Atomistic Description of Thiostannate-Capped CdSe Nanocrystals: Retention of Four-Coordinate SnS4 Motif and Preservation of Cd-Rich Stoichiometry

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ABSTRACT: Colloidal semiconductor nanocrystals (NCs) are widely studied as building blocks for novel solid-state materials. Inorganic surface functionalization, used to displace native organic capping ligands from NC surfaces, has been a major enabler of electronic solid-state devices based on colloidal NCs. At the same time, very little is known about the atomistic details of the organic-to-inorganic ligand exchange and binding motifs at the NC surface, severely limiting further progress in designing all-inorganic NCs and NC solids. Taking thiostannates (K₄SnS₄, K₆Sn₂S₇) as typical examples of chalcogenidometallate ligands and oleate-capped CdSe NCs as a model NC system, in this study we address these questions through the combined application of solution ¹H NMR spectroscopy, solution and solid-state ¹¹⁹Sn NMR spectroscopy, far-infrared and X-ray absorption spectroscopies, elemental analysis, and by DFT modeling. We show that through the X-type oleate-to-thiostannate ligand exchange, CdSe NCs retain their Cd-rich stoichiometry, with a stoichiometric CdSe core and surface Cd adatoms serving as binding sites for terminal S atoms of the thiostannates ligands, leading to all-inorganic (CdSe)₄₆[Ca₄(C₆H₄S₂)₅(J₉₆₋₂m)Sn₆]shell(y) (taking Sn₂S₄⁻²⁻ as a ligand as an example). Thiostannates Sn₄S₆⁻⁴⁻ and Sn₂S₇²⁻ retain (distorted) tetrahedral SnS₄ geometry upon binding to NC surface. At the same time, experiments and simulations point to lower stability of Sn₂S₄⁻²⁻ (and SnS₂⁻²⁻) in most solvents and its lower adaptability to the NC surface caused by rigid Sn₃S₂ rings.

INTRODUCTION

In a nonvacuum environment, metal ions and atoms do not exist in a completely isolable form but in a solvated or ligand-coordinated state. Similarly, inorganic nanoparticles or nanocrystals (NCs, crystalline nanoparticles) require a shell of capping molecules, also known as ligands, to ensure their chemical and colloidal stability. Proper selection of organic surface capping ligands, such as long-chain organic molecules with a metal binding functional headgroup, has enabled the development of monodisperse colloidal NCs since the early 1990s. Capping ligands also largely dictate the individual physical and chemical properties of NCs, as well as the collective electronic properties in the densely packed NC solids. Owing to the highly insulating character of commonly used long-chain capping ligands, novel chemistries based on short-chain and conductive ligands, organic or inorganic, were required for demonstration of NC-based solar cells, light-emitting diodes, photodetectors, thermoelectrics, transistors, and integrated electronic circuits. In this regard, colloidal, inorganic NCs are readily obtained by solution-phase exchange of organic ligands with common inorganic anions such as metal chalcogenide complexes (MCCs, also known as chalcogenidometallates), metal-free ions (S²⁻, HS⁻, Se²⁻, OH⁻, SCN⁻, Γ, etc.), oxo- and polyoxometallates, and metal halide complexes (halometallates). In addition, a powerful and complementary methodology is the formation of cationic and naked, but colloidally stable, NCs upon controlled stripping of the strongly bound native organic ligands with the simultaneous coordination of

Received: October 24, 2014
Published: January 17, 2015

DOI: 10.1021/ja510862c
J. Am. Chem. Soc. 2015, 137, 1862−1874
metal cations on the NC surface with weakly nucleophilic ligands.\textsuperscript{13}

Overall, the inorganic surface functionalization of semiconductor NCs has been the major enabler of NC-based electronic and optoelectronic devices in the last 5 years. Thus far, particularly efficient inorganic ligands, in terms of the speed of ligand-exchange (LE) reactions, affinity to and compatibility with various NCs, have been MCCs due to the high affinity of terminal chalcogen atoms to undercoordinated metal atoms on the NC surface. In highly polar solvents, such as water or methylformamide (MFA), these NCs are electrostatically stabilized due to adsorption of anionic ligands onto the NC surface and electrostatic dissociation of the counterions. Not only are the integrity and size-tunable optical properties of NCs fully preserved, but also the charge transport in the solids comprising such all-inorganic NCs is greatly improved, and electronic mobilities of $5-35$ cm$^2$ V$^{-1}$ s$^{-1}$ are now routinely obtained.\textsuperscript{7,8,14} Additionally, these all-inorganic colloids of semiconductor NCs have enabled photodetectors with detectivities of up to $10^{13}$ Jones,\textsuperscript{15} improved electrocatalytic properties of CdSe NCs (hydrogen evolution),\textsuperscript{16} and enhanced electronic transport in NC-based Li-ion batteries.\textsuperscript{17} Inorganic-capped NCs have also served as fully inorganic inks for solution-deposited CuInS$_2$, Cu(In$_{1−x}$Ga$_x$)$_2$Se$_2$, Cu$_2$ZnSn(S,Se)$_4$ (CZTS), and PbS phases as thin-film absorbers for photovoltaics,\textsuperscript{18} ionically conductive composites of Ag$_2$S NCs embedded into a GeS$_2$ matrix\textsuperscript{19} or Sb$_2$Te$_3$-based nano-composites for thermoelectrics;\textsuperscript{6a,d} for integration of highly transparent matrices;\textsuperscript{20} and for design of NC-in-glass windows and solar cells.\textsuperscript{18,21} Solution-phase or solid-state preparation of NCs with either partial or full surface coverage by halide ions has also been reported by several groups.\textsuperscript{22} Halide ion ligands provide improved electronic passivation of semiconductor NCs, high oxidative stability, and power conversion efficiencies of up to 8.6% in PbS NC-based photovoltaics.\textsuperscript{13}

The aforementioned superior electrical characteristics of the solids composed of inorganically capped NCs have stimulated this study. Here, we aim to better understand the underlying chemistry of the organic-to-inorganic LE and to unveil the mechanism of the LE reactions with MCCs and other inorganic ligands hinders the rational design of new materials and our ability to further tune their electronic and optical characteristics.

An atomically precise image of the NC surface is not yet available, nor are the NCs surfaces atomically precise and static. Faceting, surface reconstructions, and the dynamic nature of these phenomena complicate the task.\textsuperscript{24} Furthermore, the techniques that are used to determine the atomic coordinates in crystalline inorganic materials are inherently blind to the surfaces (e.g., X-ray or electron diffraction). Therefore, building the atomistic picture of ligand-capped NCs requires a powerful combination of modern experimental tools and atomistic modeling. In this study, several experimental techniques (nuclear magnetic resonance, X-ray absorption, Raman and far-infrared spectroscopies, and elemental analysis) were combined with atomistic simulations at density functional theory level (DFT) in order to understand the LE reactions involving carboxylate-capped CdSe NCs and thiostannate ligands (Sn$_2$S$_4$$^{-6}$, Sn$_2$S$_6$$^{-6}$, Sn$_2$S$_7$$^{-6}$). Our study has concentrated on these air-stable, sulfide-based ligands to minimize the effects caused by the degradation of the ligands. The majority of results concern Sn−S MCCs, due to high suitability of the $^{119}$Sn isotope for solution and solid-state NMR studies and because we also wanted to shed light onto the solution-based equilibria between several Sn−S ligands. In particular, $^{119}$Sn solution NMR spectroscopy allowed us to identify the ligands and their equilibria in various solvents, while $^{119}$Sn solid-state NMR provides insight into their surface-bound state. CdSe NCs serve as a convenient model NC system due to extensive prior work on their synthesis, surface chemistry, and photophysics. In particular, carboxylate-capped CdSe NCs were previously shown to consist of a stoichiometric CdSe core covered with a layer of Cd(O$_2$CR)$_2$.\textsuperscript{21−h} Thus, an important question specific to LE with MCCs is whether carboxylate is replaced as an anionic moiety (X-type exchange) or is detached as molecular complex Cd(O$_2$CR)$_2$.\textsuperscript{3}

