



Characterization of coordination complexes by desorption electrospray mass spectrometry with a capillary target

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ABSTRACT

Metal coordination complexes were formed directly from liquid surfaces using desorption electrospray ionization (DESI) mass spectrometry, in which the analyte solutions were furnished by a target capillary that protrudes into the ESI spray. The approach is attractive because it separates complexities of ESI spray droplet formation from delivery of the analyte solution, and thereby gets around difficulty resulting from alteration of the spray process by changes in solution chemistry. Cs^+ , Ba^{2+} , and La^{3+} coordination complexes were formed using 18-crown-6 (18c6) and triethylphosphate (TEP) as ligands (L), that had the general formula $[\text{M}^{n+}(\text{NO}_3^-)_{n-1}(\text{L})_m]^+$. Formation of singly charged cation complexes was preferred, with charge reduction at the metal site accomplished by attachment of nitrate. Using TEP as a model phosphoryl ligand, alkali metals coordinate with up to three ligands, with Cs^+ preferring fewer than Na^+ . Ba^{2+} and La^{3+} are formed as ion pair complexes $[\text{Ba}(\text{NO}_3)]^+$ and $[\text{La}(\text{NO}_3)_2]^+$, and both will coordinate with up to four TEP ligands. Using 18c6, Cs^+ forms a bis-ligand complex. In contrast, $[\text{Ba}(\text{NO}_3)]^+$ prefers a single 18c6 ligand, while La forms mainly $[\text{La}(\text{NO}_3)_2(18\text{c6})]^+$, for which DFT calculations suggested a structure in which the nitrate ligands occupy pseudo-axial positions on opposing sides of the crown. Lower abundances of bis-18c6 complexes were also formed together with doubly charged $[\text{La}(\text{NO}_3)(18\text{c6})_n]^{2+}$ complexes ($n = 2-4$). The results suggest an alternative strategy for probing metal speciation in solution that is less perturbed by the droplet formation and ionization mechanisms operating in conventional electrospray ionization mass spectrometry.

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1. Introduction

Desorption electrospray ionization mass spectrometry (DESI) has been utilized in many applications for measuring mass spectra of a wide variety of analytes [1–3]. The combination of analysis at atmospheric pressure with direct surface analysis is very appealing because sample preparation is limited, and consequently measurement can be extremely fast, with some applications reporting analysis conducted every few seconds [4,5]. The technique is especially effective for acquiring mass spectra of organics that have significant Bronsted acid–base character, or that exist as pre-formed ions in the condensed phase. Modifications of the DESI technique have extended its applicability to additional types of compounds by manipulating redox properties [6] or by incorporating anion attachment [7].

DESI may also be useful for measuring mass spectra of organometallic or inorganic species, as suggested by the fact conventional electrospray ionization (ESI) mass spectrometry has been

used for metal coordination complexes and inorganic species. Moulin and coworkers in particular used ESI to examine f-element speciation and concluded that the ESI mass spectra could be correlated with solution phase speciation [8–14]. In addition to these studies, ESI has been used widely to generate metal cation coordination complexes in the gas phase for reactivity [15–18] or ion spectroscopy measurements [19–22]. Thus the use of electrospray for measuring solution phase speciation of metal-containing molecules remains an intriguing possibility, however DESI has not been used as extensively for analysis of organometallic or inorganic species, the recent report by Miao and Chen being perhaps the salient example [23]. Using the related technique of extractive ESI, uranyl acetate complexes were measured with remarkable sensitivity by Luo et al. [24]. Considering the area of ambient mass spectrometry more generally, DART [3,25] has recently been used successfully for the analysis of a variety of organometallic compounds [26].

However ESI is not universally applicable to metal speciation problems because of constraints imposed by the need to reliably operate the ESI capillary, which can necessitate modification of the spray solution. Such modification will cause changes in the metal speciation in many cases, as a result of changing metal concentration, ionic strength, pH, and the nature of the solvent system.

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Changes to the ESI solvent system are driven by the need to reduce the surface tension of the ESI droplets and increase evaporation rates, which is normally accomplished by addition of organic solvents like methanol or acetonitrile. Furthermore ESI can induce redox reactions [27], which would also change metal speciation. Finally, direct analysis of solutions having higher concentrations of metal ions, higher ionic strengths, or extreme pH values may cause ESI capillary clogging or degradation. For these reasons, decoupling ESI spray droplet formation from the analyte solution might be highly desirable.

