); assignment of Reactions (6)–(9) is further confirmed by independent CID spectra of mass-selected $[CoO_2H_2]^+$ and $Co(NO_3)^+$, respectively, which show the listed reactions as major fragmentation channels. Further, note that Reactions (6) and (7) provide gas-phase routes for the generation of the cobalt oxide cation CoO^+, which is capable of activating small alkanes.[28,29] The assignment of CoO_2 rather than Co + O_2 or CoO + O as the neutral product of Reaction (9) is based on ab initio studies of this system, which predict the dioxide CoO_2 as the energetically preferred species.[30,31]

$$[(H_2O)Co(NO_3)]^+ \rightarrow Co(NO_3)^+ + H_2O \tag{4}$$

$$[(H_2O)Co(NO_3)]^+ \rightarrow [CoO_2H_2]^+ + NO_2 \tag{5}$$

$$[CoO_2H_2]^+ \rightarrow CoO^+ + H_2O \tag{6}$$

$$Co(NO_3)^+ \rightarrow CoO^+ + NO_2 \tag{7}$$

$$Co(NO_3)^+ \rightarrow NO_2{}^+ + CoO \tag{8}$$

$$Co(NO_3)^+ \rightarrow NO^+ + CoO_2 \tag{9}$$

Whereas Reaction (4) is a mere ligand loss from the hydrated monocation, Reaction (5) is associated with the loss of an open-shell species and hence a change in the oxidation state of the metal, which increases from Co^{II} in the precursor salt as well as in the parent ion $[(H_2O)Co(NO_3)]^+$ to formal Co^{III} in the $[CoO_2H_2]^+$ cation.

Figure 1 shows the corresponding energy behavior for the relative abundances of the parent ion and the major fragments $[CoO_2H_2]^+$ and $Co(NO_3)^+$ as a function of collision energy; note that the secondary fragments are summed into the primary fragments.[32] Loss of a water ligand requires an appearance energy of $AE(4) = (1.7 \pm 0.2)$ eV, a value which is right in the ballpark of water binding energies for bare or singly ligated metal cations,[20,27,33,34] lending confidence to the method for the approximate determination of appearance energies applied here.[35] In contrast, Reaction (5) has a considerably lower threshold of only $AE(5) = (1.0 \pm 0.2)$ eV. Despite the lower energy demand of Reaction (5), however, ligand loss according to Reaction (4) can effectively compete with the former at elevated collision energies (Figure 1). We note in passing that at low collision energies, but not under thermal conditions, small signals due to $[(Xe)Co(NO_3)]^+$ with a characteristic isotope pattern are observed, which can be attributed to endothermic exchange of the water ligand in $[(H_2O)Co(NO_3)]^+$ by xenon serving as the collision gas.[36]

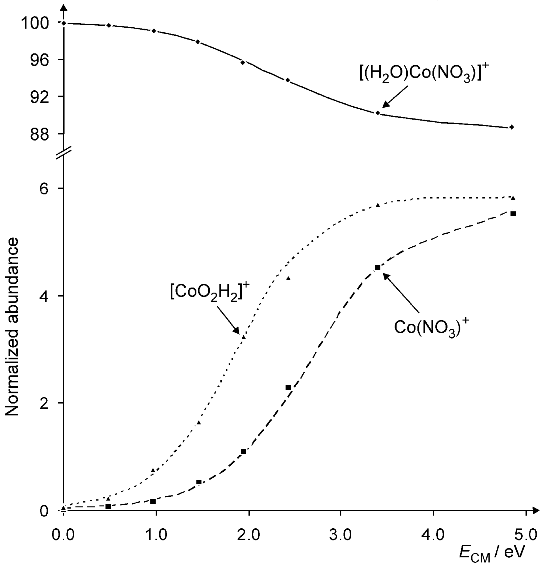
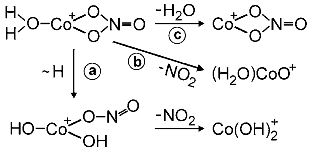


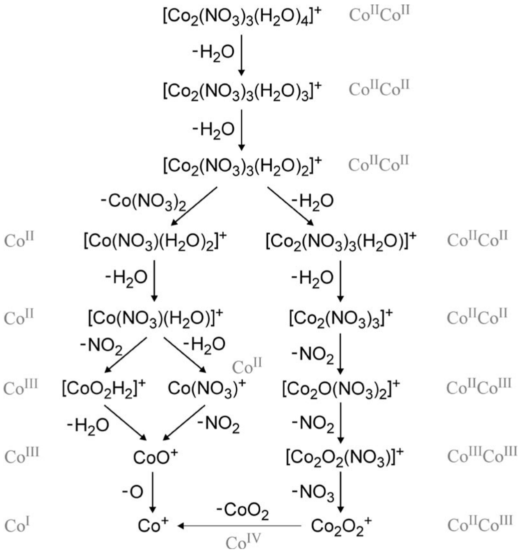
Figure 1. Fragmentation of mass-selected $[(H_2O)Co(NO_3)]^+$ (m/z = 139, ♦) into $[CoO_2H_2]^+$ (loss of NO_2, ▲) and $Co(NO_3)^+$ (loss of water, ■) as a function of the collision energy given in the center-of-mass frame. The lines are the results of the fitting of the ion intensities by using sigmoid functions; see Experimental Section. Note the interruption in the vertical axis. Further, only the parent ion and the two most abundant fragments are shown.