The key findings of this study are as follows. First, we identify the presence of Sn$_2$S$_4$$^{-6}$ ions and their role as a predominant form of thiostannate in N-methylformamide (MFA). Second, the LE reaction with all studied thiostannate and other MCC ligands retains the Cd-rich stoichiometry of CdSe NC surface, with a purely X-type displacement of the initial oleate ligand. This study also compares relative binding strengths of MCC ligands and simple S$^{-2}$ ions, including several MCCs that had not been used as capping ligands before (GeS$_2$$^{-4}$, SbS$_3$$^{-3}$, and SnS$_2$$^{-5}$). Thiostannate ligands SnS$_2$$^{-4}$, Sn$_2$S$_4$$^{-4}$, and Sn$_2$S$_6$$^{-6}$ convert into each other upon dissolution in various solvents, pointing to the importance of solution equilibria. Thiostannate ions largely maintain a tetrahedral SnS$_4$ motif after the binding to the NC surface. The multidentate nature of MCCs allows a broad spectrum of binding modes. Atomistic simulations support this observation and suggest polydentate binding of Sn$_2$S$_4$$^{-4}$ and Sn$_2$S$_6$$^{-6}$ ions as most plausible forms of Sn−S adsorbates on CdSe NC surfaces. Finally, atomistic simulations also corroborate previously reported optical and charge transport measurements, showing the key role played by the ligand in quenching the photoluminescence and for stable n-type doping. Knowledge obtained for CdSe−thiostannate system may shed light onto behavior of other technologically important NC−MCC systems.
**EXPERIMENTAL SECTION**

**Materials.** Selenium dioxide (SeO₂, 99.9+%, Strem), oleic acid (OA, 90%, Aldrich), 1-octadecene (ODE, 90%, Aldrich), methanol (Aldrich, 98%), cadmium nitrate tetrahydrate (Cd(NO₃)₂ × 4H₂O, 99.99%, Aldrich), CdO (99.99+, Sigma-Aldrich), myristic acid (MA, 99%, Aldrich), sodium hydroxide (NaOH, Aldrich), hexane (~95% Sigma-Aldrich), ethanol (99.8%, Fluka), toluene (99%, Fischer), formamide (FA, 99.5+%, Aldrich), acetonitrile (MeCN, 99.9%, Sigma-Aldrich), N-methyl formamide (MFA, 99%, Aldrich), dimethylformamide (DMF, 99.8%, Sigma-Aldrich), hydrazine (98%, anhydrous, Aldrich), potassium sulfamate (DMF, 99.8%, Sigma-Aldrich), myristic acid (MA, 99%, Aldrich), potassium sulimate (K₂S, 99.5%, Strem), ammonium sulfide (48% solution in water, Aldrich), antimony(III) sulfide (Sb₂S₃, 99.99%, Aldrich), germanium(II) sulfide (GeS₂, 99.99%, Aldrich), sulfur (99.998%, Sigma-Aldrich), As₂S₅ (99.99%, Sigma-Aldrich), K₄SnS₄, N₄Sn2S₆, and Sn(CH₃)₄. The latter, sealed in a capillary, was also used as an internal standard for accurate normalization of all spectra enabling the quantification of the amounts of absorbed thioantannates. Liquid state ¹¹⁹Sn NMR spectra were recorded using Bruker 250 and 300 MHz spectrometers. Spectra were obtained at room temperature without deuterium locking of the main magnetic field. The pulse width was set at 10 µs, and the relaxation delay was 0.5 s. The number of scans used for experiments was 4000. The NMR samples were prepared in 5 mm tube in glovebox/air using high purity solvents (C ~ 0.05 M). All ¹¹⁹Sn chemical shifts were referenced to Sn(CH₃)₄. The latter, sealed in a capillary, was also used as an internal standard for accurate normalization of all spectra enabling the quantification of the amounts of absorbed thioantannates. Liquid state ¹H NMR spectra were recorded using Bruker 250 and 300 MHz spectrometers. Spectra were obtained at room temperature with locking of the main magnetic field. The pulse width was set at 11.5 µs, and the relaxation delay was 2 s. The number of scans used for experiments was 32. The NMR samples were prepared in 5 mm tubes using C₆D₆ or DMSO-d₆ as solvents. All spectra were referenced to tetramethylsilane. Solid-state CPMG spectra are shown in their echo reconstructed form. They were obtained by summing the whole echoes of the FIDs in the time domain, followed by Fourier transform and application of a first order phase correction. CPMG spectra are shown in their echo reconstructed form. They were obtained by summing the whole echoes of the FIDs in the time domain, followed by Fourier transform and application of a first order phase correction.

**Synthesis of CdSe NCs.** CdSe NCs were synthesized following the established procedure.²⁵ For preparing the cadmium myristate precursor, cadmium nitrate solution in MeOH (5 mmol/50 mL) was added dropwise into Na myristate solution (obtained by dissolving 15 mg of Na myristate in 0.5 mL of methanol). The resulting white precipitate was washed with methanol three times, and then dried at 70 °C. In a typical synthesis of CdSe NCs, cadmium myristate (1.132 g) and SeO₂ (0.222 g) were mixed with dried ODE (128 mL) in a 500 mL three-neck flask and heated to 240 °C at a rate of 20 °C/min (the solution has dried for 30 min at 100 °C). After 3 min at 240 °C, 2 mL of dried oleic acid was injected, and the solution was cooled to ca. 140 °C, followed by the removal of ODE via vacuum distillation. After 30 min, when ca. 20 mL of ODE was left in the flask, the solution was cooled down to RT and CdSe NCs were washed 3 times with hexane and ethanol. After this purification step, CdSe NCs were redispersed in hexane and used for further experiments. For comparison, we also replaced Cd myristate by Cd oleate and obtained identical results in terms of particle size and chemical composition. The cadmium oleate precursor was prepared by mixing 0.25 g of CdO (2 mmol) and 6 mL of OA in 128 mL of ODE, heating to 240 °C until the mixture become colorless, followed by cooling to 100 °C, and drying under vacuum for 1 h.

**Synthesis of Inorganic Ligands.** SnS₅ was prepared according to ref 9a. (N₂H₅)₄Sn₂S₆ was obtained by dissolving elemental tin (118.7 mg, 1 mmol) in 3 mL of 1 M S/N₂H₄ solution and 1 mL of N₂H₄ (48% solution in water, Aldrich). The mixture was vigorously stirred for 30 min until the hexane phase became colorless and all NCs migrated into polar solvent. The hexane layer was carefully removed, and the polar phase was rinsed 3 times with pure hexane, and then filtered through a 0.2-μm filter. CdSe NCs were precipitated with a minimal amount of MeCN. For more efficient precipitation, MeCN can be mixed with a small amount of toluene (e.g., 10:1 ratio). For elemental analysis, NCs were dispersed in MFA and precipitated once again with MeCN. Analogous ligand exchange reactions were conducted with other solvents: H₂O (K₂SnS₄) and N₂H₄ (for the (N₂H₅)₄Sn₂S₆ ligand). In the case of N₂H₄, all steps were carried out in a glovebox. Ligand removal with Et₃OBF₄ was carried out according to known procedure.¹³b and stabilization with (NH₄)SCN was performed according to the established procedure.¹⁰d

**Nuclear Magnetic Resonance (NMR) Spectroscopy.** Liquid state ¹¹⁹Sn NMR spectra were recorded at 186.5 MHz using a Bruker 500 MHz DRX spectrometer. Spectra were obtained at room temperature without deuterium locking of the main magnetic field. The pulse width was set at 10 µs, and the relaxation delay was 0.5 s. The number of scans used for experiments was 4000. The NMR samples were prepared in 5 mm tube in glovebox/air using high purity solvents (C ~ 0.05 M). All ¹¹⁹Sn chemical shifts were referenced to Sn(CH₃)₄. The latter, sealed in a capillary, was also used as an internal standard for accurate normalization of all spectra enabling the quantification of the amounts of absorbed thioantannates. Liquid state ¹H NMR spectra were recorded using Bruker 250 and 300 MHz spectrometers. Spectra were obtained at room temperature with locking of the main magnetic field. The pulse width was set at 11.5 µs, and the relaxation delay was 2 s. The number of scans used for experiments was 32. The NMR samples were prepared in 5 mm tubes using C₆D₆ or DMSO-d₆ as solvents. All spectra were referenced to tetramethylsilane. Solid-state CPMG spectra are shown in their echo reconstructed form. They were obtained by summing the whole echoes of the FIDs in the time domain, followed by Fourier transform and application of a first order phase correction. CPMG spectra are shown in their echo reconstructed form. They were obtained by summing the whole echoes of the FIDs in the time domain, followed by Fourier transform and application of a first order phase correction.