DESI represents a potentially attractive approach to overcoming these difficulties because it bombards sample surfaces with charged solvent droplets, an action that produces progeny droplets containing solutes originally present in or on the sample. Most DESI studies have concluded that the ESI spray first wets the sample surface, and that the solvent deposited then extracts analyte molecules from the surface. Impacts of subsequent ESI droplets from the ESI spray onto the wetted surface serve to “splash” progeny droplets into the gas phase [28,29]. Progeny droplets are charged and undergo evaporation and leading to Rayleigh discharge events [30,31] that produce solute ions in much the same way as do conventional ESI droplets. Conceptually, DESI would seem to be well suited for measuring mass spectra of metal-containing solutions. However the need to add organic modifiers to the spray solution may have other consequences, specifically that solubility of inorganic or organometallic species may be significantly reduced. This is important because solubility correlates strongly with DESI ion formation efficacy. The overwhelming choices for DESI spray are aqueous methanol solutions [32] with acetonitrile occasionally demonstrating better performance [33]; however alternative solvent systems in general are not as effective for ion generation.

The need to pre-wet the sample target might be obviated by utilizing a liquid target in which the analyte is already dissolved, as suggested by Mulligan et al. [7]. Subsequent to that study, three additional reports have appeared in which DESI targets have liquids extruded from capillary openings: this research has suggested a wide range of measurement possibilities including derivatization and oxidation using an electrochemical cell [23,34,35]. And the extractive ESI [36] study of the uranium coordination complexes [24] also support the idea that bombardment of a liquid target (a droplet in this study) would be effective for generating relatively unperturbed speciation data. In the present study, we report formation of coordination complexes from three different metals Cs^+ , Ba^{2+} , and La^{3+} , using a DESI experiment in which the analyte solutions were supplied by means of a target capillary oriented orthogonally to the path ESI droplets take as they traverse the space between the ESI capillary and the mass spectrometer sampling cone. The experiment eliminates the need for pre-wetting the surface and provides a means for analyzing solutions that would otherwise be problematic for standard ESI analysis as a result of plugging, or chemical alteration.

2. Experimental methods

2.1. Metal nitrate – ligand solutions

Solutions of Cs nitrate (Morton Thiokol Inc., Alfa, Danvers, MA), Ba nitrate (Fisher Scientific Company, Fair Lawn, NJ) and La nitrate pentahydrate (Aldrich, Milwaukee, WI) were mixed with methanolic solutions of 18-crown-6 or triethylphosphate (both ligands from Aldrich, Milwaukee, WI) such that the final solutions were 1.6 mM in metal and ligand. Solutions were presented to the ESI spray droplets via a target capillary at a rate of 1.7–2.8 $\mu\text{L}/\text{min}$ by a 500 μL syringe pumped with a Sage Instruments syringe pump.

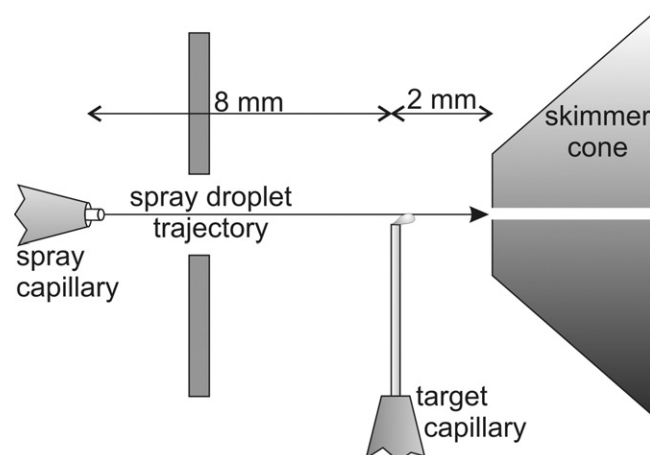


Fig. 1. Diagram of the capillary-DESI source. Spray droplets traverse the source approximately following the path indicated by the arrow, and intersect the sample droplet at the end of the target capillary.

