1058 *Inorg. Chem.* **2011**, *50*, 1058–1072
DOI: 10.1021/ic1017714

Inorganic Chemistry
Article

Coordination Chemistry Study of Hydrated and Solvated Lead(II) Ions in Solution and Solid State

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Received September 1, 2010

The coordination chemistry of lead(II) in the oxygen donor solvents water, dimethylsulfoxide (dmso, Me_2SO), *N,N*-dimethylformamide (dmf), *N,N*-dimethylacetamide (dma), *N,N'*-dimethylpropyleneurea (dmpu), and 1,1,3,3-tetramethylurea (tmu), as well as in the sulfur donor solvent *N,N*-dimethylthioformamide (dmtf), has been investigated by extended X-ray absorption fine structure (EXAFS) and/or large angle X-ray scattering (LAXS) in solution, and by single crystal X-ray diffraction and/or EXAFS of solid hydrates and solvates. Lead(II) may either form *hemi*directed complexes with large bond distance distribution and an apparent gap for excess electron density, or *holo*directed ones with a symmetric coordination sphere with normal bond distance distribution, depending on the strength of antibonding lead 6s/ligand np molecular orbital interactions and ligand−ligand interactions. The crystallographic data show that the solid lead(II) perchlorate and trifluoromethanesulfonate hydrate structures are hemidirected, while the solid lead(II) solvates of dma and dmpu have regular octahedral configuration with holodirected geometry and mean Pb−O bond distances in the range 2.50−2.52 Å. EXAFS data on the hydrated lead(II) ion in aqueous solution show broad bond distance distribution and a lack of inner-core multiple scattering contributions strongly indicating a hemidirected structure. The Pb−O bond distances found both by EXAFS and LAXS, 2.54(1) Å, point to a six-coordinate hydrated lead(II) ion in hemidirected fashion with an unevenly distributed electron density. The results obtained for the dmso solvated lead(II) ion in solution are ambiguous, but for the most part support a six-coordinate hemidirected complex. The mean Pb−O bond distances determined in dmf and dma solution by LAXS, 2.55(1) and 2.48(1) Å, respectively, indicate that in both solvate complexes lead(II) binds six solvent molecules with the former complex being hemidirected whereas the latter is holodirected. The dmpu and tmu solvated lead(II) ions have a regular holodirected octahedral configuration, as expected given their space-demanding characteristics and ligand−ligand intermolecular interactions. The dmtf solvated lead(II) ion in solution is most likely five-coordinate in a hemidirected configuration, with a mean Pb−S bond distance of 2.908(4) Å. New and improved ionic radii for the lead(II) ion in 4−8-coordination in hemi and holodirected configurations are proposed using crystallographic data.

Introduction

In accordance with the general rule concerning oxidation states of the p block elements, lead as a group 14 element, displays the oxidation states +II and +IV with preference for the former. The tendency of the heavier main group elements to adopt an oxidation state two steps below the highest possible oxidation state has been attributed to the effect of the so-called "inert electron-pair".[1] This property was explained by the relativistic stabilization of the 6s orbital, caused by the direct relativistic effect and the presence of the filled 4f subshell. The lead(IV) compounds are strong oxidants in aqueous systems, being spontaneously reduced to lead(II) under formation of oxygen gas.

The broad range of coordination numbers from 2 to 12 exhibited by lead(II), if counting all nearest neighbors, results in a large variety of configurations of its complexes and compounds.[2,3] According to the valence bond theory, the inert electron-pair can either occupy a hybrid orbital formed by mixing the 6s and 6p orbitals on the metal ion and as such becoming stereochemically active, or be a pure s^2 electron-pair and thereby stereochemically inactive. In terms of coordination number, this means that the hybrid orbital with

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a lone electron-pair can be considered an additional ligand in the coordination sphere normally even taking up *more* space than that of an ordinary ligand.[4] However, according to molecular orbital theory the classical conception of 6s/6p orbital hybridization on the lead(II) ion is regarded as incorrect. This is because the energy levels of these orbitals are too dissimilar, and the different spatial distribution of their corresponding wave functions.[5−8] Instead, the stereochemical activity observed in lead(II) complexes should be seen as a result of an antibonding lead 6s-ligand np (6s/np) interaction which causes structural distortions to energetically minimize these unfavorable covalent interactions.[5−8] Two general structural types of lead(II) complexes are identified, *hemidirected* and *holodirected*, as proposed by Shimoni-Livny et al.[9] In the former, the electron distribution around the metal ion is greatly unevenly distributed, caused by antibonding metal−ligand interactions creating a visual gap in the coordination sphere, while in the latter the electron distribution, as well as the coordination sphere, is symmetric.

Despite the large number of coordination compounds of lead(II) reported in the solid state,[2,3] extremely little is known about its coordination chemistry in solution including hydrate and solvate complexes. The presence of six water molecules in the first coordination sphere of lead(II) ion was reported by Swift and Sayre on the basis of NMR measurements.[10] Bargar et al. estimated the mean Pb−O bond length to 2.50 Å in an acidic aqueous solution of lead(II) nitrate by means of EXAFS.[11] Varying results have been presented after computer simulations on the structure of the hydrated lead(II) ion depending on the method used. The structure of the hydrated lead(II) ion in gaseous phase has been simulated using DFT and polarized continuum models.[12] Hexa-, hepta-, and octaaqualead(II) ions are very similar in energy, with the latter, with a square antiprismatic configuration, as the most favored one, and which was also believed to be present in solution.[12] According to an ab initio quantum mechanical charge field molecular dynamics (QMCF MD) simulation, 7−9 water molecules surround the lead(II) ion in aqueous solution with the square antiprismatic octaaqualead(II) ion as the dominating species with a mean Pb−O bond length of 2.72 Å.[13] A hepta-coordinate lead(II) ion in a distorted pentagonal bipyramid with the mean Pb−O bond length of 2.70 Å was predicted by means of static and Car−Parrinello molecular dynamics (CPMD) studies within the framework of a DFT approach.[14] The generally longer Pb−O bond distances and sometimes larger coordination numbers obtained in theoretical simulations are due to difficulties, in the Hartree−Fock calculations, with electron correlation and relativistic effects of heavy elements, such as lead.[14]

