Experimental Evidence for a Variable First Coordination Shell of the Cadmium(II) Ion in Aqueous, Dimethyl Sulfoxide, and *N,N*′-Dimethylpropyleneurea Solution

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A combined extended X-ray absorption fine structure (EXAFS) and large angle X-ray scattering (LAXS) investigation has been performed to evaluate the coordination structure of the cadmium(II) ion in aqueous, dimethyl sulfoxide, and *N,N*′-dimethylpropyleneurea (dmpu) solutions. This approach has singled out the existence of a flexible coordination shell around the cadmium(II) ion in aqueous and dimethyl sulfoxide solutions, whereas a regular octahedral complex is detected in dmpu. The EXAFS and LAXS techniques provide different values of the Cd−O first shell distance (2.27(1) Å and 2.302(5) Å, respectively) for the hydrated and dimethyl sulfoxide solvated complexes, and this discrepancy is originated by the simultaneous presence of hexa- and heptacoordinated complexes in solution, giving rise to a broad distribution of distances around the ion. These findings demonstrate that, in solution, the cadmium(II) ion forms quite flexible hydration and dimethyl sulfoxide solvate complexes undergoing a solvent exchange with unusually stable seven-coordinated intermediate complexes, and therefore the mean ion−solvent distance is longer in solution than in the solid state. In the dmpu solution, due to the bulkiness of the solvent molecules, the octahedral cadmium(II) solvate is extremely crowded and it is not possible for a seventh ligand to enter the inner-coordination shell. This investigation shows that the combined analysis of the EXAFS and LAXS data allows a reliable determination of the structural properties of electrolyte solutions, also in the presence of flexible coordination shell with a variable number of coordinating molecules.

1. Introduction

The structures of solvated metal ions of the transition series have been the subject of numerous experimental and theoretical investigations.[1−5] In solution, or in comparable solid compounds, changes in the geometrical structure of the solvate complexes along the 3d transition series display similar trends for different ligands with the same donor atom, and the variations are often ascribed to the influence of the surrounding atoms on the d-electron shell of the metal atom. A natural starting point for the study of the structure of the hydrated 3d transition divalent metal ions is to consider hexacoordinated $[M(H_2O)_6]^{2+}$ ions, since they have mainly electrostatic bonding characteristics, and their ionic radii and the atomic radius of oxygen in water (1.34 Å),[6] as well as in most oxygen donor solvents, make the octahedral hydrate/solvate complexes to be predominant.[1] However, 3d transition metal ions display a large variation in the rate of water substitution reactions,[1] suggesting a different stability of the first hydration sphere. Depending on the relative lifetime of a solvated species and its transition state complex at solvent exchange, more than one solvated metal complex can contribute to the mean structure in solution.

The structure of the hydrated cadmium(II) ion has been extensively investigated by means of large angle X-ray scattering (LAXS), and the reported Cd−O bond distances are 2.289, 2.292, and 2.31 Å.[7] In all cases octahedral complexes were assumed "a priori", as the structures of all isolated hydrated cadmium(II) ions in the solid state display an octahedral configuration, with a mean Cd−O bond distance of 2.278 Å.[8] The Cd−O bond distance of 2.199 Å reported for a hexaaqua-cadmium(II) ion by Ka-Luo et al.[9] seems to be unrealistically short, and it has not been included in the mean Cd−O value. All of the six crystal structures with isolated dimethyl sulfoxide solvated cadmium(II) ions are octahedral and have a mean Cd−O bond distance of 2.273 Å,[10] thus, very close to the average value of the solid hydrates. *N,N*′-Dimethylpropyleneurea (dmpu) is an unusually bulky oxygen donor solvent, with which cadmium(II) forms a hexasolvate in solid state with a mean Cd−O bond distance of 2.257 Å.[11] This complex is extremely crowded around the cadmium(II) ion making it impossible to add a seventh dmpu molecule to the first coordination sphere.

The cadmium(II) ion shows a tendency to form innersphere complexes with anions and a strong variation of the hydration number has been observed depending on the counterion concentration indicating a large flexibility of the first hydration sphere.[12] The structures of 24 seven-coordinated cadmium complexes from the CSD and ICSD databases[13] are all mixed complexes with counterions as nitrate, acetate, oxalate, water, or organic oxygen donor ligands. In these complexes, the mean Cd−O bond distance is 2.356 Å, but very frequently, one or

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two of the ligands are weakly coordinated, with Cd−O bond distances in the range 2.45−2.60 Å, whereas the remaining ligands have Cd−O bond distances close to 2.30 Å or shorter.[13] The structures of 24 eight-coordinated cadmium complexes from the CSD and ICSD databases are tetranitrato, tetracarboxylato, and tetraether complexes with a mean Cd−O bond distance of 2.411 Å.[13] The bond distance distribution is somewhat narrower in the six- and eight-coordinated complexes than in the seven-coordinated ones. This shows clearly the flexibility and nature of the coordination properties of the cadmium(II) ion. A conclusive description of the dynamical and static properties of the hydration structure of the cadmium(II) ion is difficult to obtain as they cannot be easily studied by means of experimental techniques such as EPR and NMR.

Recently, we have carried out a combined ab initio and molecular dynamics study showing that the cadmium(II) ion has a very flexible first coordination shell which transits between hexa- and heptahydrated complexes.[14] From this investigation, a dynamical picture of the water exchange process emerges that takes place through an associative mechanism for the solvent substitution reaction and this mechanism is supported by a negative activation volume.[15] These results prompt a reevaluation of the standard view of the structural and dynamic properties of the solvated cadmium(II) ion.