2.2. DESI instrumentation

The instrument utilized in these experiments was a Thermo LCQ-DECA XP Max quadrupole ion trap electrospray ionization mass spectrometer modified to enable conduct of DESI. The ESI source was re-positioned from the conventional orthogonal orientation such that the ESI spray was co-axial with the aperture of the sampling cone of the ESI source (Fig. 1). Distance between the ESI spray capillary and the sampling cone aperture was approximately 10 mm. The ESI source was fitted with a gas flow meter that enabled measurement of the sheath gas flow. Sheath gas (N_2) was admitted together with the ESI flow in a co-axial arrangement such that upon exiting the ESI capillary, the ESI flow was jacketed by the sheath gas. Typical settings for the ESI source were $V_{\text{ESI}} = 2.6 \text{ kV}$, Sheath Gas Flow = $18 \text{ cm}^3/\text{min}$, and ESI flow = $5\text{--}10 \mu\text{L}/\text{min}$. The $V_{\text{sampling cone}} = 30 \text{ V}$, $V_{\text{tube lens offset}} = 25 \text{ V}$, and transfer capillary temperature = 125°C . The target capillary was positioned between the ESI spray capillary and the sampling cone, 8 mm from the spray capillary, and 2 mm from the sampling cone. The fused silica target capillary diameter is $190 \mu\text{m}$, o.d. and $100 \mu\text{m}$, i.d. Positioning was achieved by marking the tip of the target capillary with a red Sharpie marker, and monitoring the Rhodamine 6 G [37,38] ion sig-

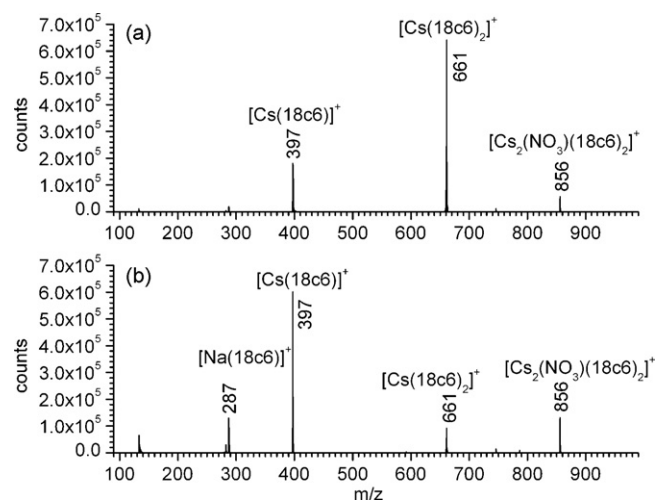


Fig. 2. DESI mass spectra of cesium nitrate/18-crown-6 solution. (a) Spectrum collected from a fully formed droplet and (b) spectrum collected from the surface of the droplet-depleted target capillary.

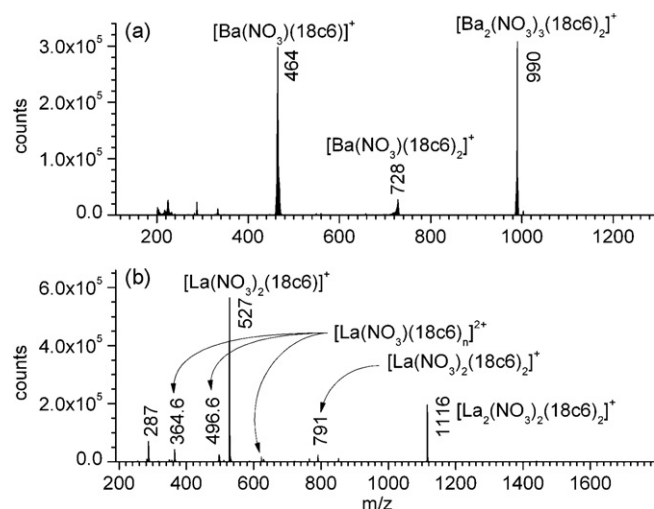


Fig. 3. DESI mass spectra of (a) barium nitrate/18-crown-6 solution, and (b) DESI mass spectra of lanthanum nitrate/18-crown-6 solution.

nal at m/z 443 as the target capillary and ESI spray capillary were adjusted.