The lead(II) ion undergoes hydrolysis in weak acidic aqueous solution. The primary products of hydrolysis are the mononuclear $[Pb(OH)]^+$ complex ($pK_a = 7.9$) in dilute solutions and the tetranuclear $[Pb_4(OH)_4]^{4+}$ complex in more concentrated ones.[15,16] Also, the composition of the dominating polynuclear lead(II) hydrolysis complexes changes with increasing pH: $[Pb_4(OH)_4]^{4+}$, $[Pb_3(OH)_4]^{2+}$, and $[Pb_6O(OH)_6]^{4+}$, in the pH range 5−8.5, respectively.[15,17] The structures of these polynuclear species have been reported in both solution and in solid state, though without indicating whether the configuration around the lead(II) ions in aqueous solution is hemi or holodirected.[17,18]

The lead(II) ion is weakly hydrated because of its low charge density. Lead(II) compounds normally crystallize without coordinated water molecules or with only a limited number of water molecules and thereby are unable to form a complete hydration shell. Additionally, only a few homoleptic lead(II) complexes with neutral and monodentate ligands have been reported and structurally characterized in the solid state: $[C_8H_{18}N_2][Pb(OCHN(CH_3)_2)_6][Pb_5I_{14}]$,[19] $[Pb(OC_{11}H_{12}N_2)_6](ClO_4)_2$,[20] $[Pb(O_5C_{19}H_{31}N_5Si)_8](C_6H_2N_3O_7)_2$,[21] $[Pb(SC(NH_2)_2)_6](ClO_4)_2$,[22] and $[Pb(SC(N(C_6H_{12})_2)_2)_6](SCN)_2$.[23] The structure of the hexakis(*N,N*-dimethylformamide)lead(II) ion is clearly hemidirected with a mean Pb−O bond distance of 2.536 Å (range 2.374−2.637 Å).[19] The hexakis(antipyrine)lead(II) ion, on the other hand, is holodirected with an almost regular octahedral configuration with O−Pb−O bond angles of 85.42, 94.58, and 180.00°, and an equidistant Pb−O bond length of 2.446 Å.[20] Antipyrine is space-demanding upon coordination, and it is apparently energetically favorable for lead(II) to form a holodirected octahedral complex instead of a hemidirected one with lower coordination number. The oxygens in the holodirected octakis((D)-(5′-(*t*-butyldimethylsilyl)-2′,3′-di-*O*-isopropylidene)guanosine)lead(II) complex form a distorted cube around lead(II), with a mean Pb−O bond distance of 2.668 Å (range 2.603−2.739 Å).[21] The lead(II) ion also forms a ten-coordinate solvate complex with the bidentate acetylacetone, $[Pb(Hacac)_5]^{2+}$, in solution with a mean Pb−O bond distance of 2.724(5) Å.[24] This complex is

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certainly holodirected, as it is typical for lead(II) complexes with coordination numbers of nine or higher.[9] In contrast, all four- and five-coordinate lead(II) complexes with oxygen and sulfur donor ligands are clearly hemidirected, Supporting Information, Table S1.[2,3] The hexakis(thiourea)lead(II) ion is six-coordinate with a distorted octahedral configuration with S−Pb−S bond angles of 79.79, 100.21, and 180.00°, and a wide bond distance distribution with mean Pb−S bond length of 3.110 Å (range 2.862−3.239 Å) showing the typical signs of a hemidirected complex.[22] A wide range of six-coordinate lead(II) complexes with bidentate sulfur donor ligands have the very same configuration and are all regarded as hemidirected, Supporting Information, Table S1. On the other hand, the six-coordinate lead(II) complex of the space-demanding ligand *N,N′*-dicyclohexylthiourea has a narrow bond distance distribution (range 2.961−2.964 Å), and S−Pb−S bond angles in the range of 74.10−105.90° (and 180°).[23] Even though the hexakis(*N,N′*-dicyclohexylthiourea)lead complex has S−Pb−S angles different from 90° it may be regarded as holodirected, based on the bond distance distribution, the only one listed in Cambridge Structural Database.[2]

Lead(II) is six- to eight-coordinate in dimethylsulfoxide (dmso) solvated lead(II) perchlorate compounds.[25] In one of the compounds, lead(II) forms two complexes in the same compound where it is six-coordinate in $[(O_3ClO)((CH_3)_2SO)_3Pb(\mu^2\text{-}ClO_4)_2Pb(OS(CH_3)_2)_3(OClO_3)]$ in slightly distorted octahedral fashion, and eight-coordinate in $[(\kappa^2\text{-}O_2ClO_2)_2(OS(CH_3)_2)_2Pb(\mu^2\text{-}OS(CH_3)_2)_2Pb(OS(CH_3)_2)_2(\kappa^2\text{-}O_2ClO_2)_2]$ in slightly distorted octahedral fashion, if the bidentate perchlorates are considered to occupy one coordination site each. This view is justified as the $Pb-O_{ClO4}$ bond distance is much longer than the $Pb-O_{dmso}$ ones. At the same time, the distance between the binding perchlorate oxygens is short, making the cone angle (see definition below) fairly small and the spatial requirement for the bidentate perchlorate ligand is similar to an ordinary bound dmso molecule. In fact, in both complexes the dmso molecules are much more strongly bound than the perchlorate ions indicated by the about 0.6 Å shorter mean Pb−O bond length. In the other compound, $[Pb(OS(CH_3)_2)_5(\kappa_2\text{-}O_2ClO_2)](ClO_4)$, lead(II) binds five dmso stronger, mean Pb−O bond distance 2.446 Å, than the two oxygens from the perchlorate ion, mean Pb−O bond distance 3.143 Å. Also in this structure, if the bidentate perchlorate ion is considered to occupy one coordination site, the ligands form a slightly distorted octahedron around lead(II). These lead(II) dmso/perchlorate complexes are all holodirected, which is unusual for ligands not considered space-demanding in a complex with such a low coordination number. The crystal structure of a third compound, $[Pb((CH_3)_2SO)_6](ClO_4)_2$, was not possible to solve[25] and confirmed by us in this study, possibly because of severe twin formation of the crystals. The hexagonal symmetry of the unit cell of this compound, however, supports an octahedral geometry of the hexakis(dimethylsulfoxide)lead(II) ion.