By reference to the closely related $[FeO_2H_2]^+$ cations,[27,37–40] this particular energy behavior can be understood[16,35] by the involvement of an entropically demanding step in Reaction (5) in comparison to Reaction (4). A plausible option in this respect is the formation of the genuine cobalt dihydroxide cation[27,41] through hydrogen migration from the water ligand to one of the oxygen atoms of the nitrato ligand (Scheme 1, path a) or the possible barrier imposed by the structural changes in a bidentate nitrato ligand to monodentate coordination prior to N–O bond cleavage, which affords the hydrated cobalt oxide cation (Scheme 1, path b); note that path b is also slightly disfavored enthalpically relative to the formation of $Co(OH)_2{}^+$ in path a.[27] As the direct loss of water (path c) does not impose any entropic restrictions to ion dissociation, it can effectively compete at elevated collision energy, even though it is enthalpically more demanding.



Scheme 1. Loss of neutral NO_2 from $[(H_2O)Co(NO_3)]^+$ preceded by hydrogen migration (path a) compared to the direct losses of NO_2 and water (paths b and c), respectively.

Further noteworthy is the fragmentation of the metal nitrate cluster ions under enforced conditions of ESI, in which multiple collisions in the medium-pressure region of the ion source allow extensive fragmentations, which inter alia leads to the generation of metal oxide cluster ions in the gas phase.[15,18,26,42] In the case of the $[Co_m(NO_3)_{2m-1}(H_2O)_n]^+$ ions mentioned above, cluster degradation to mononuclear cations and their subsequent fragmentation to CoO^+ and even atomic Co^+ predominates under harsh ESI conditions. In addition, however, a series of cluster ions is formed under these conditions in appreciable yields, which can compete with other, more complicated approaches for the generation of $Co_mO_n{}^{+/-}$ cluster ions.[43–46] Particularly noteworthy is that the use of cobalt(II) nitrate as a precursor allows the generation of oxygen-rich $Co_mO_n{}^+$ clusters, for which other methods are less suitable. Among the cluster ions possible to generate in yields sufficient for further reactivity studies are the species $[Co_mO_m(H_2O)_n]^+$ (m = 2–5, n = 0–3), which all contain one formal cobalt(III) and can be unsolvated to the binary clusters $Co_2O_2{}^+$, $Co_3O_3{}^+$, $Co_4O_4{}^+$, and $Co_5O_5{}^+$. A simplified fragmentation sequence of the binuclear nitrato cluster $[Co_2(NO_3)_3(H_2O)_4]^+$ as derived from a series of individual CID experiments is shown in Scheme 2.



Scheme 2. Simplified sequence for the sequential degradation of the binuclear nitrato cluster $[Co_2(NO_3)_3(H_2O)_4]^+$ into mono- and dinuclear cobalt oxide cations. The different valence states of cobalt along the pathways are indicated in gray.

Generally, similar results are obtained upon ESI of an aqueous solution of nickel(II) nitrate, that is, under mild conditions $[Ni_m(NO_3)_{2m-1}(H_2O)_n]^+$ cations with m and n up to 4 are observed in reasonable abundances with average hydration numbers n_{av} of about 3. Under harsher ESI conditions, these microhydrated complexes undergo loss of water, cluster degradation through expulsion of neutral $Ni(NO_3)_2$, as well as redox reactions to afford cationic $Ni_mO_n^+$ species in analogy to Reactions (1)–(3) of the cobalt analogues. At high cone voltages, this approach also permits the generation of ions such as NiO^+ (m/z = 74)[47] and $Ni_2O_2^+$ (m/z = 148),[48] which have already been shown to be able to act as oxidation reagents in the gas phase. However, rather than $Ni_mO_n^+$ formation, the nickel system displays a significantly higher tendency to yield bare, unsolvated nitrato clusters of the type $[Ni_m(NO_3)_{2m-1}]^+$ under enforced ionization conditions, for example, $[Ni_2(NO_3)_3]^+$ (m/z = 302 for the ^{58}Ni isotope), $[Ni_3(NO_3)_5]^+$ (m/z = 484), $[Ni_4(NO_3)_7]^+$ (m/z = 666), and $[Ni_5(NO_3)_9]^+$ (m/z = 848). The lower tendency for the formation of oxide cations is further confirmed by the CID behavior of these nitrato clusters, in which cluster degradation [Reaction (10)] efficiently competes with N–O bond cleavage of the nitrato ligand. Thus, for the larger clusters with $m > 2$, Reaction (10) occurs almost exclusively and only for $m = 2$ oxide formation is observed [Reaction (11)]. Moreover, the higher ionization energies of the nickel oxides[49,50] favor the elimination of neutral metal species [e.g., Reaction (11′)]. Therefore, the yields achievable for the $Ni_mO_n^+$ cations by using the ESI approach are still sufficient for further experiments, but yet significantly lower than in the case of cobalt.

$$[Ni_m(NO_3)_{2m-1}]^+ \rightarrow [Ni_{m-1}(NO_3)_{2m-3}]^+ + Ni(NO_3)_2 \tag{10}$$

$$[Ni_2(NO_3)_3]^+ \rightarrow [Ni_2O(NO_3)_2]^+ + NO_2 \tag{11}$$

$$[Ni_2(NO_3)_3]^+ \rightarrow NO_2^+ + [Ni_2O(NO_3)_2] \tag{11′}$$

With respect to the hydrated nickel nitrate cations $[Ni_m(NO_3)_{2m-1}(H_2O)_n]^+$, again the CID pattern of the monohydrated, mononuclear nickel–nitrato cation $[(H_2O)Ni(NO_3)]^+$ is of particular interest and worth a more detailed discussion, whereas the other hydrated clusters $[(H_2O)_nNi(NO_3)]^+$ (n = 2–4) show exclusive eliminations of water ligands.