X-ray absorption spectroscopy (XAS) has been often used to investigate the coordination structure of electrolyte solutions. The great advantage of XAS as compared to diffraction techniques is its short-range order and site selective sensitivity that makes this spectroscopy a unique probe of static distortions and anharmonic vibrational effects in systems with well-defined first coordination shells. Although a very accurate determination of the first shell structure can be obtained for hydration and coordination complexes with a regular octahedral symmetry,[4,5] a proper extended X-ray absorption fine structure (EXAFS) analysis is a much more delicate exercise in the case of ions with nonregular coordination geometries. In the presence of large disorder, the XAS technique determines with low accuracy the coordination numbers and gives little or no information on the higher-shell distributions. In this case, the use of information derived from other experimental techniques, such as large angle X-ray scattering, can be essential to provide a conclusive determination of the solvation structure in a wide distance range. A comparison of the intensity functions of the EXAFS and LAXS methods shows that the amplitude is much faster damped in the former, which means that long distances with relatively large distributions are not seen in EXAFS, although they can be clearly detected in LAXS.[16] For this reason, these two techniques are complementary, and their combined use allows one to gain additional insights into the structural properties of electrolyte solutions.

Here, a full examination of the structure and stability of the hydrated, the dimethyl sulfoxide and *N,N′*-dimethylpropyleneurea solvated cadmium(II) ions is presented. A combined EXAFS and LAXS study is used to provide additional insights, which are key to obtaining an accurate structural and dynamic description of the solvation structure of the cadmium(II) ion.

2. Methods

2.1. Chemicals. Aqueous solutions of cadmium(II) were prepared by dissolving weighed amounts of cadmium nitrate tetrahydrate, $Cd(NO_3)_2 \cdot 4H_2O$ (Aldrich), in water, slightly acidified with nitric acid to avoid hydrolysis. Saturated dimethyl sulfoxide solutions of cadmium(II) were prepared by dissolving the appropriate amount of hexakis(dimethyl sulfoxide) cadmium

TABLE 1: Concentrations (mol dm^{-3}), Densities (ρ/g, cm^{-3}), and Linear Absorption Coefficients (μ/cm^{-1}) of the Aqueous, Dimethyl Sulfoxide (Me$_2$SO) and *N,N′*-Dimethylpropyleneurea (dmpu) Solutions Used in the LAXS (L) and EXAFS (E) Measurements

sample	[M^{2+}]	[X$^-$]	[solvent]	ρ/ g cm^{-3}	μ/ cm^{-1}	method
Cd(ClO$_4$)$_2$ in water	1.499	3.009	48.33	1.3384	5.15	L
Cd(NO$_3$)$_2$ in water	0.200	0.400				E
Cd(ClO$_4$)$_2$ in Me$_2$SO	0.685	1.370	13.330	1.2548	7.38	L
Cd(ClO$_4$)$_2$ in Me$_2$SO	0.685	1.370				E
Cd(CF$_3$SO$_3$)$_2$ in dmpu	0.300	0.600	7.486	1.0827	1.94	L

perchlorate, $[Cd(OS(CH_3)_2)_6](ClO_4)_2$, prepared as described previously,[17] in freshly distilled dimethyl sulfoxide. Anhydrous $Cd(CF_3SO_3)_2$ was dissolved in *N,N′*-dimethylpropyleneurea (1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone) and the compositions of the studied samples are given in Table 1.

2.2. EXAFS Measurements. The XAS spectrum of the aqueous cadmium(II) solution was recorded in transmission mode using the EMBL spectrometer at DESY.[18] The measurements were performed at room temperature with a [Si 311] double-crystal monochromator and 30% harmonic rejection achieved by slightly detuning the two crystals from parallel alignment.[19] Three spectra were recorded and averaged after performing an absolute energy calibration.[19,20] The DORIS III storage ring was running at an energy of 4.4 GeV with positron currents between 70 and 40 mA. The sample was kept in cells with Kapton film windows and Teflon spacers of 3 mm. The XAS data on the dimethyl sulfoxide solution of cadmium perchlorate were collected in transmission mode at beam line 2−3, Stanford Synchrotron Radiation Laboratory (SSRL), under dedicated conditions; SSRL did operate at 3.0 GeV and a maximum current of 100 mA. A [Si 220] double-crystal monochromator was detuned to 30% of the maximum intensity at the end of the scans to discard higher order harmonics. The solution was kept in cells with 6.5 μm X-ray polypropylene film windows and a 3 mm Teflon spacer. The energy calibration of the X-ray absorption spectra was performed by simultaneously recording the spectrum of a cadmium foil, and assigning the first K edge inflection point to 26711 eV.[21] Five scans were recorded, energy calibrated, and averaged.

2.3. EXAFS Data Analysis. To extract structural information from the XAS spectra, we used an advanced theoretical scheme based on the multiple-scattering (MS) formalism. The data analysis was performed by means of the GNXAS code, which is based on the calculation of the EXAFS signal and a subsequent refinement of the structural parameters.[22,23] The GNXAS method accounts for MS paths, with correct treatment of the configurational average of all of the MS signals to allow fitting of correlated distances and bond distance variances (Debye−Waller factors). A correct description of the first coordination sphere of hydrated/solvated metal complexes has to account for asymmetry in the distribution of the ion−solvent distances.[24,25] Therefore, the Cd−O two-body signals associated with the first coordination shells were modeled with Γ-like distribution functions which depend on four parameters, namely the coordination number N, the average distance R, the mean-square variation σ, and the skewness β. The β term is related to the third cumulant C_3 through the relation $C_3 = \sigma^3\beta$, and R is the first moment of the function $4\pi \int g(r)^2 \, dr$. It is important to stress that R is the average distance and not the position of the maximum of the distribution (R_m).