Apart from some data for the hydrate and some hydrolysis products in aqueous solution[10,11,15] and for the acetylacetone solvated lead(II) ion in solution,[24] no other experimental structural information is available for solvated lead(II) ions in any other solvent. In this investigation a series of oxygen donor solvents with different physicochemical properties and steric demands upon coordination has been used to study the coordination chemistry of lead(II) in solution. The molecules of water, dmso, and dmf occupy a smaller space around the metal atom than more space demanding ligands like dma, dmpu, and tmu. To compare the bulkiness of the studied ligands we assign for each of them a value resembling the ligand cone angle introduced by Tolman for phosphines.[26] These approximated values increase from 28° for water to 84° for tmu, Table 1. For water the angle was calculated assuming an O−H bond length of 0.96 Å and an H−O−H angle of 104.45°, and for the rest of the ligands they were taken from crystal structural data as referenced.

Table 1. Solvents, Their Respective Formulas and Calculated Cone Angles for the Donor Solvents Used in This Study[a]

solvent, chemical formula	cone angle/deg	reference
water, H_2O	28	*n*/*a*[b]
N,N-dimethylthioformamide, $(CH_3)_2NCHS$	42	[c]
N,N-dimethylformamide, $(CH_3)_2NCHO$	45	19
dimethylsulfoxide, $(CH_3)_2SO$	54	25
N,N-dimethylacetamide, $(CH_3)_2NC(CH_3)O$	68	this work, **5**
N,N′-dimethylpropyleneurea, $(CH_2)_3(NCH_3)_2CO$	81	this work, **6**
1,1,3,3-tetramethylurea, $(CH_3)_2NCON(CH_3)_2$	84	27[d]

[a] Determined by placing the metal atom in the apex and choosing the two terminal atoms yielding the largest value of the angle with a M−O or M−S bond length 2.5 or 2.9 Å, respectively. [b] For water the angle was calculated assuming an O−H bond length of 0.96 Å and an H−O−H angle of 104.45°. [c] The cone angle for dmtf was calculated using $[Cd(dmtf)_6](ClO_4)_2$ as a starting point. [d] As no crystalline lead(II) tmu compound has been reported, $Ce(tmu)(C_5H_5)_3$ was used as model.

As an aprotic ambidentate solvent with a high donor number, $D_S = 27.5$,[28] dmso usually coordinates via the oxygen atom, but for noble metal ions such as rhodium(III), ruthenium(II,III), palladium(II), and platinum(II) coordination takes place also via the sulfur atom.[29] *N,N′*-dimethylpropyleneurea (dmpu) is an monodentate oxygen donor solvent with good electron-pair donating ability, $D_S = 34$, and space-demanding properties upon coordination. This manifests itself in many metal ions as a lower coordination number than in corresponding hydrates and dmso solvates.[30,31] 1,1,3,3-Tetramethylurea (tmu) is a solvent similar to dmpu but with a less rigid structure and lower donor strength, $D_S = 24$.[28] *N,N*-dimethylformamide (dmf) and *N,N*-dimethylacetamide (dma) are aprotic solvents with very similar chemical properties and relatively good electron-pair donor properties, $D_S = 24$ for both solvents, though, it can be expected that dma requires slightly more space at coordination than dmf does based on the shape of the molecule. *N,N*-Dimethylthioformamide (dmtf) is the corresponding sulfur donor solvent to dmf with some hydrogen bonding ability.[32] It has soft Lewis base character, $D_S = 52$, which results in strong interactions with soft electron-pair acceptors.

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The coordination chemistry of lead(II) is unique from several points of view. There is obviously a thin balance between hemi and holodirected complexes, which needs to be further studied and systematically described. The coordination of hydrates and solvates are preferably studied in solution as lattice energies are certainly large enough to force a change in the type of configuration. The aim of the present work is to investigate the structure of the solvated lead(II) ion in a series of oxygen donor solvents, water, dmso, dmf, dma, dmpu, and tmu, and in the sulfur donor solvent dmtf by means of large-angle X-ray scattering, LAXS, and/or extended X-ray absorption fine structure, EXAFS, spectroscopy. The crystal structures of diaquatetra(perchlorato)dilead(II) monohydrate, monoaquabis(trifluoromethanesulfonato)lead(II), hexakis(dmpu)lead(II) trifluoromethanesulfonate, and hexakis(dma)lead(II) perchlorate were solved to support the structure determination in solution, and to get more detailed information of hemi and holodirected complexes.

Experimental Section

Solvents. All *water* used was Milli-Q-filtered. *Dimethylsulfoxide*, $(CH_3)_2SO$ (Merck), *N,N′-dimethylpropyleneurea*, $OCN_2(CH_3)_2(CH_2)_3$ (Aldrich), *1,1,3,3-tetramethylurea*, $OCN((CH_3)_2)_2$ (Aldrich) were distilled over calcium hydride (Aldrich) under reduced pressure before use. *N,N-Dimethylformamide*, $(CH_3)_2NCHO$ (Aldrich, 99%), and *N,N-dimethylacetamide*, $(CH_3)_2NC(CH_3)O$ (Aldrich, 99%) were used as purchased without further purification. *N,N-Dimethylthioformamide*, $SCHN(CH_3)_2$, was prepared from *N,N*-dimethylformamide (Aldrich) and phosphorus pentasulfide (Merck) following the procedure described by Gutmann et al.[33,34]