In notable difference to the cobalt congener, the CID patterns of the monohydrated ion $[(H_2O)Ni(NO_3)]^+$ (Figure 2) show a very similar energy behavior for the losses of water [Reaction (12)] and neutral NO_2 [Reaction (13)]. Moreover, additional fragments due to expulsion of NO and O_2 according to Reactions (14) and (15) are observed, though in small abundance only. We note in passing that according to recent computational studies, the $[NiO_2H_2]^+$ species formed in Reaction (13) most likely corresponds to the hydrated nickel oxide cation $(H_2O)NiO^+$, which is predicted to be 0.2 eV more stable than isomeric $Ni(OH)_2^+$.[27]

$$[(H_2O)Ni(NO_3)]^+ \rightarrow [NiNO_3]^+ + H_2O \tag{12}$$

$$[(H_2O)Ni(NO_3)]^+ \rightarrow [NiO_2H_2]^+ + NO_2 \tag{13}$$

$$[(H_2O)Ni(NO_3)]^+ \rightarrow [NiO_3H_2]^+ + NO \tag{14}$$

$$[(H_2O)Ni(NO_3)]^+ \rightarrow [NiNO_2H_2]^+ + O_2 \tag{15}$$

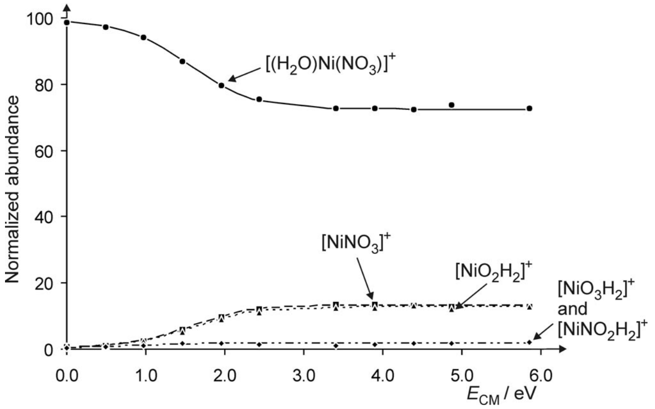
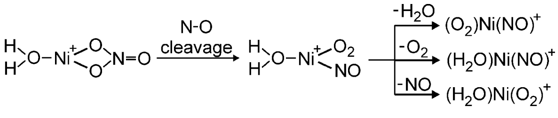


Figure 2. Fragmentation of $[(H_2O)Ni(NO_3)]^+$ (m/z = 138, ●) into $[NiO_2H_2]^+$ (loss of NO_2, ▲), [Ni,N,O_3]$^+$ (loss of water, ■), $[NiNO_2H_2]^+$, and $[NiO_3H_2]^+$ (summed losses of NO and O_2, symbol ♦) as a function of the collision energy given in the center-of-mass frame. The lines are the results of the fitting of the ion intensities by using sigmoid functions; see Experimental Section. We note that much like for the cobalt congener, small signals due to [(Xe)$Ni(NO_3)$]$^+$ are also observed at low collision energies (not shown).

Indicative with regard to ion structures is that the apparent threshold for the loss of water, $AE(12) = (0.9 \pm 0.2)$ eV, as well as neutral NO_2, $AE(13) = (0.8 \pm 0.2)$ eV, are significantly lower than for the cobalt case; a water binding energy of only 0.9 eV is certainly much lower than expected for a monohydrated transition-metal cation.[20,33] Moreover, side Reactions (14) and (15) − despite their rather low yields − occur already at very low energies (formal AE values of about 0.1 eV) and are not compatible with the presence of an intact nitrato ligand. Instead, the low appearance energy of Reaction (12) in conjunction with the observation of Reactions (14) and (15) suggest isomerization of the parent ion, which either already occurs upon ion generation or has a very low barrier (Scheme 3). Note that this suggested isomerism also sheds doubt on the structure of the $[NiNO_3]^+$ fragment formed in Reaction (12), which could either be the genuine "naked" nickel nitrate cation $Ni(NO_3)^+$ or an already rearranged complex, such as $(O_2)Ni(NO)^+$.[51] Quite obviously, the chemistry of bare metal nitrate ions still bears quite a bit of facets to be explored.



Scheme 3. Possible low-energy rearrangement of $[(H_2O)Ni(NO_3)]^+$ through N–O bond cleavage to afford the formal Ni^I complex $[(H_2O)Ni(O_2)(NO)]^+$ from which all three ligands formed can be lost in competition. Deliberately, no specification of the binding mode of the NO and O_2 ligands are made.[51,52]

Ion/Molecule Reactions with NO

With respect to the recent observation that addition of NO during thermal decomposition of metal nitrates can be advantageous for the formation of structured metal oxide nanomaterials,[3,4] the metal–nitrato cations formed upon ESI were mass selected and allowed to interact with neutral nitrogen monoxide in the hexapole region of the mass spectrometer at a collision energy nominally set to zero.[53] Under these experimental conditions, quasithermal ion/molecule reactions can be probed rapidly,[15–17,25c,35,54] although usage of a multipole set-up has some inherent limitations.[33]