Several EXAFS analyses on hydrated 3d transition metal ion complexes have pointed out the importance of accounting for MS effects within the first hydration shell.[4,5] The strongest MS

contributions are generated by the three linear O−ion−O scattering paths in octahedral complexes. However, in the case of the hydrated cadmium(II) ion, due to the longer Cd−O first shell bond distance as compared to first raw metal transition ions, these MS effects have been found to provide a negligible contribution. In the case of the dimethyl sulfoxide solution, the MS signal associated with the three-body Cd−O−S distribution has been calculated by means of the GNXAS program and the structural parameters used in the minimizations were the Cd−O and S−O bond distances, the Cd−O−S bond angle, and the six covariance matrix elements. Additional nonstructural parameters were refined, namely E_0 (core ionization threshold) and S_0^2 (many-body amplitude reduction factor). The model $\chi(k)$ signal (defined as the oscillation with respect to the atomic background cross-section normalized to the corresponding K-edge channel cross-section) was refined against the experimental data by using a least-squares minimization procedure in which structural and nonstructural parameters were allowed to float.[23] The quality of the fits was determined by the goodness-of-fit parameter, R_i,[23] and by careful inspection of the EXAFS residuals and their Fourier transforms. Phase shifts were calculated using muffin-tin potentials and advanced models for the exchange-correlation self-energy (Hedin-Lundqvist).[26] The muffin-tin radii were chosen according to the Norman criterion with 3% of overlapping.[27]

2.4. Large-Angle X-ray Scattering Measurements and Data Analysis. The scattering of Mo Kα X-ray radiation ($\lambda = 0.7107$ Å) from the free surfaces of aqueous, dimethyl sulfoxide, and N,N'-dimethylpropyleneurea solutions of cadmium perchlorate was measured by means of a large angle $\Theta-\Theta$ diffractometer. The solutions were kept in a Teflon cup inside an airtight radiation shield with beryllium windows. The scattered radiation was monochromatized in a focusing LiF crystal monochromator and the intensity was measured at 450 discrete angles in the range $1 < \Theta < 65°$ where 2Θ is the scattering angle. The scattering variable s is defined as $s = 4\pi\lambda^{-1}\sin\Theta$. A total of 100 000 counts were accumulated at each pre-set angle, and the entire angular range was scanned twice, which corresponds to a statistical error of about 0.3%. The divergence of the primary X-ray beam was limited by $1°$, $1/4°$, or $1/12°$ slits for different Θ regions, with overlapping data for scaling purposes. The experimental setup and the theory of the data treatment and modeling have been presented elsewhere.[28] All data treatment was carried out by means of the KURVLR program.[29] The experimental intensities were normalized to a stoichiometric unit of volume containing one cadmium atom, using the scattering factors f for neutral atoms, including corrections for anomalous dispersion,[30] $\Delta f'$ and $\Delta f''$, and values for Compton scattering.[31] Least squares refinements of the model parameters were carried out by means of the STEPLR program,[32] by minimizing the expression $U = \sum[si_{exp}(s) - si_c(s)]^2$, where U is the error square sum and $i(s)$ is the reduced intensity. The refinement of the model parameters was made for data in the high s region where the intensity contribution from the long-range distances can be neglected. To obtain a better alignment of the intensity function before the refinements, a Fourier back-transformation procedure was used to correct the $i_{exp}(s)$ functions by removing spurious nonphysical peaks below 1.2 Å in the experimental radial distribution function (RDF).[33]

3. Results

3.1. Hydrated Cadmium Ion. The radial distribution function from the LAXS experiment on the aqueous solution of cadmium perchlorate reveals four peaks at 1.45, 2.3, 2.9, and 4.3 Å (see Figure 1). The peaks at 2.3 and 4.3 Å correspond to the Cd−O
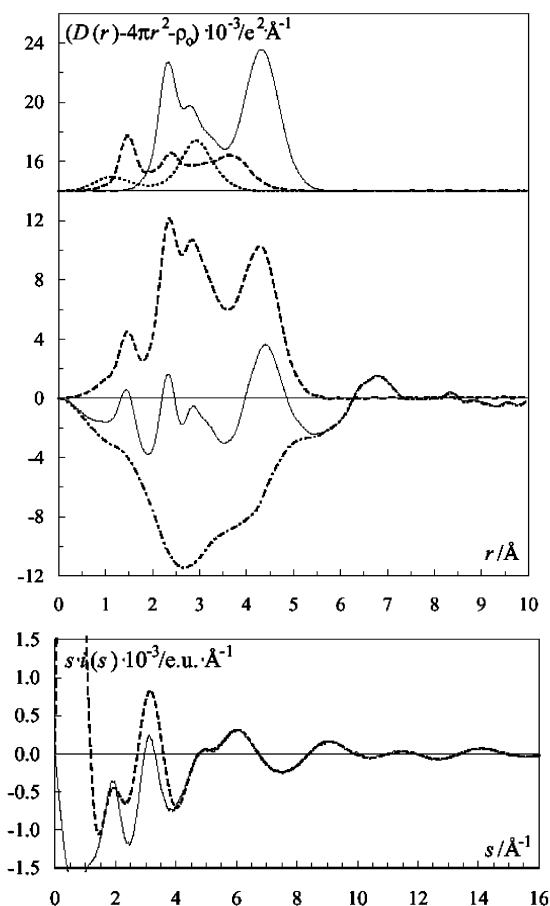

