Ceric Ammonium Nitrate (CAN)

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Revisiting the Solution Structure of Ceric Ammonium Nitrate**

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Abstract: *Ceric ammonium nitrate (CAN) is a single-electron-transfer reagent with unparalleled utility in organic synthesis, and has emerged as a vital feedstock in diverse chemical industries. Most applications use CAN in solution where it is assigned a monomeric* $[Ce^{IV}(NO_3)_6]^{2-}$ *structure; an assumption traced to half-century old studies. Using synchrotron X-rays and Raman spectroscopy we challenge this tradition, converging instead on an oxo-bridged dinuclear complex, even in strong nitric acid. Thus, one equivalent of CAN is recast as a two-electron-transfer reagent and a redox-activated super-base, raising questions regarding the origins of its reactivity with organic molecules and giving new fundamental insight into the stability of polynuclear complexes of tetravalent ions.*

Ceric ammonium nitrate (known as CAN)—$(NH_4)_2Ce(NO_3)_6$—has found widespread use as a single-electron-transfer reagent for breaking and making carbon–carbon and carbon–heteroatom bonds;[1] the crux of organic synthesis. The versatility and stability of CAN, as well as its reasonable price, has also led to its use as a precursor for myriad Ce^{IV}-based compounds that have applications beyond organic chemistry, such as photocatalysts for hydrogen generation[2] or in the synthesis of biologically active ceric oxide nanoparticles.[3] The majority of applications involving CAN start by dissolving the salt in an aqueous phase, so its solution structure is of broad fundamental importance.

Ce^{IV} in perchlorate aqueous phases has long been known to have a rich structural chemistry, with the formation of a variety of polynuclear ceric oxide species from dinuclear complexes, to polymers and nanoparticle colloids.[4] This is caused by the lack of complex formation between the perchlorate ion and the tetravalent cation, which results in hydrolysis, even in acidic solutions.[4,5] However, when in the presence of complexing ligands, such as nitrate, and under acidic conditions, Ce^{IV} ions form strong complexes so that solution-phase CAN is generally accepted to be a monomeric $[Ce(NO_3)_6]^{2-}$ ion.[4] This has led to the widely held assumption that this anionic monomer is the active CAN species that drives the renowned solution-phase electron-transfer reactions in organic synthesis.[1b]

Recent literature pertaining to the solution structure of CAN is mainly confined to text books, where it is presumed "mainly as the free ammonium ions and hexanitrated Ce^{IV}" where the structure of the hexanitrated Ce^{IV} is "similar to that of the solid state".[4] This conclusion is traced to papers published in the early-to-mid 20th century that proposes the use of $(NH_4)_2[Ce(NO_3)_6]$ as a reference for oxidimetry because of the perceived stability of the $[Ce(NO_3)_6]^{2-}$ ion in aqueous solutions, which was evidenced by salting out experiments.[6] In the 1960s, direct X-ray diffraction and vibrational spectroscopy measurements of CAN dissolved in water supported this hypothesis, with radial distribution curves interpreted to show six bidentate nitrate groups around the Ce^{IV} ion and no long-range Ce–Ce interactions that might suggest polynuclear species.[7] These studies showing monomeric CAN in solution are the basis for its categorization as a simple single-electron-transfer reagent in present day synthetic organic chemistry.