Chemicals. *Lead(II) perchlorate trihydrate*, $Pb(ClO_4)_2\cdot 3H_2O$ (Aldrich), was used as purchased. Diaquatetrakis(perchlorato)dilead(II) monohydrate (diaquabis(μ^2-perchlorato-*O*,*O′*,*O″*,*O‴*)(μ^2-perchlorato-*O*,*O′*,*O″*)(μ^2-perchlorato-*O*,*O′*)dilead(II), $[Pb_2(H_2O)_2(ClO_4)_4]_n$, **1**, was formed at recrystallization of lead(II) perchlorate trihydrate in 0.1 mol·dm^{-3} perchloric acid. *Anhydrous lead(II) trifluoromethanesulfonate*, $Pb(CF_3SO_3)_2$, was prepared from *trifluoromethanesulfonic acid*, CF_3SO_3H (Fluka) and *lead(II) oxide*, PbO (Fluka), by a method previously described.[35] *Monoaquabis(trifluoromethanesulfonato)lead(II)*, $[Pb(H_2O)(CF_3SO_3)_2]_n$, **2**, was formed at crystallization of a very concentrated solution of lead(II) trifluoromethanesulfonate in dilute trifluoromethanesulfonic acid (0.1 mol·dm^{-3}). *Hexakis(dimethylsulfoxide)lead(II) perchlorate,* $[Pb(OS(CH_3)_2)_6](ClO_4)_2$, **3**, was prepared by dissolving 0.02 mol of lead(II) perchlorate trihydrate in about 10 mL of acetone and, after a few minutes of stirring, adding 0.06 mol of 2,2-dimethoxypropane (Merck). The solution was stirred vigorously for 2 h, after which 0.12 mols of dimethylsulfoxide was added and the solution was stirred for another 30 min. The volume of this solution was halved by evaporation and put into a refrigerator, or freezer, if no precipitation takes place. The formed crystals were recrystallized from dimethylsulfoxide. The unit cell of this compound was determined to be trigonal/hexagonal, a = 20.407(6) and c = 6.759(2) Å in agreement with previous reports.[25] *Hexakis(N,N-dimethylformamide)lead(II) perchlorate,* $[Pb(OCHN(CH_3)_2)_6](ClO_4)_2$, **4**, and *hexakis(N,N-dimethylacetamide)lead(II) perchlorate,* $[Pb(OC(CH_3)N(CH_3)_2)_6](ClO_4)_2$, **5**, were prepared according the route described for **3**. **4** has a melting point of about 280 K, significantly lower than that of **5**, which melts at 337.2 K.

Table 2. Compositions (in mol·dm^{-3}), Densities (ρ), and Linear Absorption Coefficients (μ) of the aqueous, dmso, dmpu, tmu, dmf, dma, and dmtf Solutions Used in the LAXS and/or EXAFS Measurements

Sample	[Pb^{2+}]	[X$^-$]	[solvent]	ρ/g·cm^{-3}	μ/cm^{-1}
$Pb(ClO_4)_2$ in water [a,b]	1.000	2.100	52.014	1.353	27.02
$Pb(ClO_4)_2$ in water [a,b]	1.900	3.900	45.880	1.608	50.14
$Pb(NO_3)_2$ in dmso [a,b]	1.032	2.064	12.998	1.456	30.77
$Pb(CF_3SO_3)_2$ in dmpu [b]	0.300	0.600	7.512	1.114	8.36
$Pb(CF_3SO_3)_2$ in tmu [a]	0.300	0.600	8.245	1.109	8.35
$Pb(CF_3SO_3)_2$ in dmf [b]	0.736	1.471	11.554	1.216	19.68
$Pb(CF_3SO_3)_2$ in dma [b]	0.814	1.628	9.526	1.241	21.66
$Pb(CF_3SO_3)_2$ in dmtf [a,b]	1.018	2.036	9.872	1.395	29.61

[a] EXAFS. [b] LAXS.

Hexakis(dmpu)lead(II) trifluoromethanesulfonate, $[Pb(OCN(CH_3)_2(CH_2)_3)_6](CF_3SO_3)_2$, **6**, was prepared by crystallization of lead(II) trifluoromethanesulfonate in dmpu. We could not obtain any crystals from the concentrated solution of lead(II) trifluoromethanesulfonate in dmso, and of lead(II) trifluoromethanesulfonate and perchlorate in dmtf. The crystals grown in the dmso solution of lead(II) nitrate and those in tmu solution of lead(II) trifluoromethanesulfonate were extremely unstable and were left undetermined.

Preparation of Solutions. The aqueous lead(II) perchlorate solutions were prepared by dissolving lead(II) perchlorate trihydrate in 0.1 mol·dm^{-3} perchloric acid. The dmf and dma solutions were prepared by dissolving weighed amounts of **4** and **5**, respectively. The dmpu, tmu, and dmtf solutions were prepared by dissolving anhydrous lead(II) trifluoromethanesulfonate in the neat solvents, and the dmso solution by dissolving lead(II) nitrate. The lead(II) content was determined after dilution in water by EDTA titration using eriochrome black T as an indicator.[36] The compositions of the studied solutions are summarized in Table 2.

Single-Crystal X-ray Diffraction. Data were collected on an Xcalibur 2 CCD diffractometer (**1**,**6**), a Bruker SMART CCD 1 k(**2**,**5**), or a KUMA KM4 four circle diffractometer ($\mathbf{6_{RT}}$) at 100 K or ambient room temperature, Table 3. Several attempts with crystal structure measurements were carried out, and the best results are presented here. The structures were solved by standard direct methods in the SHELXTL program package[37] and refined by full matrix least-squares isotropically on F^2 and finally in anisotropic approximation on all non-hydrogen atoms, unless noted. Hydrogen atoms were detected in the difference Fourier syntheses and refined using a riding model. All calculations were performed with the SHELXTL programs in PC version (v. 5.3).[37] Selected crystal and experimental data are summarized in Table 3. The atomic coordinates, bond distances and angles are available in Crystallographic Information Files (CIFs) as Supporting Information.

The crystals of **1** are extremely hygroscopic, and the concentration range where single crystals can be obtained in the mother liquid is very narrow. The examined single crystal of **1** was taken from the mother liquid and put on a microscope glass slide placed directly on dry ice under a steady stream of dry nitrogen gas. During these conditions the crystals of **1** were stable enough to be mounted on a glass needle. The data collection was performed at 100 K under a stream of dry nitrogen gas. The other crystals were mounted in glass capillaries, which were sealed by burning immediately after mounting.