**X-ray Absorption Spectroscopy.** This was carried out at the X10DA (Super XAS) beamline at the Swiss Light Source, Villigen, Switzerland, which operated with a ring current of approximately 400 mA in top-up mode. The polychromatic radiation from a superbend magnet, with a magnetic field of 2.9 T and critical energy of 11.9 keV, was monochromatized using a channel cut Si(311) crystal monochromator. Spectra were collected on pressed pellets optimized to 1 absorption length at the Sn K-edge (29 200.1 eV) in transmission mode. For absolute energy calibration, the absorption of a Sn foil was measured simultaneously between the second ionization chamber and third ionization chamber. All 30 cm long ionization chambers were filled with Ar. Spectra were normalized using Athena,²⁷ and EXAFS spectra were fitted using FEFF²⁸ interface Artemis. Twenty-four transformation of the background-subtracted EXAFS spectra was carried out in a k-range from 3 to 12 Å⁻¹, with a δk of 1. Fitting of the EXAFS data was realized using scattering path obtained from theoretical standards for Na₃SnS₄, Na₂SnS₄, Na₂SnS₃, and Sn₃S₄. The Sn–Sn coordination shell was fitted first, in a range from 1 to 2.6 Å, without constraining the fitting parameters (amplitude reduced factor σ₀, energy shift E₀, bond distances Δr, Debye–Waller factor σ²). The amplitude reduction factors were calibrated first for the free ligands (coordination number fixed at 4). Then, for the second shell, CN, E₀, and Δr were fixed at their best value, and the fit range was extended to 4 Å in order to determine the parameters for the second shell. Cd atoms were introduced into the existing paths by replacing the Na atoms. The scattering path of the second shell Sn–Cd was added with its own set of σ₀, Δr. Fitting of both shells provided a single energy shift and Debye–Waller factor valid for both shells, as well as amplitude reduced factor and bond distances for each shell.
Inductively Coupled Plasma Optical Emission Spectrometry. (ICP-OES) was carried out using commercial ICP-OES spectrometer (Spectro Arcos, SPECTRO Analytical Instruments GmbH, Kleve, Germany). Experimental conditions for all measurements were the same and are summarized in Supporting Information Table S1. Every sample was measured 3 or 5 times, and the average result is reported. Samples were prepared by microwave-assisted digestion in a closed container of the dried materials in a mixture of 3 mL of HNO₃, 3 mL of HCl, and 0.5 mL of H₂O₂. Mn was used to control the digestion recovery. Element quantification was carried out by external calibration.

Other Characterization. UV-vis absorption spectra for colloidal solutions were collected using a Jasco V670 spectrophotometer in transmission mode. Attenuated total reflectance-Fourier-transform infrared spectra (ATR-FTIR, in mid-IR and far-IR spectral regions) were recorded using Thermo Scientific Nicolet 6700 FT-IR spectrometer. Powdered samples were deposited onto Si substrates, turned upside down, and pressed against the diamond ATR crystal. For quantifying the removal of initial organic ligands, FTIR spectra were calibrated with internal standard KCN added to the sample (CN stretches are well separated from CH). Liquid samples were measured by placing a small droplet directly onto ATR crystal. Raman spectra were recorded with a Renishaw inVia Raman microscope. Samples were run with a 785 nm laser, with 64 × 2 s scans at 2 mW power.

Calculation of the Ligand Surface Coverage. The wavelength of the 1S₅/₂−2S₁/₂ transition maximum was used to determine the mean NC diameter. From the NC size, the number of CdSe units per crystals was calculated, assuming a spherical shape and the molar volume of bulk cadmium selenide. The concentration of the NCs, the ratio of ligands per nanocrystal, and the ligand surface density assuming spherical shape were calculated from the number of CdSe units per NCs, the molar concentration of CdSe, and ligands in solutions.

DFT Simulations. Calculations were carried out using the Quickstep module of the CP2K program suite. CP2K is freely available from http://www.cp2k.org/ and utilizes a dual basis of localized Gaussians and plane waves. The plane wave cutoff was 300 Ry, appropriate for the Goedecker–Teter–Hutter pseudopotentials that we employed, and the localized basis set of double-ζ plus polarization (DZVP) quality optimized to reduce the basis set superposition errors. Calculations were performed using the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional. Simulations were performed with nonperiodic boundary conditions in a 50 × 50 × 50 Å³ unit cell for 2.5 and 3 nm NC sizes. The NC core was carved out of bulk zinc blende CdSe. All single-bonded atoms were discarded, resulting in a faceted cuboctahedron shape. Cd-rich (100) facets with two dangling bonds per atom were passivated with ligands, whereas (111) facets with one dangling bond per atom were left intact and facet passivation was achieved by adding surface vacancies, as described previously. Chlorine was used for simplicity as a ligand electronically similar to oleate, except for calculation of oleate binding energy where it was taken explicitly. Care was taken to select the stoichiometry that preserves the charge neutrality of the dot, necessary to position the Fermi level in the midgap. In case of MCC adsorption, the ligand was added together with potassium counterions in the amount required to maintain the charge neutrality. All geometries were initially propagated through a molecular dynamics simulation of at least 1 ps and then relaxed until forces on atoms reduced below 40 meV/Å. Optimized geometries and full input files for simulations are provided in Supporting Information.

RESULTS AND DISCUSSION

Carboxylate–Metal Chalcogenide Complex Ligand Exchange. It is known that carboxylate ligands can be fully exchanged with MCC ligands, but details of this process are lacking. As shown by Owen et al., carbohydrate (oleate, myristate, etc.) can be removed as an anionic (X-type) RCO₂⁻ moiety or as a Cd(O₂CR)₂ molecule, depending upon the type of incoming ligand (anionic or neutral molecule). Furthermore, the atomic structure of inorganic MCC ligands in solution at the NC surface and their bonding motifs at the NC surface are poorly understood. We have chosen ~3.5 nm carboxylate-terminated zinc blende (zb) CdSe NCs as a model system for studying the LE reactions with MCC ligands. According to the detailed surface chemistry study by Owen and co-workers, the structure of carboxylate-capped CdSe NCs can be represented with the formula (CdSe)ₙ(Cd(O₂CR)₂)ₓ, where carboxylate surface coverage is 1.5–4 carboxylates/nm², depending upon the purification procedure and nature and quantity of solvents and surfactants used. Hence the overall NC stoichiometry is Cd-rich. No other ligands such as neutral molecules of phosphines or amines (L-type ligands) were involved in the preparation of such CdSe NCs, thus providing a well-defined and simple starting material for LE reactions. We began our study by addressing the initial key question about the actual mass-balance during the LE reaction with MCCs.