Although the assumption that the monomeric hexanitrate anion dominates aqueous solutions is now seldom disputed, upon closer inspection, the early CAN literature was not unanimous in this conclusion. Solvent extraction and potentiometric experiments, published a couple of years prior to the X-ray diffraction studies appear to question the hypothesis that the monomeric hexanitrato anion dominates under all conditions. In one comprehensive report published in the Russian literature, Levin et al. suggested that the hexanitrato Ce^{IV} anion is only significant in nitric acid solutions of more than 2 M concentration, with dissociated cationic complexes (aquated Ce^{IV}, $[CeNO_3]^{3+}$, $[Ce(NO_3)_2]^{2+}$, etc.) pertaining under lower nitrate concentrations.[8] This conclusion was supported by Wylie who reported the extraction of the hexanitrato anion only at high acid concentrations, inferring the existence of hydrolyzed Ce-OH complexes at lower acidity.[9] Even more unorthodox were the findings published by Blaustein and Gryder about a decade earlier, asserting that polymeric hydrolyzed Ce–Ce complexes are the dominant extracted species even at high (5.5 M) concentrations of nitric acid.[10] Although these hydrolyzed polynuclear species were largely refuted by the subsequent direct spectroscopic studies,[7] recent literature on the generation of nanoparticles and formate clusters from aqueous Ce^{IV} nitrate solutions suggests the presence of polynuclear oxo-bridged precursor clusters.[11] These clusters were reported in electrolyzed Ce^{III} nitrate solutions[11a] (as well as in solutions of CAN subjected to

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hydrothermal synthesis)[11b] under concentrated conditions with little or no excess nitrate and very weak acidity so as to favor agglomeration. The findings invite us to question the assertion that a simple monomeric anion dominates the solution chemistry of CAN.

As CAN has become such an important chemical feedstock, we thought it timely to re-visit the structure of CAN in aqueous solutions using modern techniques. Herein we explore the structure of CAN in aqueous systems of relevance to synthetic applications (i.e. non-hydrolyzing/acidic conditions),[12] and refute the assertion of a single mononuclear anion. Our results have far-reaching consequence for organic synthesis and other applications of CAN that are important in current and emerging applied chemistry. We probed the solution structure of CAN in 3 M nitric acid by direct dissolution of the solid salt at 0.04 M and 0.4 M. The high proton activity, excess nitrate ion and low-to-medium concentration of Ce^{IV} is designed to minimize hydrolysis and agglomeration, thus favoring the monomeric $[Ce(NO_3)_6]^{2-}$ ion thought to be the active species in organic synthesis. The structure was probed using a combination of synchrotron X-ray and vibrational spectroscopies.

X-ray absorption spectroscopy (XAS) was used to simultaneously diagnose the oxidation-state purity of cerium and to provide information on the coordination environments of the Ce^{IV} centers. Spectra were collected from 0.04 M and 0.4 M solutions of CAN and for the CAN solid itself. The Ce L_3-edge X-ray absorption near-edge structure (XANES) for the solutions and the solid have two strong resonances, consistent with purely tetravalent Ce and with previous measurements of CAN.[13] The data for the dilute solution and the solid are provided in Figure 1 a. The complementary Ce L_1-edge XANES are provided in Figure 1 b. The $k^3\chi(k)$ extended X-ray absorption fine structure (EXAFS) data and the corresponding Fourier transform (FT) data for the dilute solution and the solid are plotted in Figure 2. The responses for the solid-state CAN and the solution CAN are clearly different. The readily apparent disparities (for example, in the L_1-edge XANES and in the FT data of the EXAFS) between the solid salt and upon its dissolution in aqueous HNO_3 have been noted in the literature beforehand[13,14] without comment about their physical significance. The variations in the XANES of Figure 1 as well as the EXAFS of Figure 2 are diagnostic of a reorganization of the hexanitrato, 12-oxygen coordination environment about Ce^{IV} in solid CAN, $[Ce(NO_3)_6]^{2-}$,[15] following its dissolution in acid. The FTs (Figure 2 b) reveal a marked diminution of the primary peak (at ca. 2 Å, before phase-shift correction) upon dissolution, suggesting a decrease in the O coordination number (CN) in the solution compared to the solid. The FT for the solid has a distant, medium intensity peak at 3.62 Å, which is attributed to the backscattering from the six distal O atom, one from each of the six bidentate-coordinating nitrate groups. The higher than anticipated intensity is renown in the literature of metal(IV) nitrate coordination chemistry.[11a,16] The FT for the solution exhibits weak features at 2.69 Å and 3.44 Å that are wholly inconsistent with the FT data for the $[Ce(NO_3)_6]^{2-}$ structure of the solid.[15]