Of all cobalt-containing ions investigated, however, only the mononuclear, monohydrated cation $[(H_2O)Co(NO_3)]^+$ showed a significant reactivity towards NO; mere associations of NO with several larger clusters and H_2O/NO ligand exchanges of the solvated ions were observed, but are not considered as chemically relevant reactivity in the present context. As shown in Figure 3, the interaction of $[(H_2O)Co(NO_3)]^+$ with NO leads to three product ions with m/z = 30, 48, and 123, none of which could be due to CID under these conditions. Specifically, the nitrosyl cation NO^+ (m/z = 30) is formed from $[(H_2O)Co(NO_3)]^+$ only at much larger collision energies (see above) and the ions with m/z = 48 as well as m/z = 123 are not formed at all upon CID of $[(H_2O)Co(NO_3)]^+$ with xenon. Hence, Figure 3 indicates the occurrence of thermal ion/molecule reactions of $[(H_2O)Co(NO_3)]^+$. With regard to the structures of the neutral products, the present data do not permit a more definitive assignment, because more sophisticated mass spectrometric experiments for the characterization of neutral transition-metal species formed in gas-phase reactions[55,56] cannot be applied in this particular case for instrumental circumstances. On the basis of analogies between the ionic and neutral products and additional thermochemical considerations outlined below, we tentatively propose the occurrence of Reactions (16), (17), and (18).

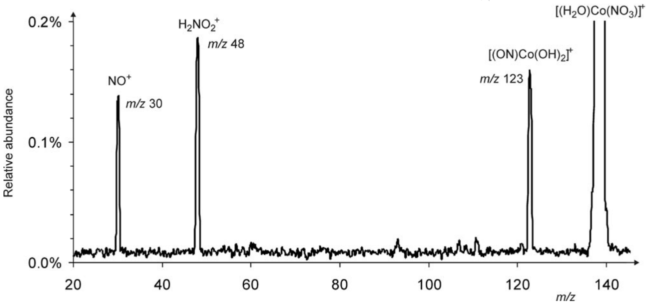


Figure 3. Ion/molecule reaction of mass-selected $[(H_2O)Co(NO_3)]^+$ (m/z = 139) with neutral nitrogen monoxide at a collision energy set nominally to E_{CM} = 0 eV.

$$[(H_2O)Co(NO_3)]^+ + NO \rightarrow NO^+ + Co(OH)_2 + NO_2 \quad (16)$$

$$[(H_2O)Co(NO_3)]^+ + NO_2 \rightarrow H_2NO_2^+ + [CoNO_3] \quad (17)$$

$$[(H_2O)Co(NO_3)]^+ + NO \rightarrow [(ON)Co(OH)_2]^+ + NO_2 \quad (18)$$

Although the formation of NO^+ in Reaction (16) might also be interpreted as a mere electron transfer between the reactants, this scenario appears quite unlikely for the formal cobalt(II) compound $[(H_2O)Co(NO_3)]^+$, because related Co^{II} species have ionization energies considerably lower than IE(NO) = 9.25 eV, for example, IE(CoOH) = 7.74 eV[57] and IE(CoCl) = 8.71 eV,[58] and the additional water ligand present in $[(H_2O)Co(NO_3)]^+$ should further lower the IE of the corresponding neutral counterpart.[33,40] Accordingly, a redox process is more likely to account for the experimental findings, and in this respect, Reaction (16) appears as a plausible option, because $IE\{Co(OH)_2\}$ can be expected to be well above IE(NO) = 9.25 eV.[39,40] Reaction (17) leading to protonated nitrous acid[59] can be associated by either $Co(NO_3)$ or a rearranged form, for example, $(O_2)Co(NO)$. The occurrence of a formal oxygen-atom transfer in Reaction (18) could either be associated by rearrangement of the nitrato ligand to $[(ON)Co(OH)_2]^+$ and hence an oxidation from Co^{II} to Co^{III} or involve reduction to a nitrito ligand, that is, $[(H_2O)Co(NO_2)]^+$, without a change in the formal oxidation state of cobalt. Alternatively, direct loss of NO_2 from the nitrato ligand of the intermediate collision complex $[(H_2O)(NO)Co(NO_3)]^+$ may lead to $[(H_2O)(NO)CoO]^+$ as the ionic product, which can be viewed as either Co^{III} or Co^{IV}, depending on the view of the NO ligand as formal $NO^{\cdot}$ or NO^-, respectively. In any case, occurrence of Reaction (18) establishes that bond-activation reactions occur upon interaction of the nitrato cation with neutral NO.[60] This parallels the facilitated pyrolysis of solid metal nitrates in the presence of NO,[3] and a conceivable explanation for this effect is that the open-shell character of NO enables formally spin-forbidden transitions in the decomposition of the nitrato complex.[61]

In contrast to the cobalt species, the corresponding nickel-containing ion $[(H_2O)Ni(NO_3)]^+$ does not show any significant reactivity towards NO under thermal conditions. Also, reactivity screening of several of the other nickel clusters formed upon ESI does not reveal occurrence of oxygen-atom transfer processes similar to Reaction (18). If any thermal reactivity is observed at all, it is associated with either electron transfer from neutral NO to the metal, cluster degradation, or mere association, for example, Reactions (19), (20), and (21). We note, however, that Reaction (20) is a genuine ion/molecule process occurring with neutral NO, because CID of mass-selected $[Ni_2(NO_3)_3]^+$ does not afford this particular product ion. Accordingly, we suggest Reaction (20) to occur as a replacement of the $Ni(NO_3)_2$ unit in $[Ni_2(NO_3)_3]^+$ by an NO ligand formally yielding the nickel–nitrosyl complex $[(ON)Ni(NO_3)]^+$; generation of the isomeric, formal Ni^{III} species $[Ni(NO_2)_2]^+$ cannot be ruled out, however. In this respect, experiments with either ^{15}N- or ^{18}O-labeled reactants might provide further insight into the details of the reactions.[62]