Figure 1. (Top) LAXS radial distribution curves for the aqueous solution of cadmium(II) perchlorate. Upper part: Separate model contributions: the hydrated cadmium(II) ion including the second hydration sphere (solid line), the hydrated perchlorate ion (dashed line) and $O_w \cdots O_w$ in the aqueous bulk (dotted line). (Middle) Experimental RDF: $D(r) - 4\pi r^2 r_0$ (solid line); sum of model contributions (dashed line); difference (dashed−dotted line). (Bottom) Reduced LAXS intensity functions $si(s)$ (solid line); model $si_c(s)$ (dashed line).

bond length and to the distance between the cadmium ion and the water molecules in the second hydration sphere, $Cd \cdots O_{II}$, respectively. The peak at 1.45 Å corresponds to the Cl−O bond distances in the perchlorate ion; the $O \cdots O$ distance in the perchlorate ion becomes then 2.37 Å (Figure 1). The peak at 2.9 Å is related to the $O(-H) \cdots O$ distances in the aqueous bulk and between the first and second hydration sphere (Figure 1).

The results of the refinements of the structural parameters of the assumed hexaaquacadmium(II) ion, and the perchlorate ion and the aqueous bulk are summarized in Table 2. The obtained results are in close agreement with the previously reported structures of the cadmium(II) ion aqueous solution.[7] The LAXS method cannot distinguish between an octahedral and a seven-coordinated cadmium(II) hydrated ion from the experimental data. However, the mean Cd−O bond distance of the first hydration shell obtained by the LAXS technique, 2.302 Å, is significantly longer than the mean Cd−O bond distance of the isolated octahedral hexaaquacadmium(II) ion reported in the solid state, 2.278 Å.[8] This difference is normally not seen between hexaaqua ions in the solid state and aqueous solution. Note that the Cl−O and $O_{aq} \cdots O_{aq}$ distances in this study are in very close agreement with the observation of other aqueous perchlorate solutions.[34]

The EXAFS data analysis of the aqueous cadmium(II) solution has been performed assuming an octahedral first

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TABLE 2: Structural Parameters for the Hydrated, the Dimethyl Sulfoxide, and the *N,N′*-Dimethylpropyleneurea Solvated Cadmium(II) Ions in Solution Obtained from the LAXS (L) and EXAFS (E) Data Analyses[a]

solvent	interaction	N	R/Å	σ^2/Å^2	β	method
Cd(ClO$_4$)$_2$ in water	Cd—O	6	2.302(5)	0.0057(5)		L
	Cd···O$_{II}$	12	4.284(17)	0.046(3)		
	OI···O$_{II}$	2	2.788(11)	0.0055(12)		
	Cl—O	4	1.453(3)	0.0020(2)		
	(Cl-)O···O$_w$	8	3.04(5)	0.023(3)		
	Cl—(O)···O$_w$	8	3.69(2)	0.038(2)		
	O$_{aq}$···O$_{aq}$	2	2.906(3)	0.0168(4)		
Cd(NO$_3$)$_2$ in water	Cd—O	6	2.27(1)	0.0075(20)	0.2(3)	E
Cd(ClO$_4$)$_2$ in Me$_2$SO	Cd—O	6	2.300(13)	0.0062(8)		L
	Cd···S	6	3.453(6)	0.0167(8)		
	Cl—O	4	1.433(4)	0.0023(2)		
Cd(ClO$_4$)$_2$ in Me$_2$SO	Cd—O	6	2.27(1)	0.0067(20)	0.0(2)	E
	S—O	6	1.50(2)	0.004(2)		
	Cd···S	6	3.39(5)	0.018(8)		
Cd(CF$_3$SO$_3$)$_2$ in dmpu	Cd—O	6	2.26(1)	0.006(1)		L
	Cd···C	6	3.39(2)	0.008(2)		

[a] The parameters are as follows: the mean bond distance R, the distance mean-square deviation σ^2, and the asymmetry parameter β. The coordination numbers, N, are fixed parameters. The estimated standard deviations are given in parentheses.
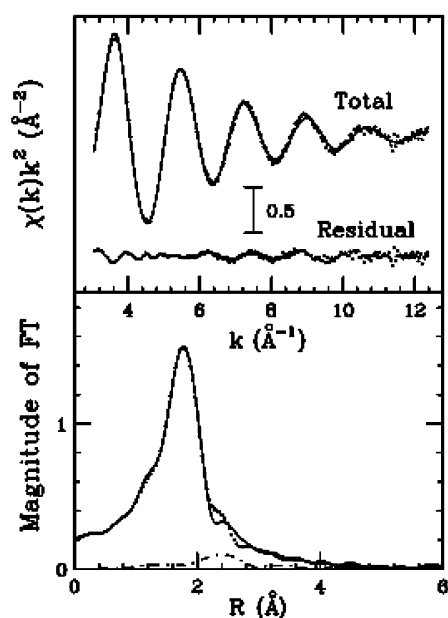

