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Chemical evidence of the stability of praseodymium(V) in gas-phase oxide nitrate complexes†

Bernardo Monteiro,[a] Nuno A. G. Bandeira,*[b] Célia Lourenço,[a ‡] Ana F. Lucena,[a] José M. Carretas,[a] John K. Gibson[c] and Joaquim Marçalo*[a]

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The diverse reactivity of $[LnO_2(NO_3)_2]^-$ complexes with water in the gas phase, for Ln = Ce, Pr and Nd, examined in a quadrupole ion trap and complemented by *ab initio* computations, illuminates the chemical stability of Pr in the unusual +5 oxidation state.

Li, Zhou and co-workers recently reported the synthesis, in the gas phase and/or in solid noble-gas matrices, of molecular Pr species that were shown to contain Pr in the +5 oxidation state (OS) by infrared spectroscopy and quantum chemistry studies.[1, 2] This was the first definite identification of such a high OS in the lanthanide (Ln) series. The +3 OS dominates Ln coordination chemistry and only Ce yields molecular complexes in the tetravalent OS, although with important limitations.[3-5] Therefore, producing molecular species containing high-valent Ln ions remains a challenge. Notably, the first structurally characterized Tb^{4+} complexes have just been reported[6, 7] and this is an important advance towards the access to high OSs along the Ln series. OS is a key concept in chemistry, particularly for establishing chemical trends, directing syntheses and analysing bonding. Recently, the highest OS in the Periodic Table was extended to IX in a gas-phase Ir species and the possibility of reaching OS X was evaluated.[8-10] Gas-phase ion chemistry experiments, e.g. in a quadrupole ion trap (QIT),[11] in combination with computational studies, can provide important contributions to this research.

The formation of molecular Pr(V) species in the gas phase may have been previously observed, such as in the case of the PrO_2^+ ions produced in reaction of PrO^+ with NO_2 in a selected-ion flow tube (SIFT), as described by Bohme and co-workers,[12] but there was no computational examination of the structure of PrO_2^+. Recently, Dau et al. have also been able to produce PrO_2^+ ion in a QIT using a similar reaction process.[13] The capacity to generate a high OS in isolated gas-phase molecules results from the absence of solvents or other interacting species that would reduce chemically fragile species in condensed phases.[10]

We have shown previously that trivalent lanthanide tetranitrate anions, $[Ln(NO_3)_4]^-$, easily produced by electrospray ionization (ESI), give rise to oxide nitrate anions, $[LnO(NO_3)_3]^-$, by low-energy collision induced dissociation (CID) in a QIT, through NO_2 elimination.[14] The nature of the $[LnO(NO_3)_3]^-$ products was experimentally evaluated by their hydrolysis to yield $[Ln(OH)(NO_3)_3]^-$ and by density functional theory (DFT) computations of the energetics of hydrolysis and bonding analysis of representative oxide and hydroxide nitrate Ln ions. The experimental and computational results clearly showed that the hydrolysis rates were related to the intrinsic stability of the Ln +4 OS.

For the specific cases of Ce, Pr and Nd, the $[LnO(NO_3)_3]^-$ ions displayed a clear stability and we decided to examine their CID behaviour under similar experimental conditions (see the Supplementary Information (SI) for details). We have previously obtained evidence of the formation of $[PrO_2(NO_3)_2]^-$ ions in CID of $[Pr(NO_3)_4]^-$ in a QIT, under somewhat different experimental conditions, by sequential elimination of two NO_2 in a single CID stage.[15] In the present study, CID of isolated $[LnO(NO_3)_3]^-$, obtained from CID of $[Ln(NO_3)_4]^-$, readily gave rise to $[LnO_2(NO_3)_2]^-$ ions, as shown in Fig. 1 for Pr and in Figs. S3 and S4 of the SI for Ce and Nd, respectively.

The formation of these $[LnO_2(NO_3)_2]^-$ ions does not directly reveal their structure or the metal OS. Therefore, we proceeded to assess the geometric and electronic properties of the synthesized Ln complexes by *ab initio* calculations[16-18] following a DLPNO-CCSD(T)/SARC-TZVPP//MP2/SARC-TZVPP protocol (see the SI for details). In Fig. 2 we show the computed ground state structures of the three $[LnO_2(NO_3)_2]^-$ ions.