$$[Ni_2O(NO_3)_2]^+ + NO \rightarrow NO^+ + [Ni_2O(NO_3)_2] \quad (19)$$

$$[Ni_2(NO_3)_3]^+ + NO \rightarrow [(ON)Ni(NO_3)]^+ + Ni(NO_3)_2 \quad (20)$$

$$[Ni_2(NO_3)_3]^+ + NO \rightarrow [Ni_2(NO_3)_3(NO)]^+ \quad (21)$$

Conclusions

ESI of aqueous solutions of metal nitrates can serve as a simple method for the generation of gaseous cobalt and nickel oxide cluster cations of medium size and relatively high oxidation states. In this respect, ESI provides an alternative that circumvents some of the problems inherent to other approaches for the generation of metal oxide cluster ions. A key requisite is the ability to employ pure water as a solvent,[24] because other solvents suitable for ESI are likely to undergo oxidation by the highly reactive metal–oxo ions formed. Interestingly, N–O bond cleavage of the nitrato ligand in $[(H_2O)Co(NO_3)]^+$ does not only occur upon energizing collisions, but it can also be induced under thermal conditions when neutral nitrogen monoxide is used as a reaction partner. The gas-phase reaction with nitrogen monoxide thereby reveals a parallel to the facilitated pyrolysis of cobalt and nickel nitrates in the presence of NO. Further, as far as the mononuclear species are concerned, all data for the cobalt complexes are consistent with their description as simple hydrated metal–nitrato cations, $[(H_2O)_n\text{-}Co(NO_3)]^+$, whereas, at least for $m = 1$, the corresponding cation of nickel has easily accessible rearrangement pathways that lead to the decomposition of the nitrato ligand into NO and O_2.

Experimental Section

Most measurements were performed by using a VG Bio-Q mass spectrometer described elsewhere.[25a] Briefly, the VG Bio-Q is a commercial instrument that consists of an ESI source combined with a tandem mass spectrometer of QHQ configuration (Q stands for quadrupole and H for hexapole). In the present experiments, millimolar solutions of $Co(NO_3)_2$ or $Ni(NO_3)_2$ in distilled water were introduced through a fused-silica capillary to the ESI source by a syringe pump (5 μL min^{-1}). Nitrogen was used as the nebulizing and drying gas at a source temperature of 120 °C. By variation of the cone voltage U_C in the transfer zone of the source, the ionization conditions in the ESI source can gradually be varied from very mild (highly solvated ions, U_C = 0–15 V), by a moderate degree of collisional activation in the transfer zone (medium solvated ions, U_C = 15–45 V), to harsh (mono- and nonsolvated ions, U_C = 45–70 V) and even very harsh (bare metal ions or clusters, $U_C > 70$ V).[35a] For collision-induced dissociation (CID), the ions of interest were mass selected by using Q1, interacted with xenon as a collision gas in the hexapole H under single-collision conditions (typically 2×10^{-4} mbar) at variable collision energies (E_{lab} = 0–15 eV), while scanning Q2 to monitor the ionic products. In all MS–MS experiments, both mass analyzers were kept at good unit-mass resolution, ensuring the exclusion of parent ions with mass differences of $\Delta m > 0.5$ amu and the proper determination of the number of hydrogen atoms in the ionic products. Ion/molecule reactions at quasithermal energy were performed in the same manner with the interaction energy set to a nominal value E_{lab} = 0 eV;[33] previous experiments have demonstrated that the thermal reactivity of mass-selected gaseous ions can be probed in this manner,[15,16,54,63] and the ions emerging from the ESI source are thus assumed to be equilibrated to room temperature in collisions with nitrogen during the transfer from the source to the vacuum manifold of the instrument. Further, it should be noted explicitly that, unless an excessive pretreatment is performed, reactions with NO in a high-vacuum system are almost always associated with some undesired processes that are either due to volatiles (primarily HNO_2 and HNO_3, but also unidentified organic compounds[64]) formed from attack of instrument components by the aggressive NO or due to nitrogen dioxide (NO_2), which is rapidly formed upon contact of NO with trace amounts of air. Such side reactions were observed in the present experiments and identified by following the dependences of the respective product ions from the pressure of NO (p_{NO}), because the impurities originating from the background do not proportionally rise with p_{NO}, whereas the true reaction products do. The data given below are accordingly corrected for the side reactions of the impurities.

As pointed out previously, the VG Bio-Q does not allow quantitative threshold information from CID experiments to be directly extracted as a result of several limitations of the commercial instrument.[25a] For weakly bound ions,[65] for example, even at E_{lab} = 0 eV a non-negligible amount of ion decay is observed, which is in part attributed to the presence of collision gas not only in the hexapole, but also in the focusing regions between the mass analyzers. To a first approximation, however, the energy dependence of the product distributions in the CID spectra can be approximated by sigmoid functions,[66] which allow some semiquantitative information about the energetics of the ions examined to be extracted.[26] The energy dependence of the CID fragments can hence be approximated by functions of the type $I_i(E_{CM}) = \{BR_i/[1 + e^{(E_{1/2,i} - E_{CM})b_i}]\}$ by using a least-square criterion; for the parent ion M, the relation is: $I_M(E_{CM}) = \{1 - \Sigma[BR_i/(1 + e^{(E_{1/2,i} - E_{CM})b_i})]\}$. Here, BR_i stands for the branching ratio of a particular product ion ($\Sigma BR_i = 1$), $E_{1/2}$ is the energy at which the sigmoid function has reached half of its maximum, E_{CM} is the collision energy in the center-of-mass frame [$E_{CM} = zmT/(mT + m_I)E_{lab}$, where z is the charge of the ion, mT and m_I stand for the masses of the collision gas and the ion, respectively], and b (in eV^{-1}) describes the rise of the sigmoid curve and thus the phenomenological energy dependence. In consecutive dissociations, all higher-order product ions are added to the intensity of the primary fragment. Further, non-negligible ion decay at E_{lab} = 0 eV as well as the fraction of non-fragmenting parent ions under single collision conditions are acknowledged by means of appropriate scaling and normalization procedures and the kinetic energy width of the incident beam (FWHM = 1.1 eV in E_{lab}) is unconvoluted from the data. Phenomenological threshold energies are then derived from linear extrapolations of the rise of the sigmoid curves at $E_{1/2}$ to the base line. This empirical, yet physically reasonable approach is able to reproduce the measured ion yields quite well. It is obvious, however, that the term $E_{1/2}$ used in the exponent does not correspond to the intrinsic appearance energies of the fragmentation of interest. Nevertheless, we have demonstrated in earlier work that this approach provides a quantitative frame for the energy demands of the various fragmentations.[35,54d,63,67]