2.3. Molecular structure calculations using density functional theory

DFT calculations were performed for several of the complexes in order to form an idea of the possible structures of the complexes. Calculations were performed using the P91 exchange functional executed with [30,39–42] in DMol³ suite [43,44]. The so-called density functional semicore pseudopotential (DSPP) was used [45], which accounts for scalar relativistic effects and includes 60 electrons in the uranium core (comparable to Stuttgart/Dresden small core ECPs), combined with the use of polarized numerical basis sets (DNP) for the active electrons. A fine (10^{-8}) energy convergence criterion was employed to ensure optimal geometries and repre-

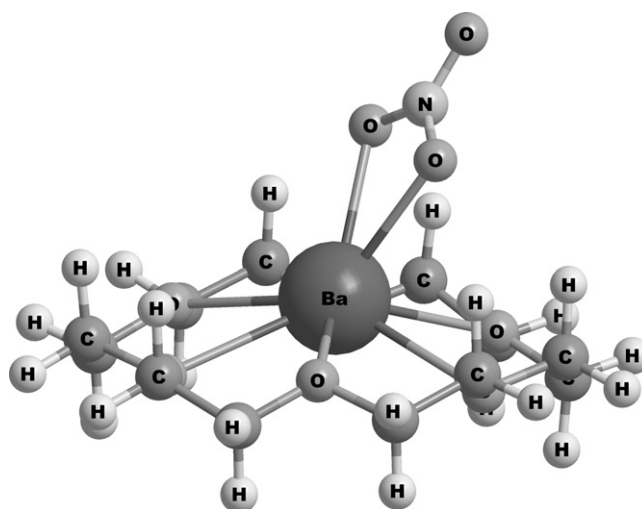


Fig. 4. Structure calculated for the $[\text{Ba}(\text{NO}_3)(18\text{c}6)]^+$ complex.

sentative vibrational frequencies. Calculations were initiated using the coordinates generated by Buhl and Wipff using DFT calculations [46].

3. Results and discussion

Initial studies focused on formation of 18-crown-6 coordination complexes because these are easy to generate in the condensed phase, are stable as gas phase species [47–51], and have a significant history regarding complex formation, stability and structure. Subsequent studies examined triethyl phosphate complexes in order to evaluate DESI for formation of coordination complexes where the ligands are bound in a monodentate fashion. TEP is also a good surrogate for tributyl phosphate, which is an important ligand in separations of metals in solutions produced from spent nuclear fuel recycling [52].

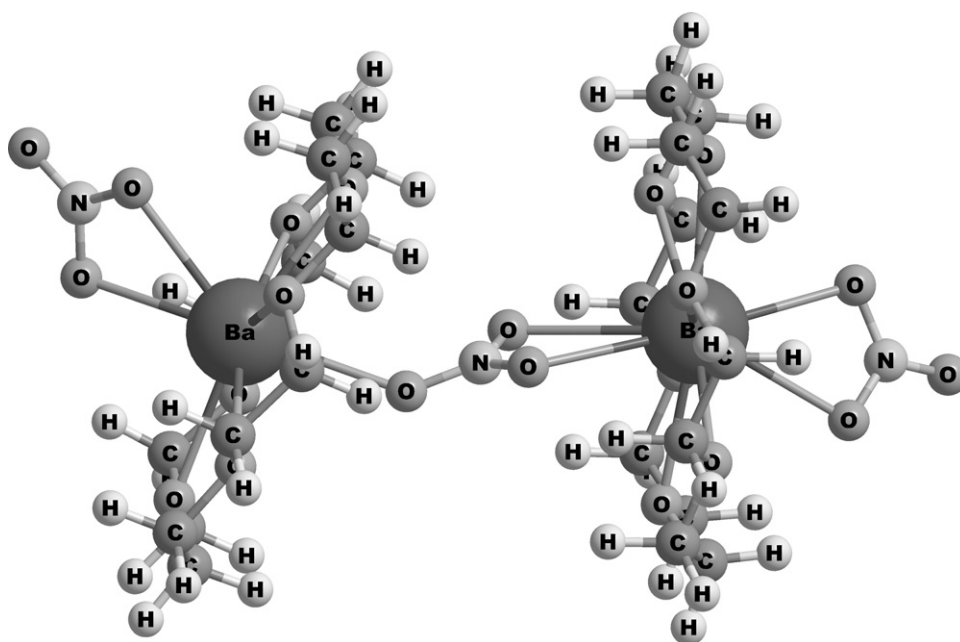


Fig. 5. Structure calculated for the $[\text{Ba}_2(\text{NO}_3)_3(18\text{c}6)_2]^+$ complex.