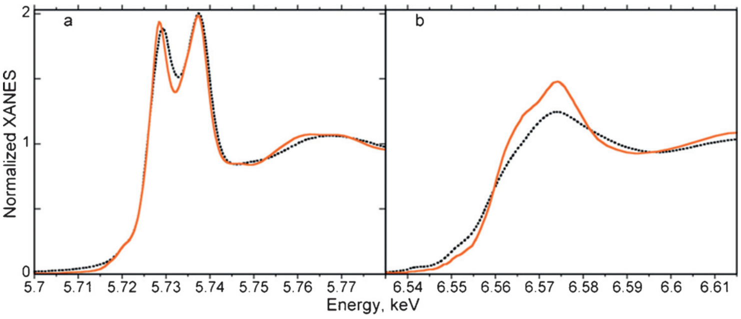

Figure 1. The Ce L_3-edge (a) and L_1-edge (b) XANES for CAN solid (solid orange line) and the 0.04 M solution (black dashed line). Beyond the two sharp electronic resonances at 5.7285–5.7292 and 5.7373–5.7374 keV in the L_3-XANES, the broad scattering signals (between 5.75 and 5.78 keV) for the solid and solution are out of phase. The L_1-XANES shows even more pronounced variations that are indicative of different coordination environments of Ce^{IV} for the solid and solution.

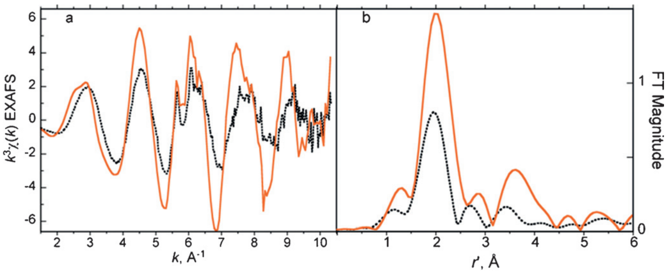

Figure 2. The $k^3\chi(k)$ EXAFS (a) and the Fourier transform (FT) data (b, uncorrected for phase shift) for CAN solid (solid orange line) and the 0.04 M solution (black dashed line). The narrow peaks at approximately 5.6 and 6.0 $Å^{-1}$ in the EXAFS (a) are multi-electron resonances that are commonly observed in L_3-edge EXAFS of Ce^{IV} compounds.[19] Based upon the X-ray crystallographic structure of $[Ce(NO_3)_6]^{2-}$, the main peak at 2.02 Å and the distant one at 3.62 Å in the FT (b) of the solid CAN are attributed to backscattering by Ce–O/N and Ce–O, respectively. Our data are of insufficient resolution to separate the close Ce–O and Ce–N correlations. No physical significance is ascribed to the small peaks at 1.30 and 2.86 Å surrounding the main peak. For the FT of the solution data, the peaks at 2.69 and 3.44 Å beyond the main one (at 1.97 Å) are inconsistent with the response for CAN, and the peak at 1.13 Å does not carry any physical significance.

To obtain metrical information from the peaks in the FT data, the $k^3\chi(k)$ EXAFS was curve fit using shell models. In view of the small range of primary data available (2.0–10.3 $Å^{-1}$) in the Ce L_3-edge EXAFS, a conservative approach was taken to fit the intense primary peaks in the FT data in as rigorous a manner as allowed with the number of independent data points (7). In this regard, the utility and value of Ce K-edge EXAFS has already been demonstrated for the CAN salt, in particular,[11a] and cerium compounds, in general.[17] Modeling the minor and distant secondary peaks in the FT data for the solution and the CAN solid is neither viable nor is it necessary to prove our point that their Ce^{IV} speciation is significantly different.