A few complementary ESI measurements of the title ions were performed with a TSQ Classic triple quadrupole mass spectrometer,[68] which has a very similar configuration as the VG BioQ, but offers a better mass resolution.[69]

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[1] C. C. Addison, B. F. G. Johnson, N. Logan, *J. Chem. Soc.* **1965**, 4490–4494.
[2] J. G. Jackson, A. Novichikhin, R. W. Fonseca, J. A. Holcombe, *Spectrochim. Acta B* **1995**, *50*, 1423–1426.
[3] J. R. A. Sietsma, J. D. Meeldijk, J. P. den Breejen, M. Versluijs-Helder, A. J. van Dillen, P. E. de Jongh, K. P. de Jong, *Angew. Chem.* **2007**, *119*, 4631–4633; *Angew. Chem. Int. Ed.* **2007**, *46*, 4547–4549.
[4] J. R. A. Sietsma, J. D. Meeldijk, M. Versluijs-Helder, A. Broersma, A. J. van Dillen, P. E. de Jongh, K. P. de Jong, *Chem. Mater.* **2008**, *20*, 2921–2931.
[5] H. Friedrich, J. R. A. Sietsma, P. E. de Jongh, A. J. Verkleij, K. P. de Jong, *J. Am. Chem. Soc.* **2007**, *129*, 10249–10254.
[6] J. R. A. Sietsma, H. Friedrich, A. Broersma, M. Versluijs-Helder, A. J. van Dillen, P. E. de Jong, K. P. de Jong, *J. Catal.* **2008**, *260*, 227–235.
[7] A. M. Gadalla, H. F. Yu, *J. Therm. Anal.* **1991**, *37*, 319–331.
[8] S. Bordere, F. Rouquerol, P. L. Llewellyn, J. Rouquerol, *Thermochim. Acta* **1996**, *283*, 1–11.
[9] S. Bordere, P. L. Llewellyn, F. Rouquerol, J. Rouquerol, *Langmuir* **1998**, *14*, 4217–4221.
[10] Z. D. Wei, W. Z. Huang, S. T. Zhang, J. Tan, *J. Appl. Electrochem.* **2000**, *30*, 1133–1136.
[11] G. Singh, C. P. Singh, S. M. Mannan, *J. Hazard. Mater.* **2005**, *122*, 111–117.
[12] G. Singh, C. P. Singh, S. M. Mannan, *J. Hazard. Mater.* **2006**, *135*, 10–14.
[13] Z. L. Cheng, K. W. M. Siu, R. Guevremont, S. S. Berman, *Org. Mass Spectrom.* **1992**, *27*, 1370–1376.
[14] R. Frański, *Eur. J. Mass Spectrom.* **2006**, *12*, 199–204.
[15] D. Schröder, J. Roithová, *Angew. Chem.* **2006**, *118*, 5835–5838; *Angew. Chem. Int. Ed.* **2006**, *45*, 5705–5708.
[16] D. Schröder, J. Roithová, H. Schwarz, *Int. J. Mass Spectrom.* **2006**, *254*, 197–201.
[17] D. Schröder, M. C. Holthausen, H. Schwarz, *J. Phys. Chem. B* **2004**, *108*, 14407–14416.
[18] J. Roithová, D. Schröder, *J. Am. Chem. Soc.* **2007**, *129*, 15311–15318.
[19] V. B. Di Marco, G. G. Bombi, *Mass Spectrom. Rev.* **2006**, *25*, 347–379.
[20] M. K. Beyer, *Mass Spectrom. Rev.* **2007**, *26*, 517–541.
[21] A. J. Stace, *Phys. Chem. Chem. Phys.* **2001**, *3*, 1935–1941.
[22] A. T. Blades, M. Peschke, U. H. Verkerk, P. Kebarle, *J. Am. Chem. Soc.* **2004**, *126*, 11995–12003.
[23] D. Vukomanovic, J. A. Stone, *Int. J. Mass Spectrom.* **2000**, *202*, 251–259.
[24] N. B. Cech, C. G. Enke, *Mass Spectrom. Rev.* **2001**, *20*, 362–387.
[25] a) D. Schröder, T. Weiske, H. Schwarz, *Int. J. Mass Spectrom.* **2002**, *219*, 729–738; b) N. Tsierkezos, D. Schröder, H. Schwarz, *J. Phys. Chem. A* **2003**, *107*, 9575–9581; c) D. Schröder, H. Schwarz, *Can. J. Chem.* **2005**, *83*, 1936–1940.
[26] D. Schröder, M. Engeser, M. Brönstrup, C. Daniel, J. Spandl, H. Hartl, *Int. J. Mass Spectrom.* **2003**, *228*, 743–757.
[27] D. Schröder, S. O. Souvi, E. Alikhani, *Chem. Phys. Lett.* **2009**, *470*, 162–165.
[28] Y. M. Chen, D. E. Clemmer, P. B. Armentrout, *J. Am. Chem. Soc.* **1994**, *116*, 7815–7826.
[29] M. F. Ryan, A. Fiedler, D. Schröder, H. Schwarz, *Organometallics* **1994**, *13*, 4072–4081.