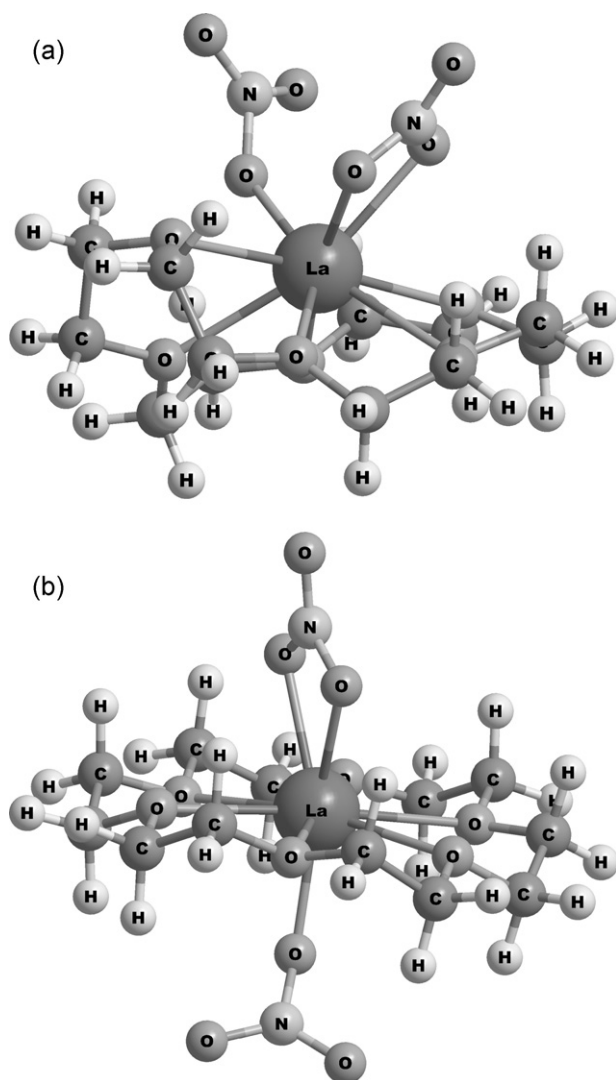


Fig. 6. Structures calculated for the $[\text{La}(\text{NO}_3)_2(18\text{c}6)]^+$ complex. Left: *cis*-nitrate conformer; Right: *trans*-nitrate conformer.

3.1. 18-Crown-6 coordination complexes

Analysis of 18c6 solutions amended with Cs^+ , Ba^{2+} and La^{3+} generated coordination complexes that were readily observed using DESI employing $\text{MeOH}:\text{H}_2\text{O}$ (95:5) as ESI spray droplets. The predominant species formed in the DESI analysis of the Cs^+ -18c6 solution were $[\text{Cs}(18\text{c}6)_2]^+$ at m/z 661 (Fig. 2). The intensity of this ion, and others in the experiment, oscillated in a rough sinusoidal fashion. The source of the oscillation is most likely due to variations in the shape of the target droplet, which periodically varied as a result of the wind caused by the high sheath gas flow. Another possible explanation is disruption of the target droplet caused by surface charge imparted by the bombarding ESI droplets. It is likely that a more stable target droplet can be generated using a syringe pump with finer control than was used in these experiments, or by altering the orientation of the target capillary. Chen [23] and Zhang [34] achieved a more stable signal by orienting their target capillary $\sim 30\text{--}50^\circ$ with respect to the ESI spray capillary axis. The present configuration has the target capillary oriented 90° to the spray capillary axis.

In addition to the $[\text{Cs}(18\text{c}6)_2]^+$, significant ions were seen at m/z 397 and 856 that corresponded to $[\text{Cs}(18\text{c}6)]^+$ and $[\text{Cs}_2(\text{NO}_3)(18\text{c}6)_2]^+$, respectively, the same ions that are seen in the

mass spectrum of the solution generated by direct ESI. Good qualitative correlation between the target capillary-DESI experiments and direct ESI was also seen for the other metal-ligand systems studied. Variations were seen in the relative abundances, and more detailed studies are planned to systematically examine these. Periodically, the target droplet was depleted (perhaps more accurately blown off the target capillary tip) by the combination of the sheath gas flow and the ESI spray. The scans that followed these events (Fig. 2b) showed a depletion of the $[\text{Cs}(18\text{c}6)_2]^+$ sandwich complex and an enhancement in the mono-crown complex at m/z 397, and in the coordination complex-salt cluster at m/z 856. These two ions are formed from liquid coating the surface of the capillary instead of from the liquid droplet, and suggest a depletion of 18c6 at this juncture in the experiment. This indicates that the envelope of species produced will be sensitive to changes in both the metal and ligand concentrations and their ratio. Such changes will entail changes in the solution speciation in many systems, and modifications seen in the mass spectra due to this versus the ion formation process constitute an intriguing question.