Powder Diffraction. A powder diffraction experiment was performed on a PANalytical X'Pert PRO diffractometer on lead(II) perchlorate trihydrate to check if the commercial product was

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Table 3. Crystallographic Data and Structure Refinement Details for Lead(II) Compounds **1**, **2**, **5**, and **6**

	1	**2**	**5**	**6**	$\mathbf{6_{RT}}$
formula	$\{[Pb_2(H_2O)_2(ClO_4)_4]\}_n$ $H_4Cl_4O_{18}Pb_2$	$[Pb(H_2O)(CF_3SO_3)_2]_n$ $C_2H_2F_6O_7S_2Pb$	$[Pb(dma)_6](ClO_4)_2$ $C_{36}H_{54}N_6O_{14}Cl_2Pb$	$[Pb(dmpu)_6](CF_3SO_3)_2$ $C_{38}H_{72}N_{12}O_{12}F_6S_2Pb$	$[Pb(dmpu)_6](CF_3SO_3)_2$ $C_{38}H_{72}N_{12}O_{12}F_6S_2Pb$
M_W	848.21	523.35	928.82	1274.39	1274.39
diffractometer system	Xcalibur 2	Bruker Smart CCD	Bruker Smart CCD	Xcalibur 2	Kuma KM4
radiation, λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	trigonal	triclinic	trigonal
space group	$P2_1$ (No. 4)	$P2_1/c$ (No. 14)	$P\bar{3}$ (No. 147)	$P\bar{1}$ (No. 2)	$P\bar{3}$ (No. 147)
a/Å	7.1961(3)	10.546(2)	12.356(3)	13.5036(2)	13.841(2)
b/Å	9.8875(3)	10.303(2)	12.356(3)	15.7483(3)	13.841(2)
c/Å	12.5017(5)	22.885(5)	7.409(2)	21.7328(3)	8.4427(7)
α/deg	90	90	90	81.6924(14)	90
β/deg	90.764(4)	113.597(8)	90	72.5196(14)	90
γ/deg	90	90	120	64.9178(16)	120
V/Å^3	889.43(6)	2278.7(9)	979.6(4)	3991.76(11)	1400.8(4)
T/K	293(2)	295(2)	296(2)	100(2)	293(2)
Z	4	4	1	3	1
D_c/g cm^{-1}	3.436	3.051	1.574	1.590	1.511
F^2	840	1904	468	1944	648
μ/mm^{-1}	19.616	15.282	4.506	3.335	3.168
crystal size/mm^3	0.35 × 0.30 × 0.25	0.50 × 0.20 × 0.05	0.21 × 0.17 × 0.14	0.15 × 0.08 × 0.06	0.30 × 0.15 × 0.10
θ range/deg	5.88−30.50	2.11 - 25.03	2.75 - 24.96	3.80−25.68	
index ranges	$-10 \leq h \leq 10$ $-11 \leq k \leq 14$ $-17 \leq l \leq 16$	$-11 \leq h \leq 12$ $-12 \leq k \leq 12$ $-27 \leq l \leq 24$	$-14 \leq h \leq 14$ $-13 \leq k \leq 14$ $-8 \leq l \leq 8$	$-16 \leq h \leq 16$ $-19 \leq k \leq 18$ $-21 \leq l \leq 26$	$-11 \leq h \leq 11$ $-12 \leq k \leq 12$ $-8 \leq l \leq 8$
measured reflections	8039	10771	7313	45609	1132
unique reflections	3969	3991 (R_{int} = 0.1743)	1148 (R_{int} = 0.0276)	15126 (R_{int} = 0.0447)	824 (R_{int} = 0.0486)
data/restraints/params	2595/94/53	3991/52/311	1148/0/76	15126/422/1027	824/3/110
goodness of fit	2.350	0.747	1.071	1.012	1.093
refinement method	full-matrix least-squares on F^2				
final R_1, wR_2 [$I > 2\sigma(I)$]^a	0.1081,0.2785	0.0630, 0.1379	0.0246, 0.0634	0.0441, 0.1048	0.044, 0.1159
largest diff. peak/hole e Å^{-3}	6.277/-9.264	2.622/-2.102	0.992/-0.470	3.700/-3.553	0.939/-1.091

[a] R values are defined as: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

identical to **1** or not. Lead(II) perchlorate trihydrate showed poor crystallinity, but is most probably different from **1**.

EXAFS - Data Collection. Lead L_3-edge X-ray absorption spectra were recorded at the previous wiggler beamline 4−1 at the Stanford Synchrotron Radiation Lightsource (SSRL). The EXAFS station was equipped with a Si[220] double crystal monochromator. SSRL operated at 3.0 GeV and a maximum current of 100 mA. The data collection was performed in transmission mode and at ambient temperature. Higher order harmonics were reduced by detuning the second monochromator to 50% of maximum intensity at the end of the scans. The solutions were placed in cells with Mylar foil windows and 1−5 mm Teflon spacers depending on concentration. The energy scale of the X-ray absorption spectra was calibrated by assigning the first inflection point of the L_3 edge of a lead foil to 13038.0 eV.[38] For each sample 3−6 scans were averaged, giving satisfactory data (k^3-weighted) in the k range 2−15.5 Å. The EXAFSPAK program package was used for the primary data treatment.[39]

EXAFS - Data Analysis. The data analyses were performed by means of the GNXAS code to get the best possible splines. The GNXAS code is based on the calculation of the EXAFS signal and a subsequent refinement of the structural parameters.[40,41] The GNXAS method accounts for MS paths, with correct treatment of the configurational average of all 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 the studied complex has to account for asymmetry in the distribution of the ion−solvent distances.[41,42] Therefore the 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; β is related to the third cumulant C_3 through the relation $C_3 = \sigma^3\beta$. It is important to stress that the position of the maximum of the distribution, R_m, is different and shorter than the mean distance.

The standard deviations given for the refined parameters in the tables are obtained from k^2 weighted least-squares refinements of the EXAFS function $\chi(k)$, and do not include systematic errors of the measurements. These statistical error estimates provide a measure of the precision of the results and allow reasonable comparisons, for example, of the significance of relative shifts in the distances. However, the variations in the refined parameters, including the shift in the E_o value (for which $k = 0$), using different models and data ranges, indicate that the absolute accuracy of the distances given for the separate complexes is within ±0.005 to 0.02 Å for well-defined interactions. The "standard deviations" given in the text have been increased accordingly to include estimated additional effects of systematic errors.

Large-Angle X-ray Scattering. A large-angle $\theta-\theta$ diffractometer was used to measure the scattering of Mo Kα radiation (λ = 0.7107 Å) on the free surface of an aqueous solution of lead(II) perchlorate, a dmso solution of lead(II) nitrate, and dmf, dma, dmpu, and dmtf solutions of lead(II) trifluoromethanesulfonate. The solutions were contained in a Teflon cuvette inside a radiation shield with beryllium windows. After monochromatization of scattered radiation, by means of a focusing

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LiF crystal, the intensity was measured at 450 discrete points in the range $1 < \theta < 65°$ (the scattering angle is 2θ). A total of 100,000 counts was accumulated at each angle, and the whole angular range was scanned twice, corresponding to a statistical uncertainty of about 0.3%. The divergence of the primary X-ray beam was limited by 1° or $^{1}/_{4}$° slits for different θ regions with overlapping some part of data for scaling purposes.