The shell-fitting shows that a single O model corresponding to a simple aquated-nitrated complex does not reasonably account for the EXAFS data for the CAN salt and its solution (see Supporting Information, Figure S1, Table S1). The only way to achieve physically realistic CNs for the O coordination shells is by the addition of a Ce–N shell (2.98 ± 0.02 Å) for the solid and a uniquely short Ce–O shell (2.06 ± 0.01 Å) for the solution. With regard to the Ce–O shell, a similar and unusually short Ce–O correlation has been observed in the solid state by Guillou et al.,[18] where an oxo-bridged Ce^{IV}-O-Ce^{IV} dinuclear complex of composition $[(H_2O)_3(NO_3)_3CeOCe(NO_3)_3(H_2O)_3]$ was isolated. For a neutral entity as for this crystallographically characterized dinuclear complex, in which there are additional water molecules bound to the Ce^{IV} centers, the O coordination number for the bidentate nitrates is 6. The EXAFS determined CN (6.5) is in agreement, but the average Ce–O distance of 2.46(1) Å is indicative of water coordination rather than nitrate coordination. For example, our distance is statistically equivalent to the average $Ce{-}(OH_2)_3$ distance of 2.471(5) in the crystal structure, whereas the average $Ce{-}(O_2NO)_3$ distance of 2.515(6) Å is longer than our average result. This leads us to the conclusion that a cationic entity, such as $[(H_2O)_6Ce\text{-}O\text{-}Ce(H_2O)_6]^{6+}$ (Figure 3, inset), prevails under our solution conditions. All the parameters and additional details pertaining to the EXAFS fitting can be found in the Supporting Information. Attempts to fit the solution data directly using the crystal structure for the monomeric $[Ce(NO_3)_6]^{2-}$ ion of the solid does not yield physically meaningful parameters. Therefore, the EXAFS data indicates a short, possibly bridging Ce–O interaction in the acidic CAN solutions in which each Ce^{IV} is coordinated to 6–7 other O atoms at 2.46 ± 0.01 Å; a distance that is more consisted with water than nitrate.

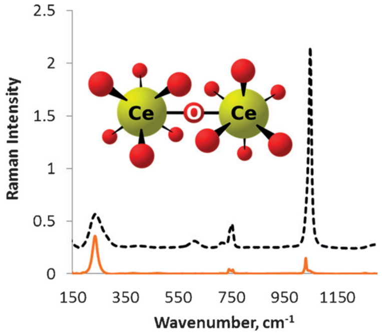

Figure 3. Raman spectra for $[(H_2O)_6Ce_2O(NO_3)_6]$ single crystal (orange line) and 0.4 M CAN in 3 M HNO_3 (black dashed line). Inset: proposed cationic dinuclear entity in solution.

Although EXAFS provides evidence for a close coordinated O donor atom that is not water or nitrate, it cannot distinguish whether this is from a bridging Ce-O-Ce interaction or merely a coordinated hydroxide or oxide on a monomer. Therefore, to explore the hypothesis that the short Ce–O interaction is from an oxo-bridged feature, we repeated the synthesis of the solid-state dinuclear complex reported by Guillou et al.[18] and collected a Raman spectrum from the $[(H_2O)_6Ce_2O(NO_3)_6]$ single crystal (Figure 3, orange line). The very intense band at 235 cm^{-1} is assigned to the Ce-O-Ce vibration and the weak bands at 740 cm^{-1}, 755 cm^{-1} and 1030 cm^{-1} are assigned to bound nitrate.[20] We compare this spectrum with the 0.4 M CAN solution in 3 M HNO_3 (black dashed line). In this case the band assigned to the Ce-O-Ce vibration, although broadened and slightly blue-shifted, remains intense and is good evidence for the presence of an oxo-bridged structure in solution. Previous Raman studies on solutions of CAN identified nitrate peaks, however the spectra presented in these publications do not cover the low wavenumber range necessary to detect the Ce-O-Ce vibration.[13] The incidence of the bridging Ce-O-Ce Raman vibration in the presence of overwhelming free nitrate in an acidic solution illustrates the stability of the bridging oxide under conditions that should be unfavorable toward hydrolysis and favorable toward the hexanitrato monomeric anion.