Figure 2. Best-fit results of the k^2-weighted EXAFS data of the hydrated cadmium(II) ion in aqueous solution. Upper panel: Comparison of the theoretical signal (solid line) with experimental data (dotted line) and residual function. Lower panel: Nonphase-shifted-corrected Fourier transforms of the experimental data (dotted line), of the theoretical signal (solid line), and of the residual curve (dashed–dotted line) calculated over the range $3.1 < k < 12.4$ Å^{-1}.

coordination sphere around the ion, and fitting procedures have been applied to the whole set of structural and nonstructural parameters mentioned above to improve, as far as possible, the agreement between the calculated signals and the experimental spectrum. The best-fit results are shown in Figure 2. In the upper panel, the comparison between the Cd—O first shell theoretical signal and the experimental spectrum and the corresponding residual is reported; all EXAFS functions shown in this paper are multiplied by k^2 for better visualization. Overall, the fitted EXAFS spectrum matches the experimental data quite well, and the weak high-frequency oscillation of the residual curve is most probably due to hydrogen atoms of the first hydration sphere. The residual value R_i, obtained from the minimization procedure, is 0.159×10^{-6}, the amplitude factor, S_0^2, is 0.80 ± 0.08 and the zero position of the theoretical scale is at 1.6 ± 1.0 eV above the first inflection point of the absorption spectrum. The consistency of the data analysis can be appreciated by looking

at the Fourier transform (FT) nonphase-shift corrected of the experimental, theoretical, and residual signals shown in the lower panel of Figure 2. As previously observed, the small peak of the residual at about 2.4 and 2.8 Å after phase shift correction, is most probably due to the presence of hydrogen atoms of the first hydration sphere; a Cd- -H bond distance should be about 2.75 Å (tetrahedral hybridization of the water oxygen) or 2.90 Å (trigonal hybridization of the water oxygen). A Cd—H distance is in agreement with the observed Cd- -O$_{II}$ distance of 4.28 Å to the second hydration sphere. Recent investigations have shown that the inclusion of hydrogen-scattering phenomena is important to perform quantitative EXAFS analysis of transition metal ionic solutions.[5,35,36] Here, the hydrogen contribution to the total $\chi(k)$ is very weak due to the longer Cd—water coordination distance as compared to the first row transition ion hydration complexes, and for this reason, it has not been taken into account in the data analysis. The EXAFS experimental spectrum is well reproduced by an asymmetric coordination shell made up of six oxygen atoms at a distance of 2.27 Å and the best-fit values for the full set of structural parameters defining the first hydration sphere of the cadmium(II) ion are listed in Table 2. To establish error limits on the refined parameters, a statistical analysis methodology using two-dimensional contour plots to selected parameters of the fit has been applied. This analysis examines the correlations among fitting parameters and evaluates statistical errors following the procedure described in details in ref 23. Figure 3a shows the contour plot of the Cd—O first shell distance vs E_0 and the innermost contour refers to the 95% error confidence interval. The Cd—O distance—asymmetry parameter correlation map is shown in Figure 3b and, as expected, the strongest correlation is detected between the first shell distance and E_0. Therefore, the statistical error on the Cd—O bond distance can be inferred from the former plot and is determined to be ± 0.01 Å. It is important to stress that this evaluation provides only statistical errors on the EXAFS refined parameters and it does not account for systematic errors in the theory or proper to the experimental technique. Figure 3c shows the contour plot for the Cd—O coordination number and Debye—Waller factor. A strong statistical correlation between the two is observed, suggesting that the determination of the two parameters has large effects on each other. This is a well-known phenomenon responsible for the large uncertainty on the coordination numbers, which is a characteristic of EXAFS. For this reason, the XAS technique alone is not able to correctly determine the number of water
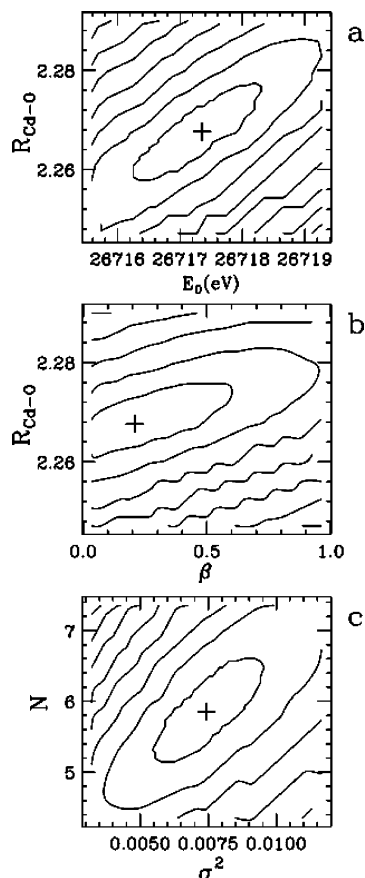
Figure 3. Two-dimensional contour plots for selected parameters in the EXAFS fit of the hydrated cadmium(II) ion in aqueous solution. (a) R_{Cd-O} vs E_0; (b) R_{Cd-O} vs β; (c) N_{Cd-O} vs σ_{Cd-O}^2. The innermost curve of each plot corresponds to the 95% confidence interval from which the statistical errors are determined.

Figure 4. (Top) LAXS radial distribution curves for the dimethyl sulfoxide solution of cadmium(II) perchlorate. Upper part: Separate model contributions: the dimethyl sulfoxide solvated cadmium(II) ion (solid line), the perchlorate ion (dashed line) and the dimethyl sulfoxide bulk (dotted line). (Middle) Experimental RDF: $D(r) - 4\pi r^2 r_0$ (solid line); sum of model contributions (dashed line); difference (dashed−dotted line). (Bottom) Reduced LAXS intensity functions $si(s)$ (solid line); model $si_c (s)$ (dashed line).

molecules bound to the cadmium(II) ion and the aid of other experimental and theoretical information is essential to quantitatively assess the coordination geometry of this ion.