The suggestion that $[\text{Cs}(18\text{c}6)]^+$ and the coordination complex-salt cluster are generated from the droplet-depleted capillary surface is supported by the coincident observation of the $[\text{Na}(18\text{c}6)]^+$ complex at m/z 287. Na^+ would be present as a contaminant from the surface of the glass capillary, at a much lower concentration compared to that of the Cs^+ , however it forms a much stronger coordination complex in the gas phase [48,53]. This suggests that formation of the Na^+ complex may be more of a gas-phase process, since complexation constants in methanol and glycerol would slightly favor Cs^+ [51]. Therefore the experiment is favoring formation of the Na^+ complex when the target droplet is depleted. The coordination complex-salt cation $[\text{Cs}_2(\text{NO}_3)(18\text{c}6)_2]^+$ most likely has a crown- Cs^+ -crown- Cs^+ -nitrate structural arrangement, with one of the Cs^+ situated slightly above the plane of the 'bridging' 18c6. In this orientation, the cation is susceptible to ion pairing, which was suggested for Cs^+ -18c6 complexes by Dang [54].

Results for the Ba^{2+} -crown solution were similar except that the $[\text{Ba}(\text{NO}_3)]^+$ ion pair is complexed with 18c6, instead of the Cs^+ cation as in the previous case. The predominant ion formed is $[\text{Ba}(\text{NO}_3)(18\text{c}6)]^+$ instead of the bis-crown complex (Fig. 3a), which probably reflects difficulty in formation of the latter as a result of crowding caused by the nitrate and the fact that the relatively small Ba^{2+} cation fits within the crown cavity. This explanation is supported by the DFT-calculated structure (Fig. 4), which shows the Ba^{2+} cation slightly out of the plane of the 18-crown-6 ligand. A bis-crown complex $[\text{Ba}(\text{NO}_3)(18\text{c}6)_2]^+$ is in fact formed but it is at significantly lower abundance. The most abundant bis-crown species formed is a coordination complex-salt cluster with the composition $[\text{Ba}_2(\text{NO}_3)_3(18\text{c}6)_2]^+$ that becomes more intense when the target droplet is depleted from the capillary tip. Its composition suggests a structure in which two $[\text{Ba}(\text{NO}_3)(18\text{c}6)]^+$ complexes are held together by a bridging nitrate, as suggested by DFT calculations (Fig. 5), and by recent IRMPD measurements of metal nitrate dimer anions [55]. Calculations for the $[\text{Ba}_2(\text{NO}_3)_3(18\text{c}6)_2]^+$ complex indicated that multiple conformers were possible that varied structurally in terms of denticity and location of the pendant nitrate groups, however the positions of the Ba atoms, the bridging nitrate and the 18c6 ligands were the same in all structures.

Analysis of the La^{3+} crown solutions generated the charge reduced $[\text{La}(\text{NO}_3)_2(18\text{c}6)]^+$ complex (m/z 527, Fig. 3b), which has an abundance significantly greater than that of the corresponding bis-crown complex at m/z 791. This is likely due to crowding around the metal center, preventing formation of abundant bis-crown complex, an idea that is supported by the DFT calculations, which showed two competitive structures. Both structures have the nitrate ligands bound to the La^{3+} metal center, one monodentate, and one bidentate. Normally narrow-bite bidentate ligands like