[30] R. J. Van Zee, Y. M. Hamrick, S. Li, W. Weltner Jr., *J. Phys. Chem.* **1992**, *96*, 7247–7251.
[31] D. Danset, M. E. Alikhani, L. Manceron, *J. Phys. Chem. A* **2005**, *109*, 97–104.
[32] Note that the MO^+ fragments can be formed from either $M(OH)_2{}^+$ or $M(NO_3)^+$ and a rigorous assignment cannot be made. However, in the range of collision energies studied here, these fragments never comprise more than 5% of the total fragment ion abundances, and equal sharing between both channels gave a reasonable fit with the experimental data in Figures 1 (M = Co) and 2 (M = Ni).
[33] P. B. Armentrout, B. L. Kickel in *Organometallic Ion Chemistry* (Ed.: B. S. Freiser), Kluwer, Dordrecht, **1996**, pp. 1–45.
[34] B. Jagoda-Cwiklik, P. Jungwirth, L. Rulišek, P. Milko, J. Roithová, J. Lemaire, P. Maitre, J. M. Ortega, D. Schröder, *ChemPhysChem* **2007**, *8*, 1629–1639.
[35] See also: a) C. Trage, M. Diefenbach, D. Schröder, H. Schwarz, *Chem. Eur. J.* **2006**, *12*, 2454–2464; b) P. Gruene, C. Trage, D. Schröder, H. Schwarz, *Eur. J. Inorg. Chem.* **2006**, 4546–4552.
[36] For a review on similar rare gas complexes, see: D. Bellert, W. H. Breckenridge, *Chem. Rev.* **2002**, *102*, 1595–1622.
[37] C. J. Cassady, B. S. Freiser, *J. Am. Chem. Soc.* **1986**, *108*, 5690–5698.
[38] a) D. Schröder, H. Schwarz, *Angew. Chem.* **1990**, *102*, 1466–1468; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1431–1433; b) M. Brönstrup, D. Schröder, H. Schwarz, *Chem. Eur. J.* **1999**, *5*, 1176–1185; c) S. Bärsch, D. Schröder, H. Schwarz, *Chem. Eur. J.* **2000**, *6*, 1789–1796.
[39] D. Schröder, H. Schwarz, *Int. J. Mass Spectrom.* **2003**, *227*, 121–134.
[40] D. Schröder, *J. Phys. Chem. A* **2008**, *112*, 13215–13224.
[41] A. Ricca, C. W. Bauschlicher Jr., *J. Phys. Chem. A* **1997**, *101*, 8949–8955.
[42] a) S. Feyel, D. Schröder, H. Schwarz, *J. Phys. Chem. A* **2006**, *110*, 2647–2654; b) S. Feyel, D. Schröder, H. Schwarz, *Eur. J. Inorg. Chem.* **2008**, 4961–4967.
[43] M. C. Oliveira, J. Marcalo, M. C. Vieira, M. A. A. Ferreira, *Int. J. Mass Spectrom.* **1999**, *187*, 825–835.
[44] B. C. Guo, K. P. Kerns, A. W. Castleman, *J. Phys. Chem.* **1992**, *96*, 6931–6937.
[45] F. Y. Liu, F. X. Li, P. B. Armentrout, *J. Chem. Phys.* **2005**, *123*, Art. No. 064304.
[46] F. Aubriet, C. Poleunis, J. F. Muller, P. Bertrand, *J. Mass Spectrom.* **2006**, *41*, 527–542.
[47] D. Schröder, A. Fiedler, M. F. Ryan, H. Schwarz, *J. Phys. Chem.* **1994**, *98*, 68–70.
[48] K. Koszinowski, M. Schlangen, D. Schröder, H. Schwarz, *Eur. J. Inorg. Chem.* **2005**, 2464–2469.
[49] For example, *IE*(CoO) = (8.9 ± 0.2) eV vs. *IE*(NiO) = (9.5 ± 0.2) eV, see: P. B. Armentour, L. F. Halle, J. L. Beauchamp, *J. Chem. Phys.* **1982**, *76*, 2449–2457.

[50] Data of the nitrogen oxides for comparison: $IE(\mathrm{NO}) = (9.2642 \pm 0.0002)$ eV and $IE(\mathrm{NO_2}) = (9.586 \pm 0.002)$ eV. Taken from: P. J. Linstrom, W. G. Mallard (Eds.), *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov.

[51] a) For matrix-isolation studies of related, neutral, and charged $\mathrm{M(NO)}_n^{+/0/-}$ complexes with M = Fe, Co, and Ni, see: M. F. Zhou, L. Andrews, *J. Phys. Chem. A* **2000**, *104*, 915–3925. b) For the complicated case of $\mathrm{Cu(NO)}_n^+$ (n = 1, 2), see: K. Koszinowski, D. Schröder, H. Schwarz, M. C. Holthausen, J. Sauer, T. Hideyaka, P. B. Armentrout, *Inorg. Chem.* **2002**, *41*, 5882–5890.