In Table 2, it is shown that the Cd−O bond distance obtained from LAXS is about 0.03 Å longer than the value determined from the EXAFS analysis. To shed light on the origin of this discrepancy, additional EXAFS least-squares fits have been performed fixing the Cd−O complex geometry to the one determined from the LAXS analysis. In particular, the first shell distance has been fixed to 2.302 Å, whereas all of the other structural and nonstructural parameters have been allowed to float. The results of this analysis are shown in Figure S1. From the minimization procedure the Cd−O Debye Waller factor is 0.0095 Å^2, the amplitude factor, S_0^2, is 0.82 ± 0.08, the zero position of the theoretical scale is found at 4.9±2.0 eV above the first inflection point of the absorption spectrum, while the residual function R_i is 0.725·10^{-6}. In this case the theoretical signal does not reproduce the experimental spectrum and the residual shows a well-defined oscillation. The FT's shown in the lower panel of Figure S1 reveals that the Cd−O distance used in the calculation of the $\chi(k)$ theoretical signal is too long and this gives rise to a spurious peak in the residual curve at about 2.30 Å after phase shift correction.

3.2. Dimethyl Sulfoxide Solvated Cadmium(II) Ion. The radial distribution function from the LAXS experiment on the dimethyl sulfoxide solution of cadmium perchlorate reveals three peaks at 1.7, 2.3, and 3.55 Å (see Figure 4). The peaks at 2.3 and 3.55 Å correspond to the Cd−O and Cd···S distances in the dimethyl sulfoxide solvated cadmium(II) ion, respectively.
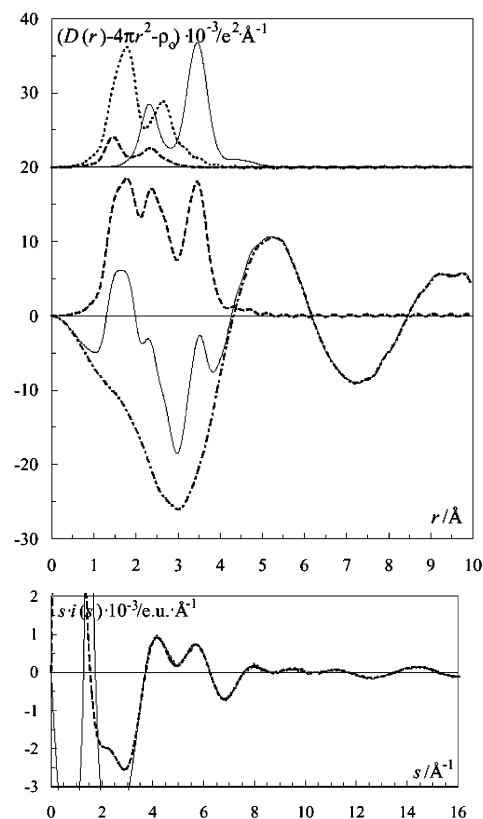
The broad peak centered around 1.7 Å is related to the intramolecular bond distances within the dimethyl sulfoxide molecules and perchlorate ion (Figure 4).

The results of the refinements of the structure parameters of the dimethyl sulfoxide solvated cadmium(II) ion and the perchlorate ion are summarized in Table 2; the structure parameters of the dimethyl sulfoxide molecules were taken from previous studies.[37] The obtained result is in close agreement with the previously reported structures of the dimethyl sulfoxide solvated cadmium(II) ion in solution.[38] The mean Cd−O bond distance of the dimethyl sulfoxide solvated cadmium(II) ion in dimethyl sulfoxide solution obtained with the LAXS technique, 2.300 Å, is significantly longer than the mean Cd−O bond distance of the isolated octahedral hexakis(dimethyl sulfoxide)-cadmium(II) ion reported in the solid state, 2.273 Å.[38] The Cd−S distance of 3.45 Å corresponds to a Cd−O−S bond angle of 127.0(1.3)° assuming a S−O bond distance of 1.54 Å.[39]

Also in this case an octahedral symmetry has been assumed in the EXAFS data analysis, and a fixed coordination number of six has been used in the minimizations. The results of the data analysis are shown in Figure 5. The first three curves from the top of the upper panel correspond to the Cd−O two-body, Cd−O−S three-body, and Cd···S two-body signals. The reminder of the figure shows the total theoretical signal compared with the experimental spectrum, and the resulting residual. The magnitudes of the FTs, nonphase-shift corrected, of the experimental, theoretical, and residual signals are shown in the lower panel of Figure 5. The agreement between the experimental and theoretical spectra is very good and the fit
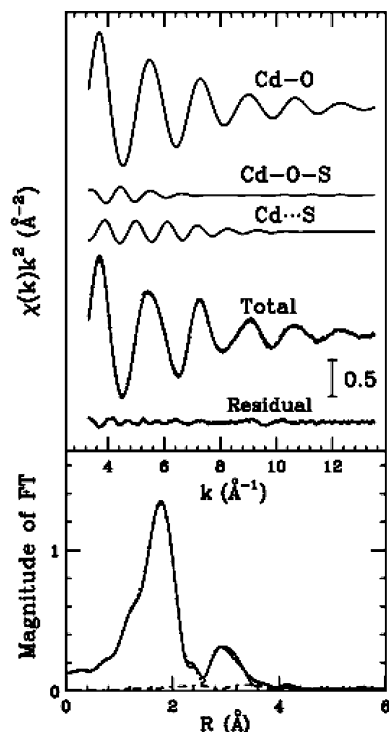
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Figure 5. Best-fit results of the k^2-weighted EXAFS data of dimethyl sulfoxide solvated cadmium(II) ion. Upper panel: from the top to the bottom of the panel the following curves are reported: Cd−O two-body signal, Cd−O−S three-body signal, Cd···S two-body signal, total theoretical signal (solid line) compared with the experimental spectrum (dotted line) and residual. Lower panel: Nonphase-shift corrected Fourier transforms of EXAFS experimental data (dotted line), of the theoretical signal (solid line), and of the residual curve (dashed−dotted line) calculated over the range $3.3 < k < 12.5$ Å^{-1}.