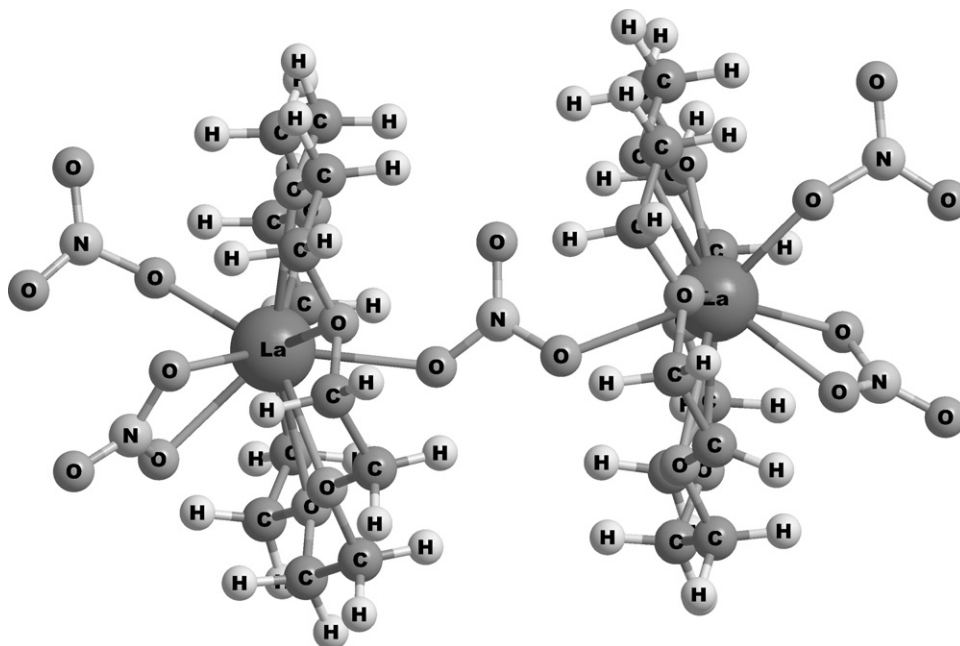


Fig. 7. Structure calculated for the $[\text{La}_2(\text{NO}_3)_5(18\text{c}6)_2]^+$ complex.

nitrate prefer to be bound in a bidentate fashion to metal cations, but complexes can adopt a mixed-denticity conformation when the metal center is crowded, as was recently shown for acetate [56]. When the two nitrates are located on the side of the metal (Fig. 6a), they serve to slightly repel the crown, and the metal appears a bit above the ring. On the other hand, when the nitrate ligands are on opposite sides of the crown, the La^{3+} is more centrally situated in the crown, slightly displaced from the center toward the bidentate nitrate (Fig. 6b). Crowding on the opposite side seems to limit nitrate to monodentate coordination. The coordination complex-salt cluster $[\text{La}_2(\text{NO}_3)_5(18\text{c}6)_2]^+$ was also produced, and DFT calculations suggest a double-decker sandwich structure similar to that of the analogous barium coordination complex-salt cluster. In this complex, two complexes $\text{cis-}[\text{La}(\text{NO}_3)_2(18\text{c}6)]^+$ molecules (analogous to those in Fig. 6a) are tethered by the a single nitrate ligand in which reaches into the center of the crown to coordinate the metal centers (Fig. 7).

3.2. Triethyl phosphate coordination complexes

The DESI analyses of the Cs^+ -TEP solutions produced abundant ions corresponding to $[\text{Cs}(\text{TEP})_2]^+$ and $[\text{Na}(\text{TEP})_3]^+$ at m/z 497 and 569 respectively, and little else (Fig. 8a). The fact that Na^+ coordinated to three TEP ligands but Cs^+ to only two is rationalized on the basis of the stronger Lewis acidity of Na^+ compared to Cs^+ . These two ions were also predominant in the spectrum of the capillary surface collected when the droplet on the tip was depleted, although $[\text{Cs}]^+$, $[\text{Cs}(\text{TEP})]^+$, and $[\text{Na}(\text{TEP})_2]^+$ were also formed (Fig. 8b). The lower coordinated species may indicate depletion of TEP from the surfaces, or a more energetic DESI mechanism operating on the surface of the liquid-depleted capillary surface. In addition, two series of salt clusters were formed corresponding to $[\text{Cs}(\text{CsNO}_3)_n]^+$ and $[\text{Na}(\text{CsNO}_3)_m]^+$. These ions also suggest depletion of TEP from the target surface.

The Ba-TEP solution provided complexes with much more extensive coordination. Abundant ions with the composition $[\text{Ba}(\text{NO}_3)(\text{TEP})_n]^+$ were generated with $n = 2, 3, 4$ (Fig. 9a). Assuming the nitrate ligand is bound in a bidentate fashion, the $n = 4$ complex is formally hexa-coordinated which is probably close to the

extent of coordination in solution. The most abundant coordination complex is the $n = 3$ version, indicating that either it is more stable or that dissociation of the more weakly bound $n = 4$ complex is occurring. A series of doubly charged complexes having the composition $[\text{Ba}(\text{TEP})_n]^{2+}$ are also formed where $n = 3, 4, 5$. In fact a hexa-coordinated version is also generated, albeit at very low abundance. In the $2+$ cations, the $n = 4$ complex is most abundant. The $[\text{Na}(\text{TEP})_{n=2,3}]^+$ adducts are also formed at m/z 389 and 569, respectively.