The EXAFS and Raman both support the presence of polynuclear Ce^{IV} complexes—constructed of bridging Ce-O-Ce motifs—in the 3 M HNO_3 solution. We therefore sought to investigate the nanostructured morphology of these clusters using synchrotron small-angle X-ray scattering (S-SAXS). With a high photon flux, S-SAXS is sensitive enough to pick out small clusters of Ce (Z = 58) against the low-Z background electrolyte (consisting of H_2O and HNO_3). S-SAXS data were collected from both the 0.04 M and 0.4 M Ce^{IV} nitric acid solutions. By subtracting the scattering contribution from the background aqueous 3 M HNO_3 solution, the scattering from the Ce^{IV} species is revealed (Figure 4). The data collected from the 0.04 M CAN solution in 3 M nitric acid gives a curved profile that progresses from a plateau at low-q to a rapid decline at high-q, typical for scattering produced by particles with little extended structure. These data were fitted using a model for a simple solid sphere to give a radius of 2.6 ± 0.2 Å (see Supporting Information). The scattering for the concentrated 0.4 M Ce^{IV} solution gives a similar profile, but this time with a hump at approximately 0.3 Å^{-1}. This is typical for a hard-sphere repulsive structure factor peak that is expected at high particle concentrations. To account for this feature, the data for the high concentration solution were fitted using a model for hard spheres to yield a spherical radius of 3.1 ± 0.3 Å (see Supporting Information). Because Ce has a much higher electron count than the background water/nitrate solvent, the radii correspond only to the Ce centers. The radii calculated from the data fitting for both solutions are significantly larger than the ionic radius of a single Ce^{IV} ion in its monomeric form (0.97 Å for CN = 6).[21] An oxo-bridged dinuclear structure is estimated to have a long-axis diameter of 4.64 Å (calculated from the ionic radii of Ce^{4+} and O^{2-}),[21] which is close to the hard sphere

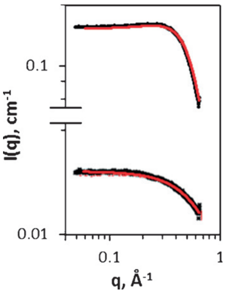

Figure 4. Experimental S-SAXS data for 0.04 M Ce^{IV} (lower series) and 0.4 M Ce^{IV} (upper series) in 3 M HNO_3 and corresponding model fits (red lines).

diameters calculated from the SAXS data (5.2–6.2 Å), re-enforcing that the Ce-O-Ce complexes are dinuclear. Therefore, the SAXS suggests that dinuclear Ce^{IV} clusters pertain in the 3 M nitric acid solution, irrespective of the Ce^{IV} concentration.

Taken together, the EXAFS, Raman, and SAXS data provide strong evidence for the oxo-bridged dinuclear complex in the 3 M nitric acid solution. This is unprecedented under the experimental conditions and has important implications in the electron-transfer reaction mechanisms that are standard in organic synthesis.

Ce^{IV} has long been considered a one-electron acceptor with a simple valence change taking place according to Equation (1):[4]

$$Ce^{IV} + e^{-} \rightleftharpoons Ce^{III} \tag{1}$$

However, recent electrochemical studies have shown that variations of nitric acid concentration exhibit pronounced effects on the voltammogram peak shapes.[22] Although the formal electrode potential for the cerium couple of Equation (1) is independent of both proton and nitrate concentrations,[22b,23] the peak current ratios are far from unity and the peak separation is much greater than 59 mV (variations from 785–124 mV have been noted for increasing $[HNO_3]$ from 0.5–6 M, respectively). Both diagnostic criteria suggest that the cerium(III/IV) redox reaction is not nearly as simple as the one-electron transfer depicted in Equation (1). Rather, the responses are typical of a redox reaction that is coupled with a chemical one involving either bonding variations between the Ce^{III} and Ce^{IV} entities and/or reorganization of the inner coordination environment.[22,23] Whereas Ce^{III} is generally acknowledged to exist as a simple aquated cation in acidic electrolytes,[24] a Ce^{IV} oxo-bridged dinuclear complex, which we find to be prevalent even in strongly acidic solutions, could account for these electrochemical results so that the electron transfer equation involves protons and becomes [Eq. (2)].