index value R_i is 0.713×10^{-7}. The structural parameters obtained from the minimization are listed in Table 2. The Cd−O−S angle is 127(3)° with a bond angle variance of 5°. According to the EXAFS results the Cd···S distance is 3.39(3) Å with a Debye−Waller factor of 0.018(4) Å^2, the zero position of the theoretical scale is 2.1 ± 1.0 eV above the first inflection point of the spectrum and the amplitude factor is equal to 0.87 $\pm$ 0.06. As shown in Table 1, the distances obtained from the LAXS and EXAFS studies are not in agreement and the Cd−O coordination distance detected by XAS is 0.03 Å shorter than the one determines by X-ray diffraction. Also in this case we have proved that this discrepancy originates from systematic errors by performing additional analyses of the EXAFS data. A second fitting procedure has been applied to the XAS experimental spectrum using a fixed Cd−O distance of 2.300 Å and refining all of the other structural and nonstructural parameters. The results of this analysis are shown in Figure S2. Similarly to what found in the case of the hydrated complex, the EXAFS theoretical curve calculated on the basis of the LAXS results is not in good agreement with the experimental data, and the residual curve shows an oscillation whose amplitude is well above the experimental noise of the spectrum. This result is corroborated by the FTs shown in the lower panel of Figure S2 (see the Supporting Information). Note that the agreement between the calculated and theoretical first shell peaks is not very good, the residual curve has a peak at about 2 Å and the fit index value becomes 0.408×10^{-6}.

3.3. *N,N′*-Dimethylpropyleneurea Solvated Cadmium(II) Ion. The radial distribution function from the LAXS experiment on the *N,N′*-dimethylpropyleneurea solution of cadmium tri-fluoromethanesulfonate reveals four peaks at 1.5, 2.5, 3.85, and
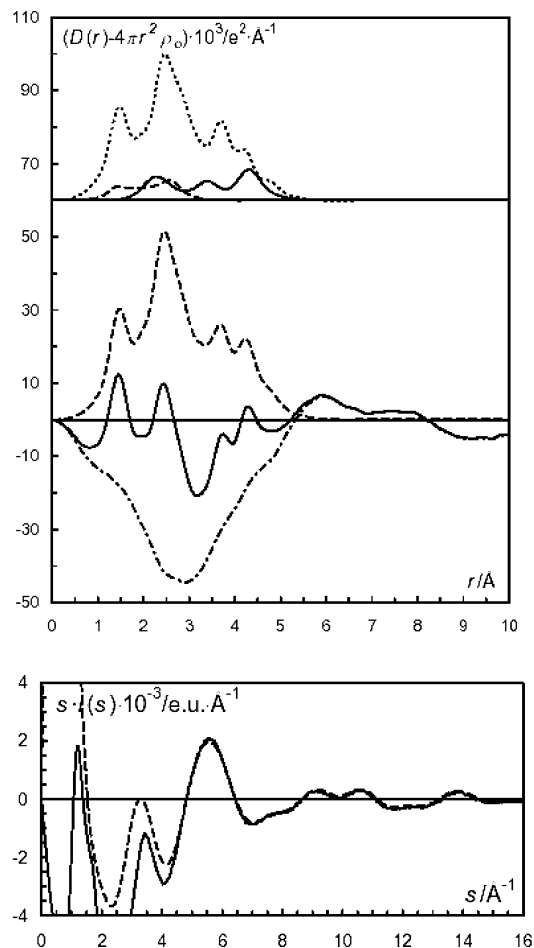

Figure 6. (Top) LAXS radial distribution curves for the *N,N′*-dimethylpropyleneurea solution of cadmium(II) trifluoromethanesulfonate. Upper part: Separate model contributions: the *N,N′*-dimethylpropyleneurea solvated cadmium(II) ion (solid line), the trifluoromethanesulfonate ion (dashed line) and the *N,N′*-dimethylpropyleneurea bulk (dotted line). (Middle) Experimental RDF: $D(r) - 4\pi r^2 r_0$ (solid line); sum of model contributions (dashed line); difference (dashed−dotted line). (Bottom) Reduced LAXS intensity functions $si(s)$ (solid line); model si_c (s) (dashed line).

4.35 Å, which are all related to the intramolecular bond distances within the *N,N′*-dimethylpropyleneurea molecules (see Figure 6). After the introduction of the solvent, two peaks at 2.3 and 3.55 Å did remain in the difference function. These correspond to the Cd−O and Cd···C distances in the *N,N′*-dimethylpropyleneurea solvated cadmium(II) ion, respectively. The result of the refinements of the structure parameters are summarized in Table 2. The structure parameters for the *N,N′*-dimethylpropyleneurea molecule and the trifluoromethanesulfonate ion are taken from previous studies. The results show that almost identical Cd−O bond distances are obtained in both solid state and solution, 2.257 and 2.26 Å, respectively.