Fate of Oleate and the Mass Balance of the LE Reaction. The organic-to-inorganic LE was carried out via a phase-transfer reaction (Scheme 1). The initially carboxylate capped CdSe NCs migrate from the nonpolar phase (hexane) to a polar phase (MFA or N₂H₄) upon LE due to the change from a hydrophobic surface functionality (with steric stabilization) to a hydrophilic surface functionality (electrostatic stabilization). Note that this is the first time that several of these MCCs have been used as capping ligands (K₅SnSe₅, K₅GeSe₅, K₅SbSe₅). For comparison, LE reactions were also performed with a metal-free S²⁻ ligand and with Et₃OBF₄ (Meerwein’s salt). To the best of our knowledge, MFA has the highest known static dielectric constant (ε = 176) for solvents; therefore, MFA enables the efficient dissociation of cations, leading to stable colloidal solutions. In order to remove any unbound ligands following LE, the NCs are precipitated from the MFA phase by adding a minimal amount of nonsolvent (usually MeCN). The nonsolvent and its quantity are chosen such that the free ligands remain soluble in the solvent/nonsolvent mixture. The LE reaction mass-balance was estimated by quantitative elemental analysis (ICP-OES, Supporting Information Tables S1 and S2), ATR-FTIR, and H and Sn NMR spectroscopies of all phases: initial oleate-capped NCs, precipitated thiooleate-capped NCs, and hexane and MFA phases collected after phase-separation,
NCs capped with the initial oleate ligand and capped with various MCCs, sulfide ions, or weakly bound BF$_4^−$ ions. The excitonic absorption peak of the MCC and sulfide capped CdSe NCs exhibit only small red shifts (1−11 nm) and a blue shift of −11 nm, respectively, in comparison to the excitonic absorption peak of the initial oleate capped NCs. This suggests that there are only small differences in the radius of the particles following LE with these inorganic ligands. On the other hand, LE with Et$_3$OBF$_4$ leads to a noticeable absorption peak of the initial oleate capped NCs. This suggests that there are only small differences in the radius of the particles following LE with these inorganic ligands. On the other hand, LE with Et$_3$OBF$_4$ leads to a noticeable absorption peak of the initial oleate capped NCs. This suggests that there are only small differences in the radius of the particles following LE with these inorganic ligands.

Figure 1. Absorption spectra of ~3.5 nm CdSe NCs capped with initial oleate ligands and, after ligand exchange, with various chalcogenidometallate complexes, sulfide ions, or weakly bound BF$_4^−$ ions.

ICP-OES elemental analysis indicates that all MCC capped NCs retain a Cd-rich stoichiometry, with Cd:Se ratios of 1.15−1.30 (Supporting Information Table S2). Increased Cd stoichiometries may be caused by partial anion exchange of Se-to-S at the NC surface. ICP-OES analysis of the hexane phase following LE shows that less than 1% of Cd remained in the hexane phase. Upon precipitation and separation of NCs, less than 0.1% of Cd can be found in MFA. Consequently, no more than 5% of the Cd from the initial Cd(O$_2$CR)$_2$ ligand shell is detached from the NC surface during the LE reactions with MCCs and sulfide as ligands. Somewhat contrary to the common notion that long-chain organic ligands should remain in the nonpolar phase, $^3$H solution NMR spectra indicate no residual oleate-anions in hexane phase after LE, but rather large amount of potassium oleate in the MFA phase following LE (Supporting Information Figure S3, vinylic hydrogens at δ = 5.1−6.1 ppm were monitored). Quantitatively, the amount of potassium oleate corresponds to ca. 2 carboxylates/nm$^2$ of the initial CdSe NCs, consistent with the density of 1.5−4 carboxylates/nm$^2$ reported by Owen et al.$^{22}$ The amount of incoming MCC ligands varies from 0.65 to 2 MCC ligands/nm$^2$. Taken together, ICP-OES and $^1$H NMR experiments on NCs and supernatant solutions provide strong evidence for the formation of the all-inorganic MCC-capped CdSe NCs with the composition expressed with formula 1 in Scheme 1. This implies the purely X-type ligand-exchange and the formation of Cd−S bonds at the NC/MCCs interface.

Solution Phase Behavior of Sn−S MCCs and Their Adsorption onto NC Surface. Sn$_2$S$_6^{4−}$ and SnS$_4^{4−}$ ions were introduced by Krebs$^{37}$ and later studied by Kanatzidis,$^{38}$ Dehnen,$^{39}$ and others. These ions are very convenient for solution NMR studies due to good sensitivity of (natural abundance) $^{119}$Sn NMR, with spin of 1/2 leading to narrow NMR peaks. Thiostannate anions often interconvert depending upon the solvent or pH while their isotropic chemical shifts (δ($^{119}$Sn)) are well-documented and rather weakly solvent or counterion dependent.$^{39a}$ δ($^{119}$Sn) values of all thiostannate anions fall in relatively narrow range 49−74 ppm indicating that the tetrahedral environment for $^{119}$Sn nuclei is maintained, whereas the change in coordination number by 1 would lead to ca. 150 ppm change in chemical shift. No SnS$_4^{3−}$ anions were observed in our solution NMR studies.$^{40}$ No other Sn species, such as tin-oxosulfide ions, were detected by NMR spectroscopy (from −1000 to 1000 ppm). SnTe$_4^{4−}$ ions differ from thiostannate ions in that they contain more polarizable Te atoms, and therefore, their $^{119}$Sn chemical shifts are highly variable due to solvation or ion-pairing effects and are generally observed between −1675 and −1825 ppm.$^{41}$ Furthermore, Se- and Te-based stannates are much more sensitive to oxygen. For these reasons, we concentrated our solution NMR studies exclusively on thiostannate ions.

Before studying the LE reaction with solution NMR spectroscopy, we studied the actual species existing in solutions of these thiostannate compounds in nonaqueous solvents commonly used in LE reactions. K$_3$SnS$_4$ and K$_3$Sn$_2$S$_6$ can be prepared in water by combining SnS$_2$ with the correct molar proportions of K$_2$S. Figure 2 shows the effect of the solvent, as observed by solution $^{119}$Sn NMR, upon dissolution of the pure substances K$_3$SnS$_4$ and K$_3$Sn$_2$S$_6$. The most interesting observation is the appearance of highly charged Sn$_3$S$_{6}^{6−}$ ions as the predominant ion in MFA solutions upon dissolving K$_3$SnS$_4$. An analogous NMR spectrum is obtained by combining SnS$_2$ and K$_2$S directly in MFA. Na$_2$Sn$_3$S$_6$ has been previously obtained by solid-state synthesis by Krebs et al.$^{57a}$ and characterized with solid-state NMR spectra by Mundus et al.$^{52}$ A clear spectroscopic signature that distinguishes Sn$_3$S$_{6}^{6−}$ from Sn$_2$S$_4^{4−}$ is the presence (in good agreement with natural
The spectra of K₄SnS₄ dissolved in H₂O (A, 74 ppm), K₄SnS₄ dissolved in terminal, one bridging), Sn₂S₆ at 347 cm⁻¹; symmetric Sn−S vibrations at 386 and 373 cm⁻¹, vibration of SnS₄ ring at 277 cm⁻¹, and Sn−S bridging vibration at 347 cm⁻¹. K₄SnS₄ exhibits only two bands at 351 and 370 cm⁻¹, characteristic of symmetric and asymmetric Sn−S modes. The spectrum of solid K₆Sn₂S₇ isolated from MFA is characterized by the strong band at ca. 360 cm⁻¹, and Sn−S vibrations (similar to SnS₄⁴⁻). The solution phase Raman spectra of SnS₄⁴⁻ in FA and SnS₆⁶⁻ in MFA resemble those of the solid-state samples. Further illustrating the effect of solvent, the pH value of the solution plays an important role as well. Sn₄S₆⁴⁻/MFA converts into SnS₄⁴⁻/MFA upon addition of KOH K₆Sn₂S₇ (that reacts with residual moisture giving KOH and KHS). This can be explained by the importance of protonation for the stability of Sn₄S₆⁴⁻. In N₂H₄, only SnS₄⁴⁻ is stable, and it does not convert into SnS₆⁶⁻ or SnS₆⁶⁻ upon addition of S²⁻ (Supporting Information Figure S4). On the basis of the above solution ¹¹⁹Sn NMR and Raman spectroscopic data, we further studied the LE with the oleate capped NCs for four ligand/solvent combinations which clearly yield a single form of anion without altering the pH of the solution (Figure 2) were chosen: SnS₄⁴⁻/H₂O, SnS₄⁴⁻/FA, SnS₆⁶⁻/N₂H₄, and SnS₆⁶⁻/MFA.