Extensive coordination was also seen in the analysis of the La^{3+} -TEP solutions (Fig. 9b). The most abundant complexes formed had the general composition $[\text{La}(\text{NO}_3)_2(\text{TEP})_n]^+$ where $n = 2, 3, 4$, with the $n = 4$ complex being most abundant. This complex presumably assumes a pseudo-octahedral geometry, which is more stable compared with Ba^{2+} as a result of the higher charge at the metal center in the present case. The other complexes seen were cluster ions consisting of the above-mentioned bis-nitrate coordination complexes

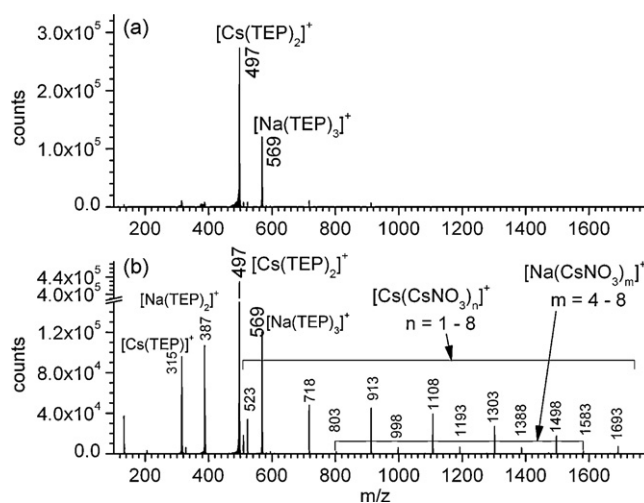


Fig. 8. DESI mass spectra of cesium nitrate/triethyl phosphate solution. (a) Spectrum collected from a fully formed droplet; (b) spectrum collected from the surface of the droplet-depleted target capillary.

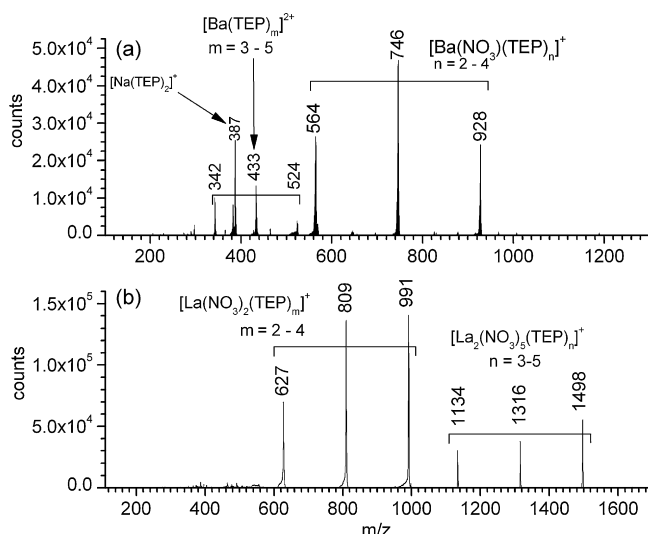


Fig. 9. (a) DESI mass spectra of barium nitrate/triethyl phosphate solution and (b) DESI mass spectra of lanthanum nitrate/triethyl phosphate solution.

and $\text{La}(\text{NO}_3)_3$. These coordination complex-salt complexes become more abundant as the target droplet is depleted and are quite stable in the gas phase as indicated by their significant abundances.

4. Conclusions

Coordination complexes of metal cations in the 1+, 2+ and 3+ charge states were formed from progeny droplets of analyte solutions using DESI. The analyte solutions were introduced as target droplets via a capillary, and were sampled by bombarding them with ESI spray droplets. This approach eliminated the need for pre-wetting the sample surface, and provided longer-lived, more stable ion signal from a relatively small volume of sample solution. We expect that separation of the sample introduction from the ESI droplet generation will lead to greater versatility in use of ESI for analysis of coordination complexes and may also reduce the quantities needed for analysis.

The changes in the spectra with changing target droplet quantity reflects alterations in the concentrations of the metal, nitrate, and ligand, which suggests that DESI of metal coordination complexes in target droplets will be quite sensitive to changes in solution phase meta speciation. Utilization of any ESI-based approach for measuring solution phase speciation will still require judicious correlation of gas-phase ions with solution phase counterparts, but the DESI strategy may cause fewer perturbations to the solution chemistry during the course of analytical measurement.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ijms.2010.07.028](https://doi.org/10.1016/j.ijms.2010.07.028).

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