4. Discussion

The results of several studies on the cadmium(II) ion in aqueous solutions by X-ray diffraction are consistent,[7] and with the assumption of a nearest-neighbor number of six, the average Cd−O internuclear distance is in the range 2.29−2.32 Å, depending on the concentration and counterion in the solution. The most recent ab initio MD simulation study was carried out imposing an octahedral symmetry for the first hydration sphere and the derived Cd−O distance was 2.33 Å.[40] Starting from these results, the present data analyses have been performed

assuming an octahedral structure of the cadmium(II) hydration complex and incongruous Cd−O first shell distances have been obtained from EXAFS and LAXS (2.27(1) Å and 2.302(5) Å, respectively). Recently, we obtained a detailed description of the structural and dynamical properties of the cadmium(II) ion in aqueous solution by means of a 100 ns long MD simulation based on accurate effective ion−water potentials.[14] The results of this investigation indicate that this ion transits between hexa- and heptahydrated complexes and the water exchange reaction follows an associative mechanism with a stable seven-coordinated intermediate complex. This is not surprising as metal ions with similar ionic radii as yttrium(III),[41] lutetium(III),[42] and calcium(II)[43] are eight-coordinated in water, and the yttrium-(III) and lutetium(III) ions have the same coordination also in dimethyl sulfoxide. Therefore, there is a lot of space in the cadmium(II) hydration sphere making it sterically very flexible, and it shall not be described in terms of a unique regular octahedral complex. The heptahydrated structure determined from the MD simulations[14] has been optimized using an ab initio procedure, and it may be depicted in the way that the water molecules are arranged in a C_2 symmetry with a spread of distances of 0.1 Å or more, similarly to what observed in solid seven-coordinated cadmium complexes.[13] Therefore, in aqueous solution, there are two species, an octahedral complex with six equal Cd−O distances, and a heptahydrated one having a less regular coordination with longer Cd−O bond lengths and a much broader bond distance distribution. However, this lengthening of the Cd−O bond distances in solution is not observed for the *N,N′*-dimethylpropyleneurea solvate and the crowdedness within the solvate structure of Cd(dmpu)$_6^{2+}$ will make an associative ligand exchange impossible. Therefore, the lifetime of the intermediate complex seems sufficiently short not to affect the observed mean structure of the octahedral solvate complex.

The structure detected by LAXS and XAS is an average of all the existing species but, due to the characteristics of the two techniques, a different mean Cd−O distance is measured. In particular, the signal from any shell is damped in LAXS and in EXAFS in such a way that the former technique is sensitive to long distances up to the second coordination sphere, whereas the latter is much more sensitive to shorter and well-defined first coordination shells. As a consequence, the heptahydrated complex provides a detectable contribution to the LAXS data and the determined Cd−O distance is longer than the one obtained from the EXAFS data analysis, which is essentially insensitive to the long distance tail of broad distributions. Similar results have been obtained in the case of the dimethyl sulfoxide solvated cadmium(II) ion. By assuming an octahedral symmetry, a shorter mean Cd−O bond distance has been obtained by EXAFS as compared to LAXS (see Table 2). The difference of about 0.03 Å between the two determinations can be explained by the presence of seven-coordinated and maybe also eight-coordinated complexes with a similar configuration as shown in the solid-state cadmium(II) complexes (see the Introduction). The coordination number does not seem to be concentration dependent as very similar results have been obtained in LAXS studies performed at different ionic concentration.

Additional insights into the solvation properties of the cadmium(II) ion can be gained by the comparison of the coordination geometries obtained in solution and in the solid sate. The hydrated, the dimethyl sulfoxide and *N,N′*-dimethyl-propyleneurea solvated cadmium ions in six-coordinated complexes in the solid state, all show a mean Cd−O bond distance of about 2.27 Å. However, the Cd−O bond distance in the hydrated and the dimethyl sulfoxide solvated cadmium(II) ions

in solution, as determined by LAXS, are both 2.30 Å, whereas the Cd−O bond distance in the dmpu solvated cadmium ion in solution remains at ca. 2.26 Å. These findings demonstrate that, in solution, the cadmium(II) ion forms quite flexible hydration and dimethyl sulfoxide solvate complexes undergoing a solvent exchange with unusually stable seven-coordinated intermediate complexes, and therefore, the mean ion−solvent distance is longer in solution than in the solid state. On the contrary, the *N,N′*-dimethylpropyleneurea molecule is very bulky, the octa-hedral solvate is extremely crowded, and a seventh ligand cannot enter the inner-coordination sphere. The crowdedness in the hydrated and the dimethyl sulfoxide solvated cadmium ions is much less and it seems very likely that a seventh solvent molecule can enter the inner coordination shell of cadmium(II). The yttrium(III) and lutetium(III) ions, which has about the same ionic radius as cadmium(II), form eight-coordinated dimethyl sulfoxide solvates, whereas the corresponding dmpu solvates are six-coordinated (results not published).

Supporting Information Available: Minimization results of the k^2-weighted EXAFS data of the hydrated cadmium(II) ion in solution (Figure S1). Minimization results of the k^2-weighted EXAFS data of cadmium(II) in dimethyl sulfoxide (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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