Upon binding of the anions to the NC the isotropic molecular tumbling slows, leading to significant broadening and attenuation of NMR signals from bound ligands. The NMR signal broadening arises from large anisotropic dipolar couplings and anisotropies of the chemical shifts which are no longer averaged away. In the case of MCC ligands bound to the NC surface, the signal mostly vanishes (Figure 4), allowing quantitative estimation of the amount of surface-bound ligands by measuring intensity from the remaining unbound ligand. Thiostannate ligands can act as polydentate ligands due to multiple terminal S atoms. On the basis of the LE reaction shown in Scheme 1, the following solution equilibrium between bound and unbound MCC ligand can be postulated assuming K₆Sn₂S₇ as a single thiostannate form in MFA:

\[
\text{(CdSe)ₙ} \cdot \text{Cd}_{m} (\text{SnS}_7^−) K(1−2m) \Rightarrow \text{(CdSe)ₙ} \cdot \text{Cd}_{m} (\text{SnS}_7^−) /3 + (y−m/3)K₆Sn₂S₇
\]

The exchange of bound and unbound MCC ligand is rather slow, as the NMR spectra for unbound ligands do not show broadening or a change in the chemical shift which would indicate fast exchange of bound and unbound ligand. Composition 1b represents an extreme case, in which full denticity of Sn₃S₇⁶⁻ is used (k⁸-Sn₃S₇⁻ in the terminology of...
coordination chemistry); that is, each \( \text{Sn}_2\text{S}_7^{6-} \) forms 6 bonds with surface \( \text{Cd}^{2+} \). An opposite extreme is the \( \kappa_1\text{Sn}_2\text{S}_7^{6-} \) bonding motif, that is, monodenticity of the ligand at \( y = 2m \).

Thus, in principle the amount of surface-bound \( \text{Sn}_2\text{S}_7^{6-} \) ligand can adopt values of \( m/3 \leq y \leq 2m \), due to facile rearrangement of Cd-MCC bonds with variable denticity of MCC ligand.

Quantitatively, after first addition of oleate-capped CdSe NCs (12 mg, Figure 3B), the K\( _6\text{Sn}_2\text{S}_7 \) ligand coverage was \( \sim 4 \) ligands nm\(^{-2} \). Note that this coverage corresponds to \( y \approx 2.5m \), which exceeds the 2\( m \) limit discussed above, but may be explained by the additional week nonspecific binding of MCCs.

After the number of CdSe particles in solution was doubled, the amount of ligands on the surface decreased to 2.2 ligands nm\(^{-2} \) for K\( _6\text{Sn}_2\text{S}_7 \), which corresponds to \( y \approx 1.4m \). This shows that the initial binding of K\( _6\text{Sn}_2\text{S}_7 \) is labile and K\( _6\text{Sn}_2\text{S}_7 \) can detach and engage in a LE reaction with the oleate-capped CdSe, in agreement with postulated equilibrium reaction 1. After double precipitation with MeCN, the ICP-OES analysis shows 1.2 L nm\(^{-2} \), that is \( y \approx 0.7m \). Note that single-washed NCs are still well-dispersible in MFA, whereas double-washed NCs show much lower solubility in MFA, the difference which is best seen for larger NCs. When \( y \) approaches \( m/3 \) (composition 1b) due to further washing steps, particles should contain no K’ rendering them fully insoluble in polar solvents. Fully analogous observations are found for K\( _4\text{Sn}_2\text{S}_6 \) and other MCC ligands.

It is also important to note that the reverse exchange, e.g., displacement of MCCs by K-oleate and transfer of CdSe NCs back to the nonpolar phase, requires 20-fold molar excess of oleate, and takes up to 1–2 weeks, compared to minutes for direct LE. This is again in agreement with strong multidentate binding of thoistannate ligands to the NCs surface.

**Concurrent MCC LE Reactions.** Convenient monitoring of thoistannate concentrations by \( ^{119}\text{Sn} \) solution NMR also allows qualitative comparison of concurrent LE reactions with other MCC ligands. For example, when a 1:1 molar mixture of K\( _6\text{Sn}_2\text{S}_7 \) and K\( _3\text{SbS}_4 \) (Figure 5) or K\( _6\text{Sn}_2\text{S}_7 \) and K\( _3\text{AsS}_4 \) (Supporting Information Figure S5) is reacted with oleate-capped CdSe NCs the solution \( ^{119}\text{Sn} \) NMR signal in NMR spectra decreases at the same rate as for pure K\( _6\text{Sn}_2\text{S}_7 \), pointing to preferential binding of \( \text{Sn}_2\text{S}_7^{6-} \) ions as compared to the other MCC. However, a K\( _6\text{Sn}_2\text{S}_7\text{S}_4 \text{GeS}_4 \) mixture shows no signs of K\( _6\text{Sn}_2\text{S}_7 \) binding to the NC surface during the phase transfer of CdSe NCs, suggesting that Ge\( _4\text{S}_4^{4-} \) has a stronger binding affinity. The comparison of metal-free \( \text{S}^2^- \) with MCCs is another important point, especially because \( \text{S}^2^- \) is expected in

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**Figure 4.** Solution \( ^{119}\text{Sn} \) NMR spectra for K\( _3\text{Sn}_2\text{S}_6 \text{FA} \) and K\( _3\text{Sn}_2\text{S}_7 \text{MFA} \) solutions before LE, and after LE with increasing amounts of CdSe NCs. Note that 24 mg of CdSe NCs corresponds to \( y/m \) ratio of ca. 2–2.2 in eq 1; i.e., the amount of thoistannate ligand is sufficiently high for monodentate binding to all surface Cd atoms. Inset shows NMR tubes before and after LE.

**Figure 5.** Concurrent LE reaction by adding oleate-capped CdSe NCs into solutions of (A) K\( _6\text{Sn}_2\text{S}_7 \) and K\( _3\text{SbS}_4 \) or (B) K\( _6\text{Sn}_2\text{S}_7 \) and K\( _3\text{AsS}_4 \). (C) A graph illustrating the decrease of the integrals of the \( ^{119}\text{Sn} \) NMR signal upon titration with oleate-capped CdSe NCs (6 mg = 32 \( \mu \)mol). The initial K\( _6\text{Sn}_2\text{S}_7 \) was 5 mg (7 \( \mu \)mol) in a 0.5 mL reaction volume. All ligand mixtures are equimolar, except where 10-fold access is indicated.
the solutions of most MCCs. Only when a 10-fold excess of K₂S with respect to K₂SnS₄ is added do we notice a slower decrease in the Sn signal in comparison with pure K₂SnS₄-based LE (Figure 5C). Hence a binding affinity sequence K₂GeS₄ > K₂SnS₄ > K₂SbS₄ (K₂AsS₄) > K₂S can be established for the organic-to-inorganic LE.

**Solid-State ¹¹⁹Sn NMR Observation of Thiostannate Ligands Bound to the NC Surface.** Having confirmed that thiostannate ions disappear from the solution and bind to the NC surface as a result of the LE reaction, we now turn our focus on the establishing bonding motifs at the NC/MCC surface. We used solid-state magic angle spinning (MAS) ¹¹⁹Sn NMR spectroscopy to average the anisotropic NMR interactions and obtain solution-like NMR spectra of the MCC capped NCs.40,47, The ¹¹⁹Sn solid-state NMR spectra of the MCC capped NCs are compared to spectra of the pure solid unbound ligands and with the solution ¹¹⁹Sn NMR chemical shifts of the dissolved ligands (Figure 6).