[52] D. Schröder, A. Fiedler, W. A. Herrmann, H. Schwarz, *Angew. Chem.* **1995**, *107*, 2714–2716; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2517–2520.

[53] For extensive studies of gas-phase reactions of metal cations with neutral NO, see: a) V. Blagojevic, M. J. Y. Jarvis, E. Flaim, G. K. Koyanagi, V. V. Lavrov, D. K. Bohme, *Angew. Chem. Int. Ed.* **2003**, *42*, 4923–4927; b) V. V. Lavrov, V. Blagojevic, G. K. Koyanagi, G. Orlova, D. K. Bohme, *J. Phys. Chem. A* **2004**, *108*, 5610–5624; c) M. J. Y. Jarvis, V. Blagojevic, G. K. Koyanagi, D. K. Bohme, *Chem. Phys. Lett.* **2005**, *416*, 268–271; d) V. Blagojevic, E. Flaim, M. J. Y. Jarvis, G. K. Koyanagi, D. K. Bohme, *J. Phys. Chem. A* **2005**, *109*, 11224–11235; e) V. Blagojevic, E. Flaim, M. J. Y. Jarvis, D. K. Bohme, *Int. J. Mass Spectrom.* **2006**, *249*, 385–391.

[54] a) D. Schröder, H. Schwarz, S. Schenk, E. Anders, *Angew. Chem.* **2003**, *115*, 5241–5244; *Angew. Chem. Int. Ed.* **2003**, *42*, 5087–5090; b) J. Roithová, J. Hrušák, D. Schröder, H. Schwarz, *Inorg. Chim. Acta* **2005**, *358*, 4287–4292; c) S. Feyel, D. Schröder, H. Schwarz, *J. Phys. Chem. A* **2006**, *110*, 2647–2654; d) M. Schlangen, J. Neugebauer, M. Reiher, D. Schröder, J. Pitarch López, M. Haryono, F. W. Heinemann, A. Grohmann, H. Schwarz, *J. Am. Chem. Soc.* **2008**, *130*, 4285–4294.

[55] a) D. Schröder, D. Sülzle, J. Hrušák, D. K. Böhme, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1991**, *110*, 145–156; b) D. Schröder, H. Schwarz, *Helv. Chim. Acta* **1992**, *75*, 1281–1287.

[56] D. Schröder, H. Schwarz, S. Polarz, M. Driess, *Phys. Chem. Chem. Phys.* **2005**, *7*, 1049–1053.

[57] M. Trachtman, G. D. Markham, J. P. Glusker, P. George, C. W. Bock, *Inorg. Chem.* **2001**, *40*, 4230–4241.

[58] D. L. Hildenbrand, *J. Chem. Phys.* **1995**, *103*, 2634–2641.

[59] S. Kazazić, S. P. Kazazić, L. Klasinc, S. P. McGlynn, W. A. Pryor, *J. Phys. Org. Chem.* **2002**, *15*, 728–731.

[60] For somewhat related reactions of mass-selected $\mathrm{Co}_n\mathrm{(NO)}^+$ clusters (n = 2–4) with $\mathrm{O_2}$, see: J. J. Claasen, D. B. Jacobsen, *J. Am. Chem. Soc.* **1988**, *110*, 974–976.

[61] For formally spin-forbidden reactions in the gas phase and the related concept of two-state reactivity, see: a) D. Schröder, S. Shaik, H. Schwarz, *Acc. Chem. Res.* **2000**, *33*, 139–145; b) H. Schwarz, *Int. J. Mass Spectrom.* **2004**, *237*, 75–105.

[62] For a recent example of the use of labeling for the differentiation of all atoms in the quasidegenerate $\mathrm{CO_2}^{2+}/\mathrm{CO_2}$ system, see: a) J. Roithová, C. L. Ricketts, D. Schröder, S. D. Price, *Angew. Chem. Int. Ed.* **2007**, *46*, 9316–9319; *Angew. Chem.* **2007**, *119*, 9476–9479; b) C. L. Ricketts, D. Schröder, J. Roithová, H. Schwarz, R. Thissen, O. Dutuit, J. Žabka, Z. Herman, S. D. Price, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5135–5143.

[63] D. Schröder, M. Engeser, H. Schwarz, E. C. E. Rosenthal, J. Döbler, J. Sauer, *Inorg. Chem.* **2006**, *45*, 6235–6245.

[64] C. Heinemann, H. H. Cornehl, D. Schröder, M. Dolg, H. Schwarz, *Inorg. Chem.* **1996**, *35*, 2463.

[65] D. Schröder, M. Semialjac, H. Schwarz, *Int. J. Mass Spectrom.* **2004**, *233*, 103–109.

[66] G. Bouchoux, D. Leblanc, J. Y. Salpin, *Int. J. Mass Spectrom.* **1996**, *153*, 37–48.

[67] P. Milko, J. Roithová, D. Schröder, J. Lemaire, H. Schwarz, M. C. Holthausen, *Chem. Eur. J.* **2008**, *14*, 4318–4327.

[68] J. Roithová, D. Schröder, J. Míšek, I. G. Stará, I. Starý, *J. Mass Spectrom.* **2007**, *42*, 1233–1237.

[69] a) J. Roithová, P. Milko, C. L. Ricketts, D. Schröder, T. Besson, V. Dekoj, M. Bělohradský, *J. Am. Chem. Soc.* **2007**, *129*, 10141–10148; b) B. Colasson, M. Save, O. Reinaud, P. Milko, J. Roithová, D. Schröder, *Org. Lett.* **2007**, *9*, 4987–4990.

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