All data treatment was carried out by using of the KURVLR program[43] which has been described in detail earlier.[44] The experimental intensities were normalized to a stoichiometric unit of volume containing one lead atom, using the scattering factors f for neutral atoms, including corrections for anomalous dispersion, $\Delta f'$ and $\Delta f''$,[45] and values for Compton scattering.[46] To receive a better alignment of the intensity function, a Fourier back-transformation was applied to eliminate spurious peaks not related to any interatomic distances below 1.2 Å in the radial distribution function (RDF).[47] Least-squares refinements of the model parameters were performed by means of the STEPLR program[48] to minimizing the error square sum $U = \Sigma w(s) \cdot [i_{\text{exp}}(s) - i_{\text{cal}}(s)]^2$.

Results and Discussion

Ionic Radii of Lead(II) Ion. The determination of coordination numbers from structure determinations in solution is connected with large errors, as they are strongly correlated with the Debye−Waller coefficients.[39] On the other hand, for these methods the determination of distances is very accurate, and taken into account that there is a strong correlation between coordination number and bond distance,[49] a very good estimate about the coordination number can be reached from the obtained bond distances alone. To estimate the coordination numbers from the obtained bond distances an overview of the bond distances in solid lead(II) solvates and complexes in different configurations have been made. The ionic radii listed by Shannon and Prewitt[50a] and later revised by Shannon,[50b] did not take the hemi and holodirectionality into account, Supporting Information, Table S1. However, since all reported four-coordinated lead(II) complexes are hemidirected, the given radius can be used as reference for this type of lead(II) ionic radius. Our study of lead(II) complexes with mono- and bidentate oxygen and sulfur donor ligands has resulted in new and improved ionic radii for lead(II) in four- to eight-coordination, Tables 5 and Supporting Information, Table S2. For neutral oxygen and sulfur donor ligands the atom radii are 1.34 Å[51] and 1.75 Å,[52] respectively. To account for the differences between anionic and neutral ligands, the applied values were increased 1.37 Å and 1.80 Å, respectively.[50b] The relationship between ionic radius and coordination number in hemi- and holodirected configurations are given in Figure 1. For 4- and 5-coordinate lead(II) complexes only hemidirected complexes are known, and for coordination numbers larger than eight no difference in ionic radius between hemi and holodirectionality can be distinguished, Figure 1 and Supporting Information, Table S2.

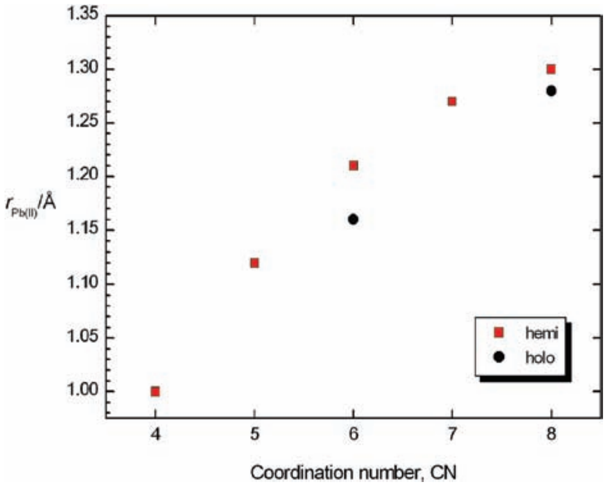

Figure 1. Relationship between ionic radius and coordination number in hemi and holodirected configurations of lead(II) complexes in the solid state, denoted by red squares and black circles, respectively; the detailed data for this figure are summarized in Supporting Information, Table S2.

Crystal Structure of Diaquatetrakis(perchlorato)dilead(II), 1. The crystal structure of **1** was very difficult to solve, likely because of severe disorder, and we have not been able to solve the structure to the normal detailed level with stable structure refinement achieved with only the lead atoms treated anisotropically. However, the basic structure and the atomic arrangement can be described, which is vital for the understanding of the coordination behavior of lead(II). **1** has a polymeric structure where the perchlorate ions link two crystallographically independent lead(II) ions into chains, Figure 2a. The lead(II) ion Pb1 binds seven perchlorate oxygens from four neighboring perchlorate ions, and Pb2 is eight-coordinate binding to two water molecules (O201, O202) and four neighboring perchlorate ions. Each lead(II) ion binds two crystallographically equivalent perchlorate ions in a bidentate fashion totalling four Pb−O bonds; Pb1 binds Cl1O_4 and Pb2 Cl2O_4 in this way, Figure 2a. One perchlorate ion, Cl3O_4, bridges the two lead ions through bidentate bonding to Pb1 (O31, O34) and monodentate to Pb2 (O33), and the last perchlorate ion, Cl4O_4, also bridges the two lead(II) ions (O42, O43). This means that only three of the perchlorate oxygens, O32, O41, and O44, do not bind to either of the crystallographically independent lead(II) ions. The coordination around Pb1 is clearly hemidirected with a large part of the coordination sphere occupied by unsymmetrically distributed electron density taking up a volume much larger than an ordinary bond, and causing a very wide Pb−O bond distribution, 2.334−3.199 Å, Figure 2 and Table 4. The coordination around Pb2 is slightly different with a coordination number of eight and a somewhat smaller gap in the coordination sphere around the lead(II) ion and bond distances in the range 2.338−3.323 Å. The crystallographic data of **1** are given in Table 3. Selected bond distances and bond angles are presented in Table 4.