![Figure 6](image_url)

**Figure 6.** (A) Solid-state MAS ¹¹⁹Sn NMR for K₄SnS₄, K₄Sn₂S₆ and K₂Sn₂S₄ powders. (B) Solid-state CPMG MAS ¹¹⁹Sn NMR for CdSe/ K₄SnS₄ (LE in H₂O), CdSe/K₄Sn₂S₆ (LE in FA), CdSe/K₂Sn₂S₄ (LE in MFA), and CdSe/K₄Sn₂S₄ (LE in N₂H₄). Three dash lines correspond to 74, 55, and 50 ppm, respectively (expected peaks for unbound ligands). *represents the spinning side bands.

Similar to solution NMR spectra, δ(¹¹⁹Sn) in the MAS ¹¹⁹Sn NMR spectra of solid free ligands falls in the range 50–74 ppm. While the spectrum of solid K₂SnS₄ is characterized by one narrow peak at 74 ppm (in good agreement with the corresponding chemical shift for K₂SnS₄ dissolved in water), the spectrum of K₄SnS₄ contains two peaks: one broad peak corresponds to K₄SnS₄ at 50 ppm42 and the narrow peak at 74 ppm from K₂SnS₄. The intensity of the isotropic K₂SnS₄ peak at 74 ppm appears to be more intense because the peaks from K₂SnS₄ are much broader and also dispersed over several spinning side bands. Keeping in mind that the longitudinal relaxation rate of the K₂SnS₄ peak also appeared to be slower, the NMR spectra indicate that at most only 10% of the K₂SnS₄ sample corresponds to K₂SnS₄. The product isolated from K₂SnS₄/MFA solution by adding acetonitrile shows signals at 74 ppm (50% integrated intensity, K₂SnS₄) and at 55 ppm (50% attributed to K₂SnS₄).

In order to overcome the low concentration of Sn atoms in the MCC capped NC samples, we applied a CPMG pulse sequence26,48 to maximize the signal-to-noise of the spectra of the NC-ligand samples (Figure 6B). Overall, the chemical shifts fall in the same range as for the free ligands, indicating very similar tetrahedral SnS₄ environment of Sn. However, the peaks are considerably broader than those observed for the pure ligand samples, which is suggestive of a spread of bonding motifs: various denticity conformations of ligands and distribution of binding sites on the NC surface (different facets, edges of facets, etc.). The downfield shifts of several ppm may arise due to binding of the thiostannate ions with the NC surface or from the formation of covalent Cd−S bonds. No unambiguous differentiation between SnS₄⁴⁺, SnS₄⁶⁻, or Sn₂S₆⁴⁻ can be made due to signal broadening. Furthermore, formation of SnS₄ on the NC surface can also be excluded, as it should manifest itself by the peak at ~765 ppm in the solid-state ¹¹⁹Sn NMR spectrum (for pure spectra of pure SnS₄ see Supporting Information Figure S6). No other Sn-containing species could be detected with solid-state NMR spectroscopy. In the case of CdSe/K₄Sn₂S₆/N₂H₄ samples, a clear splitting of ¹¹⁹Sn NMR spectrum is observed that may indicate, for instance, two distinct binding modes of a ligand or mixed SnS₄⁴⁻/SnS₄⁶⁻/SnS₄⁶⁻ surface coverage.

**Se CPMG MAS NMR spectra of CdSe NCs capped with thiostannate ligands contain a main peak at ~28.5 ppm with ~50 ppm broadening and a shoulder at ~557.4 ppm (Supporting Information Figure S7). This line shape and more negative chemical shifts as compared to bulk CdSe (~472.3 ppm) are fully consistent with quantum-size effects and core−shell distribution of chemical shifts (more negative for near surface Se layer).49**

**Observation of Thiostannate Ligands on the NC Surface with Far-IR Spectroscopy.** Far-IR spectroscopy (100−600 cm⁻¹) may serve as excellent tool for studying inorganic capping of colloidal NCs because this region corresponds to vibrational frequencies of bonds formed by heavier atoms such as Cd, Sn, and chalcogens and because organic ligands and other light-atom residues (solvents, etc.) show virtually no absorption. Previously, far-IR spectra were seldom used for characterization of colloidal NCs.50 We note that, as expected, Raman spectra were not conclusive due to the fluorescence background from NCs and due to drastic difference in scattering intensity not only between solid NC cores (very weak signals) and molecular species (much greater signals), but between various molecules. Far-IR spectra of CdSe/oleate and “ligand-free” CdSe NCs (Figure 7) are very similar and contain a relatively narrow peak at 183 cm⁻¹ characteristic of ν(Cd−Se) stretching frequencies,51 and consistent with Raman shifts of transverse optical (156 cm⁻¹) and longitudinal optical (215 cm⁻¹) phonons.52 The spectrum of CdSe/BF₄⁻ shows only peaks associated with CdSe. This is consistent with only weak electrostatic interactions between BF₄⁻ and the surface Cd²⁺ adatoms.
insights into the binding modes and bond distances were gained with X-ray absorption spectroscopy (XAS). Sn K-edge XAS spectra allow the study of the local electronic and geometric structure (up to 6 Å) around Sn atoms, and are also applicable to disordered systems such as surface-bound ligands. In order to evaluate the data from the XAS measurements we took a Fourier transform of the spectra into frequency space, which results in a radial structure function (RSF) where peaks correspond to the distances to the nearest-neighbors. Fitting of the EXAFS region was performed using theoretical Sn−S references generated from crystal structures of Na₄Sn₂S₆, Na₂Sn₃S₄ and Na₂Sn₅S₇. The value of the amplitude reduced factor (S₀²) was determined by fitting the first shell using the references (S₀² = 4.6) and the coordination number (CN), Debye−Waller factor (DW), interatomic distance (R), and edge-shift (∆E₀). For the free ligands, two major peaks could be distinguished in the RSFs (Figure 8A−C, Table 1), and they indicate close to expected interatomic distances (d) and coordination numbers (CN): only one type of Sn−S bond with d(Sn−S) = 2.4 Å and CN = 4 in K₄Sn₂S₆ and two bonds in K₄Sn₃S₄ and K₄Sn₂S₇ [Sn−S₁ (terminal, ~2.35 Å) and Sn−S₂ (bridging, ~2.50 Å)] with CN close to the expected value (CN = 1−2). The bond lengths are in good agreement with crystallographic data and with our DFT calculations.

Chemical binding of thiostannates to surface Cd atoms should modify the overall geometry of the ligand and its local coordination environment. Further, the surface conformation of a ligand will depend on the surface coverage, facet to which ligand binds, etc. It is therefore not possible to deduce the exact surface geometry, but rather to monitor the key differences to unbound ligands, primarily in the bond distances and coordination numbers. XAS studies on NCs after LE (Figure 8D−G) indicate important changes with respect to free crystalline ligands and unambiguously confirm chemical binding of thiostannate ligands onto NC surface. One important feature that was not directly observed by other techniques and reported here for the first time is that there is strong evidence for Sn−O bonds in XAS spectra of CdSe NCs capped with K₄Sn₅S₇ in H₂O (d(Sn−O) = 2.1 Å). Judging from CNs, a particularly high proportion of Sn−O bonds are found in K₄Sn₅S₇/H₂O (CN = 2.8 for Sn−O bonding) system, and only one type of Sn−S with d = 2.4 Å and CN = 1.3, suggesting an overall stoichiometry of [SnO₃S]⁺⁴⁻ (which can also correspond to a mixture of SnO₄⁴⁻ and SnO₂⁴⁺ ions). This can be explained by well-known hydrolysis of chalcogenido-metallates in water at high pH, and this may also occur in nonaqueous solutions handled in air (as in this study). Also, CdSe NCs can aid the formation of Sn−O bonds in aqueous environment and even in powdered solids through photocatalytic oxidation of Sn−S by photogenerated holes. On the contrary, for the nonaqueous LE systems we observed a much smaller proportion of Sn−O bonds (CN = 0.2−0.9, Table 1). Further, and very importantly, two types of Sn−S bonds are found for Sn₃S₄⁶⁻ and Sn₅S₇⁶⁻, and all Sn−S distances are shorter, on average by 0.1 Å as compared to reference to unbound ligands, in agreement with DFT calculations (see below). The second coordination shell was fitted by introducing Cd (or Sn) atoms into the existing scattering paths by replacing the Na atoms and optimizing the parameters (Figure 8D,F,E,G). The shortest Sn−Cd distance of 3.37−3.8 Å was found for Sn₅S₇⁶⁻ (CN ~ 1) and is attributed to Cd−Sn bridge which is in good agreement with the distances obtained by DFT modeling. We note that for NC-ligand

Figure 7. Far-IR ATR spectra for CdSe NCs with various surface chemistries. (A) CdSe/oleate (black), CdSeCdS/oleate (orange), CdSe/Br⁻ (gray), CdSe/S²⁻ (green), K₄S (dashed green spectrum). (B) CdSe/oleate (black), CdSe/S²⁻ (green), CdSe/Sn₂S₆⁻ (blue), CdSe/Sn₅S₇⁶⁻ (red).