$$[Ce^{IV}\text{-O-}Ce^{IV}]^{6+} + 2\,e^{-} + 2\,H^{+} \rightleftharpoons 2\,Ce^{III} + H_2O \tag{2}$$

Such a dinuclear structure of CAN would therefore operate as a two-electron-transfer reagent by accepting electrons on two adjacent centers on the same complex. This has important implications in synthetic organic mechanisms that involve a two-electron oxidation of one (or more) molecules, such as in the synthesis of quinones from polynuclear aromatic systems (an important commercial application of CAN).[25] Another is in reactions that involve a one-electron oxidation of two separate hydrocarbon molecules in the same vicinity and coupling them together, such as in the oxidative coupling of dialkylamines.[26] There are also important mechanistic implications that could arise from the imbedded bridging oxide that binds the dinuclear structure together; although the oxide ion is apparently stable under acidic conditions, upon reduction of the Ce^{IV} centers it would become available as a proton sponge. This would make CAN a two-electron one-step redox-activated superbase that is capable of deprotonating weakly acidic molecules as well as donating an oxide ion in a reaction mechanism. In this regard, there are myriad examples of reactions that involve the formation of a C–O bond using CAN.[1b]

Our results strongly suggest that the structure of CAN in acidic nitrate solution is an oxo-bridged dinuclear complex. This structure apparently self-assembles upon dissolution of the solid salt in 3 M nitric acid. In a similar vein, independent results indicate that the electrolytic oxidation of $Ce^{III}(NO_3)_3{\cdot}6\,H_2O$ in a 0.5 M HNO_3 electrolyte leads to a predominantly dinuclear Ce^{IV} entity.[11a] Coincidentally, organic catalysis using solutions of CAN and with solutions of electrolytically oxidized $Ce^{III}(NO_3)_3$ lead to the same products, that is, oxidations of carbonyl compounds were dimerized by both systems.[27] This line of evidence suggests that the predominant solution species upon dissolution of CAN in nitric acid is the same one obtained upon electrolytic oxidation of $Ce(NO_3)_3$ in nitric acid. In both instances a dinuclear complex is the prevalent molecular entity. Based upon the results of the EXAFS analyses (Table S1), the dinuclear complex proposed in Equation (2) can be generalized as $[(H_2O)_{6-7}Ce^{IV}\text{-O-}Ce^{IV}(OH_2)_{6-7}]^{6+}$(Figure 3, inset). The stability of such an oxo-bridged dinuclear complex and its prevalence under acidic conditions and in excess nitrate is a surprising new insight into the solution chemistry of tetravalent metal ions in the presence of complexing ligands.

Experimental Section

CAN solutions were obtained by direct dissolution of the 99.98% pure ceric ammonium nitrate salt (from Sigma–Aldrich) in Optima grade nitric acid (from Fisher Scientific) diluted with ultra-high-purity water (18.2 MΩ cm). EXAFS and S-SAXS measurements were conducted at the sector 12 beamlines at the Advanced Photon Source, Argonne National Laboratory, USA. The crystal studied by Raman spectroscopy was obtained by slow evaporation during bulk electrolysis of Ce^{III} nitrate dissolved in water. Both crystal and solution drops were placed on glass slides and Raman spectra were recorded using a Renishaw in Via Raman microscope with an excitation line of 532 nm. Full experimental details are available in the Supporting Information.

Keywords: cerium · Raman spectroscopy · small-angle X-ray scattering · structure elucidation · X-ray absorption spectroscopy

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