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[a] Centro de Ciências e Tecnologias Nucleares and Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, 2695-066 Bobadela LRS, Portugal. Email: jmarcalo@ctn.tecnico.ulisboa.pt
[b] BioISI and Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal. Email: nuno.bandeira@ciencias.ulisboa.pt
[c] Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.

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‡ Present address: *Centre for Environmental and Agricultural Informatics, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK.*

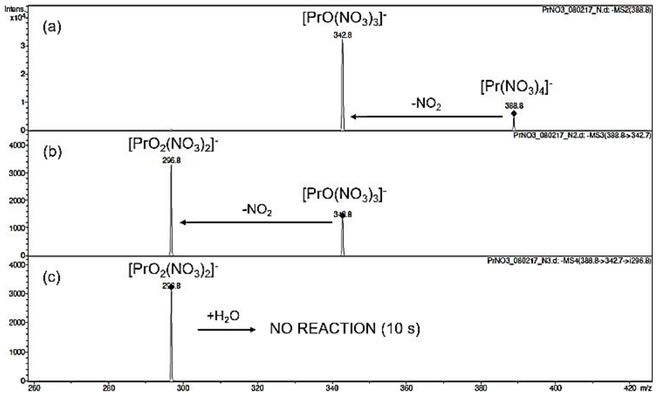

Fig. 1 – Mass spectra showing: (a) CID of isolated $[Pr(NO_3)_4]^-$ producing $[PrO(NO_3)_3]^-$; (b) CID of isolated $[PrO(NO_3)_3]^-$ producing $[PrO_2(NO_3)_2]^-$; (c) isolated $[PrO_2(NO_3)_2]^-$ in the presence of background water for 10 s.

The search for the ground state structure of these anions resulted in very different species depending on the nature of Ln. For cerium, the lowest isomer was an oxo-/oxyl- species in which an unpaired electron resides in one of the oxygen ligands. This is shown by the calculated spin density (1.02) on this fragment. The anion is best described as having an $O{=}Ce^{IV}{-}O^{\bullet}$ type of Lewis structure (ground state doublet).

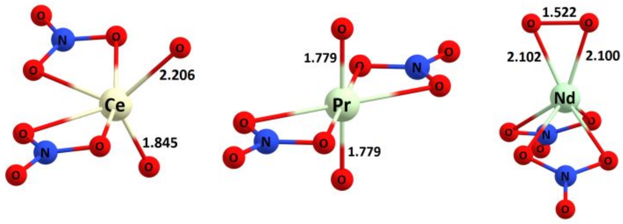

Fig. 2 – MP2/SARC-TZVPP computed ground state structures of $[LnO_2(NO_3)_2]^-$ ions for Ln = Ce, Pr, Nd, with the most relevant bond lengths in Å.

The computations of the Pr dioxide nitrate complex show that in the ground state Pr is indeed in the +5 oxidation state, while Ce and Nd are in the +4 and +3 OS, respectively. The former species can be viewed as a $[O{=}Pr^{V}{=}O]^+$ moiety coordinated by two (NO_3^-), resulting in an overall net charge of −1. The $[Pr(O)_2(NO_3)_2]^-$ ion exhibits near perfect D_{2h} point group symmetry. The Pr≡O bond length (1.779 Å) in $[PrO_2(NO_3)_2]^-$ is comparatively longer than the previously reported[1] CCSD(T) estimate (1.699 Å) in PrO_2^+ due to charge polarisation caused by the presence of nitrate ligands. The MP2 method can accurately reproduce (1.694 Å) the CCSD(T) bond length in the PrO_2^+ cation.

The Nd complex is significantly different from the remainder since the lowest energy structure corresponds to a di-haptic peroxide ($[Nd^{III}(\eta^2\text{-}O_2)(NO_3)_2]^-$). The corresponding Nd^V complex is 250.7 kJ mol^{-1} higher in energy. The energy gain resulting from multiple Nd=O bond formation does not offset the stability provided by the formation of an O-O single bond. The structures of the Ln dioxide cation cores of the two other metals are in agreement with previous computations for Ce[19] and Pr.[1]

The generation of the dioxides from the preceding monoxides was further investigated. The energetics of the collision induced dissociation of nitrogen dioxide from the $[LnO(NO_3)_3]^-$ complexes was calculated for Ln = Ce, Pr, Nd. Our computations indicate that the elimination of NO_2 is increasingly more likely with increasing electron count as shown in Table 1. For the early lanthanides this dissociation might not be the easiest route to generate dioxo species.