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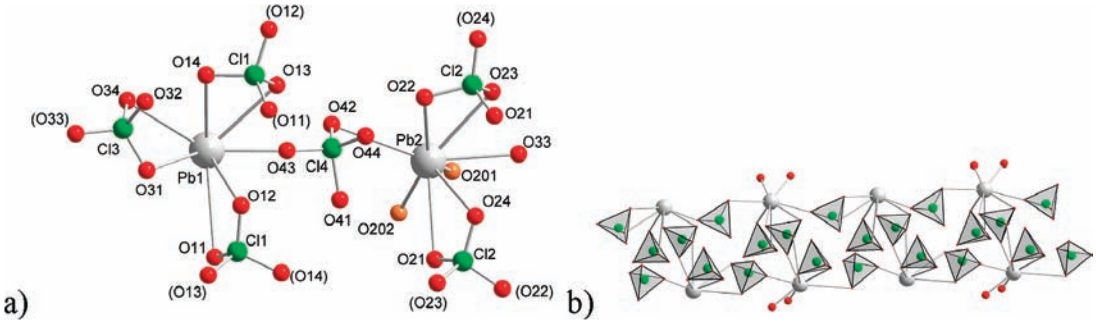

Figure 2. (a) Fragment of the polymeric grid formed by $\{[Pb_2(H_2O)_2(ClO_4)_4]\cdot H_2O\}_n$. (b) The packing of the polymeric structure, viewed along the *b* axis, showing the sheet-like arrangement of the perchlorate ions.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in **1**, **2**, **5**, and **6**

		$[Pb_2(H_2O)_2(ClO_4)_2]_n$, **1**			
Pb1−O43	2.334(14)	Pb2−O201	2.338(24)	O201−Pb2−O202	50.2(7)
Pb1−O13	2.931(15)	Pb2−O202	2.433(20)	O201−Pb2−O33	65.7(6)
Pb1−O14	2.972(16)	Pb2−O33	2.654(13)	O202−Pb2−O33	107.4(6)
Pb1−O31	3.071(14)	Pb2−O23	2.916(13)		
Pb1−O34	3.084(13)	Pb2−O22	2.928(12)		
Pb1−O12	3.128(16)	Pb2−O21	2.943(12)		
Pb1−O11	3.199(15)	Pb2−O24	3.117(15)		
		Pb2−O42	3.323(19)		
		$[Pb(H_2O)(CF_3SO_3)_2]_n$, **2**			
Pb1−O1	2.473(26)	Pb2−O2	2.459(28)	O1−Pb1−O11	66.1(7)
Pb1−O21	2.498(16)	Pb2−O23	2.472(18)	O1−Pb1−O21	83.3(6)
Pb1−O11	2.565(19)	Pb2−O13	2.511(17)	O2−Pb2−O13	82.7(7)
Pb1−O31	2.602(15)	Pb2−O42	2.537(18)	O2−Pb2−O23	73.5(7)
Pb1−O43	2.673(20)	Pb2−O33	2.638(21)		
Pb1−O41	2.716(19)	Pb2−O32	2.723(20)		
Pb1−O12	2.803(21)	Pb2−O22	2.785(19)		
		$[Pb(dma)_6](ClO_4)_2$, **5**			
Pb1−O1	2.519(3)			O1−Pb1−O1′	90.0(1)
				O1−Pb1−O1′	180.0(1)
		$[Pb(dmpu)_6](CF_3SO_3)_2$, **6**			
Pb1−O11	2.516(6)			O11−Pb1−O12	86.4(1)
Pb1−O12	2.481(5)			O12−Pb1−O13	87.7(2)
Pb1−O13	2.491(5)			O11−Pb1−O11	180.0(1)
Pb2−O21	2.536(6)			O21−Pb2−O23	88.0(2)
Pb2−O22	2.510(5)			O21−Pb2−O24	179.6(2)
Pb2−O23	2.513(5)				
Pb2−O24	2.437(6)				
Pb2−O25	2.518(5)				
Pb2−O26	2.525(5)				
		$[Pb(dmpu)_6](CF_3SO_3)_2$, $\mathbf{6_{RT}}$			
Pb−O1	2.520(6)			O1−Pb−O1′	90.2(2)
				O1−Pb−O1	89.8(2)

Crystal Structure of Monoaquabis(trifluoromethanesulfonato)lead(II), 2. **2** has a polymeric structure with the lead(II) ions situated inside the characteristic two-dimensional grid with the $-CF_3$ groups of the CF_3SO_3 moieties directed outside, Figure 3a. Although both lead(II) ions have the same coordinative environment, two crystallographically independent lead(II) ions are distinguished, Pb1 and Pb2, with somewhat different mean Pb−O bond lengths, Table 4. Each lead(II) ion binds strongly to one water molecule, with Pb−O bond lengths of 2.473(26) and 2.459(28) Å for Pb1 and Pb2, respectively, and weakly to six oxygen atoms, originating from six different trifluoromethanesulfonate ions, with bond distances in the range 2.498−2.803 and 2.472−2.785 Å for Pb1 and Pb2, respectively. Pb1 and Pb2 are both seven-coordinate with mean Pb−O bond lengths of 2.619 and 2.589 Å, respectively. The $CF_3SO_3^-$ ions display a role as *O*,*O*′,*O*″-bridges connecting three lead atoms, either two Pb1 and one Pb2 or two Pb2 and one Pb1. The unsymmetric electron distribution seems to push the surrounding oxygens to angles larger than in a regular square antiprism and thereby limiting the number of oxygens opposite to the highest electron density in the coordination shell to three because of the ligand−ligand repulsion. The geometry around the lead(II) ion in **2** is therefore hemidirected but with a smaller gap in the coordination sphere than in **1**. The unresolved electronic density around the lead atoms and possible disorder in the structure made

Table 5. New and Improved Ionic Radii for Lead(II) in Different Coordination Numbers from This Study Compared with the "IR" Values Listed by Shannon and Prewitt, r_{SP} (ref 50b) and Shannon, r_{Sh} (ref 50a)[a]

Lead(II) coord. geometry	r_{SP}/Å[b]	r_{Sh}/Å[b]	r_{new}/Å	no. struct. (r_{SP}, r_{Sh}, r_{new})
CN = 4, hemidirected	0.94	0.98 (calc.)	1.00	3, 1[c], 20*O*+7*S*
CN = 5, hemidirected	*n*/*a*	*n*/*a*	1.12	*n*/*a*, *n*/*a*, 8*O*+1*S*
CN = 6, hemidirected	*n*/*a*	[d]	1.21	*n*/*a*, 3 + 1[d], 4*O*+5*S*
CN = 6, holodirected	1.18	[d]	1.16	3, 3 + 1[d], 5*O*+1*S*
CN = 7, hemidirected	*n*/*a*	1.23 (calc.)	1.27	*n*/*a*, 2, 8*O*
CN = 8, hemidirected	[e]	[e]	1.30	5[e], 5[e], 3*O*
CN = 8, holodirected	[e]	[e]	1.28	5[e], 5[e], 5*O*