Core−shell CdSe/CdS NCs (oleate capped, 4.5 nm core and 2 nm shell) were also measured as a reference material for all MCCs in order to observe the effect of Cd−S bonds on the far-IR spectra. In CdSe/CdS NCs, a broad and intense peak at 242 cm⁻¹ characteristic of CdS shell and considerable broadening in CdSe region (with a small shoulder at 142 cm⁻¹, presumably due to the effects of strain and alloying at CdSe/CdS interface) were observed. In CdSe/S²⁻ NCs, a broad shoulder at 260 cm⁻¹ due to Cd−S bonds was slightly upshifted compared to pure CdSe due to the formation of shorter Cd−S bonds at the NC surface than in pure CdS. Broadening of CdSe features was also observed. Figure 7B compares the far-IR spectra of CdSe NCs capped with different thiostannate ligands. The major common feature is intense absorption in the 240−300 cm⁻¹ range due to the formation of Cd−S bonds. The broadening and downshift of CdSe band for CdSe/Sn₂S₆⁻ and CdSe/Sn₅S₇⁶⁻ are very similar to CdSe/S²⁻ and may also be the effect of the higher absorbance of ligands below 200 cm⁻¹ (Supporting Information Figure S8). As expected, far-IR spectra of the pure K₄Sn₂S₆, K₄Sn₃S₄ and K₄Sn₅S₇ compounds are distinctly different from each other, and from the surface-bound species, and agree well with the literature (see Supporting Information for further discussion).

Thiostannate Bonding Motifs from X-ray Absorption Spectroscopy and DFT Simulations. Qualitatively, both far-IR and NMR spectroscopy clearly indicate that thiostannate ions are covalently attached to the surface of CdSe, and on the basis of the NMR spectra, the basic four-coordinate SnS₄ coordination environment is preserved in all cases. Further researchers used theoretical Sn−S references generated from crystal structures of Na₄Sn₂S₆, Na₂Sn₃S₄ and Na₂Sn₅S₇ to fit the XAS data. The fits showed that the Sn−S bonds are primarily localized at the surface, with bond distances consistent with the literature. The fits also revealed that the Sn−O bonds, which are present in the nonaqueous LE systems, are not observed in the aqueous systems. These findings suggest that the chemical binding of thiostannate ligands to CdSe NCs is distinct in aqueous and nonaqueous environments.
samples the distances in the second shell are precisely fitted, while CN values are much less accurate.

For DFT simulations, theoretical models were prepared on the basis of the experimental findings: one terminal S atom from thiostannate ligand was coordinated to one adsorption site on the surface, displacing the original oleate (or halide) ligand, while each unbound terminal S was compensated by a potassium counterion. Calculations show that the thiostannate binding energy is 0.6 eV per site higher than for oleate, suggesting an energetically favored displacement. For a 3 nm

Table 1. Structural Information for Reference Samples and Capped NCs from Best Fitting of the EXAFS Spectra (Figure 8)\textsuperscript{a}

| sample                  | path   | CN         | $R_t$ (Å) | $R_{t\text{ DFT}}$ (Å) | DW (Å$^2$) | $E_0$ (eV) | $R$ factor |
|-------------------------|--------|------------|-----------|------------------------|------------|------------|------------|
| (free) K$_4$SnS$_4$     | Sn−S   | 4.1 ± 0.6  | 2.41 ± 0.017 | 2.4 | 0.0107 ± 0.0025 | 2.03 ± 1.74 | 0.0075    |
| (free) K$_4$SnS$_6$     | Sn−S$_{\text{dangl}}$ | 1.8 ± 0.4 | 2.34 ± 0.018 | 2.35 | 0.0010 ± 0.0019 | 6.68 ± 1.37 | 0.0043    |
|                         | Sn−S$_{\text{bridge}}$ | 2.0 ± 0.5 | 2.46 ± 0.018 | 2.46 |                      |            |            |
| CdSe/Sn$_2$S$_6^{4−}$/FA| Sn−S$_{\text{dangl}}$ | 1.4 ± 0.2 | 2.27 ± 0.016 | 2.37 | 0.0008 ± 0.0009 | 8.17 ± 1.17 | 0.0078    |
|                         | Sn−S$_{\text{bridge}}$ | 2.6 ± 0.7 | 2.42 ± 0.012 | 2.47 |                      |            |            |
|                         | Sn−O   | 0.7 ± 0.2  | 2.00 ± 0.019 | 2.03 | 0.0004 ± 0.0015 | 0.83 ± 0.29 | 0.0051    |
|                         | Sn−Cd  | 0.6 ± 0.2  | 3.77 ± 0.020 | 3.78 | 0.0024 ± 0.0010 | 3.59 ± 0.98 | 0.0089    |
| CdSe/Sn$_2$S$_6^{4−}$/MFA| Sn−S$_{\text{dangl}}$ | 0.7 ± 0.4 | 2.24 ± 0.057 | 2.27 | 0.0038 ± 0.0018 | 3.59 ± 0.88 | 0.0089    |
|                         | Sn−S$_{\text{bridge}}$ | 3.8 ± 0.7 | 2.41 ± 0.012 | 2.44 | 0.0038 ± 0.0018 | 3.59 ± 0.88 | 0.0089    |
|                         | Sn−Cd  | 0.9 ± 0.2  | 3.37 ± 0.012 | 3.99 | 0.0024 ± 0.0010 | 3.59 ± 0.88 | 0.0089    |
| CdSe/Sn$_2$S$_6^{4−}$/N$_2$H$_4$| Sn−S$_{\text{dangl}}$ | 1.1 ± 0.1 | 2.30 ± 0.009 | 2.25 | 0.0002 ± 0.0003 | 4.14 ± 0.91 | 0.0078    |
|                         | Sn−S$_{\text{bridge}}$ | 1.7 ± 0.2 | 2.44 ± 0.007 | 2.48 | 0.0002 ± 0.0003 | 4.14 ± 0.91 | 0.0078    |
|                         | Sn−O   | 0.2 ± 0.1  | 1.97 ± 0.033 | 2.00 | 0.0002 ± 0.0003 | 4.14 ± 0.91 | 0.0078    |
|                         | Sn−Cd  | 1.0 ± 0.7  | 3.51 ± 0.021 | 3.5−4.1 | 0.0063 ± 0.0063 | 3.59 ± 0.88 | 0.0089    |
| CdSe/Sn$_4^{4−}$/H$_2$O | Sn−S   | 1.3 ± 0.3  | 2.42 ± 0.020 | 2.31−2.44 | 0.0037 ± 0.0013 | 7.64 ± 0.93 | 0.0076    |
|                         | Sn−O   | 2.8 ± 0.2  | 2.06 ± 0.011 | 2.07 | 0.0037 ± 0.0013 | 7.64 ± 0.93 | 0.0076    |
|                         | Sn−Cd  | 0.5 ± 0.2  | 3.51 ± 0.015 | 3.86 | 0.0002 ± 0.0001 | 7.64 ± 0.93 | 0.0076    |

\textsuperscript{a}Coordination number (CN), bond distance from XAFS ($R_t$), bond distance from DFT ($R_{t\text{ DFT}}$), pseudo-Debye–Waller factor (DW), energy shift ($E_0$), $R$ factor obtained from the fits.
model NC with exclusively \( K_4Sn_2S_7 \) capping ligand, such a procedure leads to a stable configuration with no \( S_2^- \) or \( K_2S \) desorption, as verified by molecular dynamics. Calculated energy required for desorption of \( K_2S \) is 4.1 eV with explicit inclusion of coordinating MFA molecules. The relaxed structure with stoichiometry \( Cd_{1.18}Se_{1.08}Sn_{0.18}S_{0.63}K_{0.18} \) is shown in Figure 9a. A similarly stable configuration can be constructed with \( K_4SnS_4 \).