Table 1 – Energetics (DLPNO-CCSD(T)/SARC-TZVPP//MP2/SARC-TZVPP) of the NO_2 dissociation event for three lanthanide anions.

$[LnO(NO_3)_3]^- \rightarrow [LnO_2(NO_3)_2]^- + NO_2$	ΔE/kJ mol^{-1}
Ln = Ce	+531.2
Ln = Pr	+170.9
Ln = Nd	+35.4

The ease of access to the experimentally obtained $[LnO_2(NO_3)_2]^-$ ions for Ln = Ce, Pr and Nd prompted us to examine their reactivity with water, as this is probably the most elementary, direct probe of the chemical stability of the Ln dioxide species. As before,[14] we took advantage of water present in the background of the QIT and, by including a reaction delay in the experimental sequence, we observed that the $[LnO_2(NO_3)_2]^-$ ions had different behaviours, as depicted in the equations below:

$$[CeO_2(NO_3)_2]^- + H_2O \longrightarrow [CeO(OH)(NO_3)_2]^- + OH^{\bullet} \qquad (1)$$

$$[PrO_2(NO_3)_2]^- + H_2O \longrightarrow \textit{NO REACTION} \qquad (2)$$

$$[NdO_2(NO_3)_2]^- + H_2O \longrightarrow [NdO_2(H_2O)(NO_3)_2]^- \qquad (3)$$

Representative mass spectra from these reactivity experiments are shown in Fig. 1 for Pr and in Figs. S3 and S4 of the SI for Ce and Nd, respectively. The spectra clearly indicate the absence of reactivity for Pr, a slow reaction for Ce and a very fast reaction for Nd. The measured rates for reactions 1 and 3 were k(Ce) = 0.061 s^{-1} and k(Nd) = 41.2 s^{-1}, respectively, obtained from the slope of the log of the reactant ion decay versus time. The helium pressure and the background water pressure in the QIT were nearly constant (to within <10%), as established by the reproducibility of the rates measured at different times, and thus the determined rates directly provide comparative kinetics.

For confirmation of these observations, we performed experiments in which additional water was introduced in the QIT through a variable leak valve. The resulting mass spectra are presented, together with experimental details, in Figs. S5, S6 and S7 of the SI. In the case of the Pr complex, the reaction with water continued to be absent, while for the Ce complex, a faster hydrolysis occurred as expected, with k(Ce) = 0.63 s^{-1}. $[NdO_2(NO_3)_2]^-$, due to its very fast reaction, was already totally consumed during CID of the precursor complex $[NdO(NO_3)_3]^-$.

The hydrolysis reaction of $[CeO_2(NO_3)_2]^-$, eq. 1, may be expected due to the structure of the reactant ion, where one of the oxido ligands can be considered as $O^{\bullet-}$ and, therefore, $H^{\bullet}$

abstraction from H_2O could be a favourable process. In this reaction, the Ce centre preserves a +4 OS. The structure of the $[Ce^{IV}O(OH)(NO_3)_2]^-$ product ion was computed and is displayed in Fig. 3. The energetics of reaction 1 was computed and the value obtained, ΔE(Ce) = -0.5 kJ mol^{-1}, indicates a marginal exergonicity, which seems to be in agreement with the low value obtained for the reaction rate.

In the case of of $[PrO_2(NO_3)_2]^-$, a hydrolysis reaction such as that observed for Ce could be anticipated, as the +4 OS is moderately stable for Pr. The energetics of reaction 1 was also computed for Pr and the determined value, ΔE(Pr) = +719.1 kJ mol^{-1}, clearly indicates an endergonic process, reflecting the robust character of Pr(V) in $[PrO_2(NO_3)_2]^-$. Moreover, the addition of one hydrogen atom reduces the Pr metal centre, resulting in the $[Pr^{IV}O(OH)(NO_3)_2]^-$ anion, as the ensuing spin density (1.08) is unequivocally localised in the metal. This resultant $[Pr^{IV}O(OH)]^+$ fragment is angular and less symmetric than its precursor (Fig. 3).

In the reaction of $[NdO_2(NO_3)_2]^-$ with water, eq. 3, considering that the reactant ion involves a peroxide ligand (O_2^{2-}), one could predict either a simple hydration or a hydrolysis reaction, with Nd retaining a +3 OS in both cases. The structure of the Nd hypothetical products were computed and are displayed in Fig. 3. The expected neodymium $[Nd^{III}O^{\bullet}(OH)(NO_3)_2]^-$ species undergoes peroxide cleavage which is energetically costly (ΔE = +115 kJ mol^{-1}), explaining why it is not formed. The actual obtained product from reaction 3 is $[Nd(\eta^2\text{-}O_2H)(OH)(NO_3)_2]^-$ (Fig. 3.d). The more intuitive structural isomer $[Nd(\eta^2\text{-}O_2)(H_2O)(NO_3)_2]^-$ is +71.7 kJ mol^{-1} higher in energy (cf. Fig. S18).

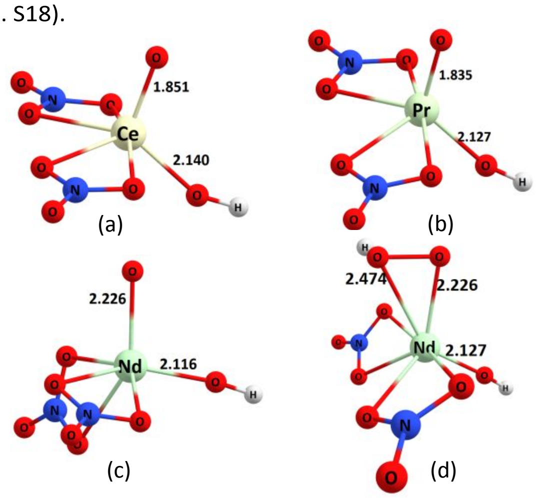

Fig. 3 – Computed ground state structures (bond lengths in Å) of the hydration products of $[LnO_2(NO_3)_2]^-$ ions, for Ln = Ce (a), Pr (b) and Nd (c), with S=0 (f^0),1/2 (f^1) and 2 (f^3), respectively; the actual Ln = Nd product formed is (d).

To further test the stability of the $[LnO_2(NO_3)_2]^-$ ions, we examined their CID behaviour. The results are depicted in Figs. S8, S9 and S10 of the SI, for Ce, Nd and Pr, respectively. For the case of Ce, NO_2 loss is again observed, leading to a $[CeO_3(NO_3)]^-$ species that promptly reacts with background water. In the case of Nd, there is loss of O_2, apparently in agreement with the computed structure of the precursor ion, followed by a very fast reaction with water. CID of $[PrO_2(NO_3)_2]^-$ at increasing fragmentation amplitudes showed only a decrease in spectrum intensity and the absence of product ions, which is also an indication of the stability of the Pr(V) complex.

Gas-phase nitrate decomposition via CID in metal complexes such as that presented here bears resemblance to condensed phase thermal decomposition of metal nitrates to form metal oxides. In both cases, the process is facilitated by the susceptibility of NO_3 towards dissociation into NO_2 and O. The evidence obtained here for the easy production of Pr(V) species starting from Pr(III) nitrates suggests that the thermal decomposition of solid Pr(III) nitrates could lead to Pr(V) oxide nitrate species such as $PrO_2(NO_3)$. However, a detailed study of the use of $Pr(NO_3)_3{\cdot}6H_2O$ as a precursor of $PrO_{1.833}$ (Pr_6O_{11}) at 600°C in an atmosphere of static air did not show any evidence of the formation of Pr(V) oxide nitrate species.[20] Possibly, only a specific combination of nitrate and other ligands in a Pr complex, together with particular conditions during thermal decomposition, can lead to a Pr(V) compound in condensed phase. Yet, other experimental approaches may be feasible, such as the ones that very recently led to the first structurally characterized Tb^{IV} complexes.[6, 7]

In conclusion, the different reactivity with water of the gas-phase complexes $[LnO_2(NO_3)_2]^-$ for Ln = Ce, Pr, Nd showed to be related to the stabilities of the +4, +5 and +3 OS, respectively. The unreactive nature of $[PrO_2(NO_3)_2]^-$ with water demonstrated the chemical stability of Pr(V) in this complex as identified by *ab initio* computations. The results show that Pr(V) is readily accessible and indicate that high OS lanthanide chemistry could be richer than previously assumed, at least in the isolated environment of the gas phase.