To study the binding geometries in details, a smaller trap-free 2.5 nm CdSe model NC with one thiostannate ligand per facet was used. The (100) facets provide a tetrahedral lattice scaffold, helping maintain the tetrahedral coordination of Sn. For a \( SnS_4 \) complex it means two S atoms bind to the surface with the other two S unbound (Figure 9b). However, such dangling S atoms are highly unfavorable, and after relaxation one of them falls onto the surface by tilting the \( SnS_4 \) tetrahedron, and forming a bond to Cd (dotted lines) that breaks the periodicity of the original lattice. The remaining S is unable to distort the \( SnS_4 \) tetrahedron sufficiently in order to reach the surface and thus stays unbound, stabilized by the available potassium counterion. In the absence of potassium ions, this S atom tends to diffuse along the surface away from the \( SnS \) complex, exposing the Sn atom, or dimerizes with other available S from the same thiostannate complex or from complexes adsorbed nearby, thus stabilizing it against desorption. Similar behavior is observed for \( Sn_2S_7^{6-} \) in which the bridging S makes the unit more rigid so that both dangling S cannot reach the surface (Figure 9c). For \( SnS_2Se^+ \), the rigid \( SnS_2 \) ring precludes compliance with the underlying lattice; however, the ligand still maximizes its denticity by distorting the \( SnS_4 \) tetrahedra (see geometries in Supporting Information). Over the duration of our molecular dynamics runs we have not observed the fragmentation of \( SnS_2^6^- \); however, we expect it to be quite possible. Overall, thiostannate complexes tend to maximize the amount of bonds to the surface, while counterions are found to be important for stabilization of Sn tetrahedral coordination. However, it is not uncommon for this tetrahedron to break.

Calculated distances in the relaxed geometries are presented in Table 1 and in general agree with EXAFS observations; the bond from Sn to dangling S is shorter, while Sn to surface-bound S and bridging S are practically identical and longer. EXAFS findings of slightly lower coordination numbers to dangling S may be indicative of rare detachment of a dangling S from Sn tetrahedra, as observed in theoretical model, but most of them remain intact. The theoretical model provides an Sn and Cd coordination numbers of 4, drastically different from EXAFS values. This can be attributed to inaccurate fitting of the second shell in EXAFS spectra of surface bound ligands. The predicted Sn–Cd distance of 3.86–3.99 Å is comparable to and slightly higher than experimental values.

The quality of surface passivation by thiostannate ions can be judged from the analysis of projected densities of states and HOMO and LUMO wave functions (Figure 9d,e). PDOS plots clearly show that thiostannate ligand creates hole traps on an initially trap-free NC which are localized mainly on dangling and bridging S atoms (Figure 9e). This is expected since the free ligand has HOMO levels deep in the bandgap of CdSe (Figure 9d). This is consistent with the low photoluminescence quantum yield (PL QY) of the MCC-capped CdSe NCs (usually below 1%) and drastically shorter ON-state in single-particle blinking trajectories of MCC-capped CdSe/CdS NCs. Surprisingly, despite all the disorder of the surface (Figure 9a), the conduction band remains clear of traps thanks to self-healing also observed previously on ligand-free CdSe NCs consistent with excellent n-type conductivity of the CdSe-MCC films.

Figure 9. DFT modeling of thiostannate-capped CdSe NCs: (a) relaxed geometry of a 3 nm CdSe NC capped with \( SnS_2^6^- \) ligands; (b) stable binding geometries of \( SnS_2^4^- \) and \( Sn_2S_7^{6-} \) ligands on (100) CdSe surface; (d) projected density of states for a free \( K_4SnS_4 \) ligand and for CdSe-\( K_4SnS_4 \) NC; (e) spatial distribution of the trap and electronic states in a 2.5 nm model.
CONCLUSIONS
In conclusion, we have conducted a detailed experimental and theoretical study of the inorganic surface functionalization of CdSe NCs by thioctannate and similar sulfur-based ligands. The combined analysis of solution $^1$H NMR, solution and solid-state $^{119}$Sn NMR, far-IR and XAS spectroscopies, and DFT modeling is consistent with the X-type ligand exchange mechanism. During the ligand exchange reaction, CdSe NCs retain their Cd-rich stoichiometry, where surface Cd adatoms serve as binding sites for terminal S atoms from chalcogenidometallate ligands leading to all-inorganic $(\text{CdSe})\text{core}(\text{Cd}_{28}(\text{SnS})_{30})^{-}\text{K}_{(6-8\text{m})}^{+}$ stoichiometry, taking $\text{SnS}_{6}^{4-}$ as inorganic ligands, and K-oleate as side product. DFT modeling combined with molecular dynamics, with or without inclusion of the polar solvent molecules into simulations (corresponding to colloidal or powdered state, respectively), confirms stable Cd-rich composition upon adsorption of $\text{SnS}_{6}^{4-}$ or $\text{SnS}_{4}^{4-}$ ligands. We note that NC compositions are very dynamic due to ligand exchange—desorption equilibria and surface reconstruction. Furthermore, thioctannates $\text{SnS}_{4}^{4-}$ and $\text{SnS}_{6}^{4-}$ retain 4-coordinate Sn, despite the occurrence of significant distortions due to surface-binding. At the same time, experiments point to the instability of $\text{Sn}_{2}\text{S}_{6}^{4-}$ due to surface-binding. At the same time, experiments and simulations of this study such as retention of metal-rich NC compositions for $\text{CdSe} \rightarrow \text{CdS}$ and $\text{CdSe} \rightarrow \text{CdS}$, respectively, confirm the stability of all-inorganic NCs. In conclusion, we have conducted a detailed experimental and theoretical study of the inorganic surface functionalization of CdSe NCs by thioctannate and similar sulfur-based ligands. The combined analysis of solution $^1$H NMR, solution and solid-state $^{119}$Sn NMR, far-IR and XAS spectroscopies, and DFT modeling is consistent with the X-type ligand exchange mechanism. During the ligand exchange reaction, CdSe NCs retain their Cd-rich stoichiometry, where surface Cd adatoms serve as binding sites for terminal S atoms from chalcogenidometallate ligands leading to all-inorganic $(\text{CdSe})\text{core}(\text{Cd}_{28}(\text{SnS})_{30})^{-}\text{K}_{(6-8\text{m})}^{+}$ stoichiometry, taking $\text{SnS}_{6}^{4-}$ as inorganic ligands, and K-oleate as side product. DFT modeling combined with molecular dynamics, with or without inclusion of the polar solvent molecules into simulations (corresponding to colloidal or powdered state, respectively), confirms stable Cd-rich composition upon adsorption of $\text{SnS}_{6}^{4-}$ or $\text{SnS}_{4}^{4-}$ ligands. We note that NC compositions are very dynamic due to ligand exchange—desorption equilibria and surface reconstruction. Furthermore, thioctannates $\text{SnS}_{4}^{4-}$ and $\text{SnS}_{6}^{4-}$ retain 4-coordinate Sn, despite the occurrence of significant distortions due to surface-binding. At the same time, experiments point to the instability of $\text{Sn}_{2}\text{S}_{6}^{4-}$ due to surface-binding. At the same time, experiments and simulations of this study such as retention of metal-rich NC compositions for $\text{CdSe} \rightarrow \text{CdS}$ and $\text{CdSe} \rightarrow \text{CdS}$, respectively, confirm the stability of all-inorganic NCs.