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A data set collection of computational results is available in the ioChem-BD repository[21] and can be accessed via https://doi.org/10.19061/iochem-bd-6-19.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1. Q. Zhang, S. X. Hu, H. Qu, J. Su, G. Wang, J. B. Lu, M. Chen, M. Zhou and J. Li, *Angew. Chem. Int. Ed. Engl.*, 2016, **55**, 6896-6900.
2. S.-X. Hu, J. Jian, J. Su, X. Wu, J. Li and M. Zhou, *Chem. Sci.*, 2017, **8**, 4035-4043.
3. N. A. Piro, J. R. Robinson, P. J. Walsh and E. J. Schelter, *Coord. Chem. Rev.*, 2014, **260**, 21-36.
4. R. Anwander, M. Dolg and F. T. Edelmann, *Chem. Soc. Rev.*, 2017, **46**, 6697-6709.
5. Y.-M. So and W.-H. Leung, *Coord. Chem. Rev.*, 2017, **340**, 172-197.
6. C. T. Palumbo, I. Zivkovic, R. Scopelliti and M. Mazzanti, *J. Am. Chem. Soc.*, 2019, **141**, 9827-9831.
7. N. T. Rice, I. A. Popov, D. R. Russo, J. Bacsa, E. R. Batista, P. Yang, J. Telser and H. S. La Pierre, *J. Am. Chem. Soc.*, 2019, **141**, 13222-13233.
8. G. Wang, M. Zhou, J. T. Goettel, G. J. Schrobilgen, J. Su, J. Li, T. Schlöder and S. Riedel, *Nature*, 2014, **514**, 475.
9. H. S. Yu and D. G. Truhlar, *Angew. Chem. Int. Ed.*, 2016, **55**, 9004 -9006.
10. S.-X. Hu, W.-L. Li, J.-B. Lu, J. L. Bao, H. S. Yu, D. G. Truhlar, J. K. Gibson, J. Marçalo, M. Zhou, S. Riedel, W. H. E. Schwarz and J. Li, *Angew. Chem.-Int. Ed.*, 2018, **57**, 3242-3245.
11. R. A. J. O'Hair, *Chem. Commun.*, 2006, 1469-1481.
12. M. J. Jarvis, V. Blagojevic, G. K. Koyanagi and D. K. Bohme, *Phys. Chem. Chem. Phys.*, 2010, **12**, 4852-4862.
13. P. D. Dau, M. Vasiliu, K. A. Peterson, D. A. Dixon and J. K. Gibson, *Chem. Eur. J.*, 2017, **23**, 17369-17379.
14. A. F. Lucena, C. Lourenço, M. C. Michelini, P. X. Rutkowski, J. M. Carretas, N. Zorz, L. Berthon, A. Dias, M. C. Oliveira, J. K. Gibson and J. Marçalo, *Phys. Chem. Chem. Phys.*, 2015, **17**, 9942-9950.
15. A. Kovacs, P. D. Dau, J. Marçalo and J. K. Gibson, *Inorg. Chem.*, 2018, **57**, 9453-9467.
16. F. Neese, *WIREs Comput. Mol. Sci.*, 2017, **8**, e1327.
17. C. Riplinger and F. Neese, *J. Chem. Phys.*, 2013, **138**, 034106.
18. C. Riplinger, P. Pinski, U. Becker, E. F. Valeev and F. Neese, *J. Chem. Phys.*, 2016, **144**, 024109.
19. C. Heinemann, H. H. Cornehl, D. Schröder, M. Dolg and H. Schwarz, *Inorg. Chem.*, 1996, **35**, 2463-2475.
20. G. A. M. Hussein, B. A. A. Balboul, M. A. A-Warith and A. G. M. Othman, *Thermochim. Acta*, 2001, **369**, 59-66.
21. M. Álvarez-Moreno, C. de Graaf, N. López, F. Maseras, J. M. Poblet and C. Bo, *J. Chem. Inf. Model.*, 2015, **55**, 95-103.

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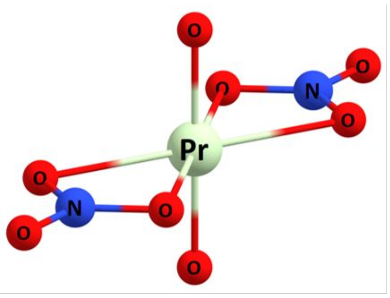

$[Ce^{IV}O_2(NO_3)_2]^- + H_2O \longrightarrow [Ce^{IV}O(OH)(NO_3)_2]^- + OH^\bullet$

$[Pr^{V}O_2(NO_3)_2]^- + H_2O \longrightarrow$ ***NO REACTION***

$[Nd^{III}(O_2)(NO_3)_2]^- + H_2O \longrightarrow [Nd^{III}(O_2H)(OH)(NO_3)_2]^-$