[a] The lead(II) radius is calculated using an oxygen radius of 1.37 Å for *O*-donor anions and 1.34 Å for neutral *O*-donor ligands, as reported for water by Beattie et al. (ref 51.), and a sulfur radius of 1.80 Å for *S*-donor anions and 1.75 Å for neutral *S*-donor ligands, as reported for dmtf by Lundberg (ref 52.). Contrary to the "IR" values, the r_{new} values are the results of studies in crystalline solvates and as such less influenced by crystal lattice energies. CN = coordination number. [b] The reported values were not classified as hemi or holodirected by Shannon and Prewitt or by Shannon, but are specified here whenever possible for comparison purposes. [c] It is unclear if only one reference was used, as the only one listed in ref 50a is one of the three given in ref 50b. This change may explain why the radius has been noted as less reliable, i.e. "(calc.)". [d] The new reference value given in Shannon's revision is an unfortunate one, as it without any doubt is a hemidirected complex. The resulting "mixed-directed" lead(II) ionic radius is reported to be 1.19 Å. [e] No distinction is made between hemi and holodirected complexes. Reported CN = 8 $r_{Pb(II)}$: 1.29 Å.

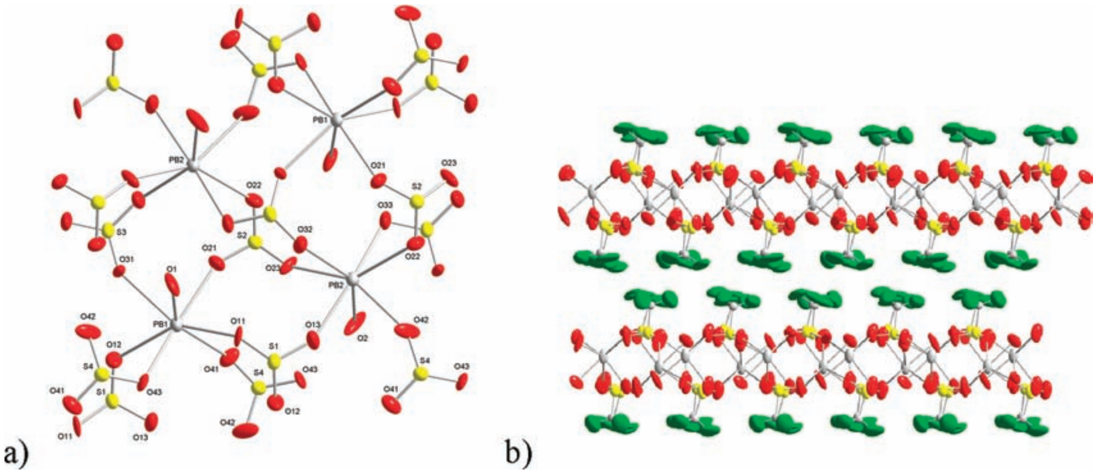

Figure 3. (a) Fragment of the polymeric grid formed by $[Pb(H_2O)(CF_3SO_3)_2]_n$, with the $-CF_3$ part of the trifluoromethanesulfonate anions omitted for clarity. (b) The packing of the polymeric structure, viewed along the *b* axis, showing the sheet-like arrangement of the trifluoromethanesulfonate ions. Thermal ellipsoids of non-hydrogen and non-carbon atoms are shown at 30% probability level.

anisotropic refinement of the trifluoromethanesulfonate carbon atoms not possible. Albeit undesirable, this ought to have little or no effect on the studied coordination properties of lead(II). The crystallographic data of **2** are given in Table 3.

In the analogous system with thallium(III), a monomeric complex, $[Tl(H_2O)_3(\kappa\text{-}OSO_2CF_3)_3]$, is formed.[53] Mercury(II) ions form a chain structure, $[Hg(H_2O)_2(\mu_2\text{-}OSO_2CF_3)_2]_\infty$,[54] where two water molecules are strongly bound in linear fashion and two trifluoromethanesulfonate oxygens connect the $Hg(H_2O)_2$ units through double bridges with Hg−O bond distances about 0.35 Å longer than those seen for the water molecules. These structures show that the trifluoromethanesulfonate ion is able to form well-defined complexes with heavy element ions as mercury(II), thallium(III), and lead(II) when crystallized from acidic aqueous solution and thereby showing a significant competitiveness with water, at least in concentrated solutions. Trifluoromethanesulfonate salts should therefore not be used as supporting electrolytes in such systems. We have also experienced that several metal ion solvates decompose much more easily in organic solvents as trifluoromethanesulfonate salts compared to the perchlorate ones. Selected bond distances and bond angles for the lead compound are presented in Table 4.

Hydrated Lead(II) Ion in Aqueous Solution. The EXAFS and LAXS data of the hydrated lead(II) ion in aqueous solution show an obvious damping in the intensity functions, (Figures 4, 5 and Supporting Information, Figure S1a) implying that the Debye−Waller factor coefficients of the Pb−O bond distances are large, and thereby with wide bond distance distribution. The EXAFS data could be well fitted with a model only containing a single Pb−O distance, including a C_3 factor for asymmetric bond distance distribution, Figures 4 and Supporting Information, Figure S1a. The refinement of the EXAFS data gave mean Pb−O bond distances of 2.541(6) and 2.543(6) Å, R_m = 2.52 Å, for the 1.0 and 1.9 mol dm^{-3} solutions, respectively. The large damping of the EXAFS functions is caused by a large Debye−Waller factor coefficient, σ^2 = 0.027(1) and 0.024(1) Å^2, respectively, Figure 4. The Pb−O distance displays only a small asymmetry with regard to the large Debye−Waller factor coefficient, $C_3 = 1.3 \times 10^{-4}$ and 3.3×10^{-4} Å^3 in the 1.0 and 1.9 mol dm^{-3} solutions, respectively.

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(53) Molla-Abbassi, A.; Eriksson, L.; Lindqvist-Reis, P.; Mink, J.; Persson, I.; Sandström, M.; Skripkin, M.; Ullström, A.-S. *J. Chem. Soc., Dalton Trans.* **2002**, 4357–4364.

(54) Molla-Abbassi, A.; Eriksson, L.; Mink, J.; Persson, I.; Sandström, M.; Skripkin, M.; Ullström, A.-S.; Lindqvist-Reis, P. *J. Chem. Soc., Dalton Trans.* **2002**, 4357–4364.

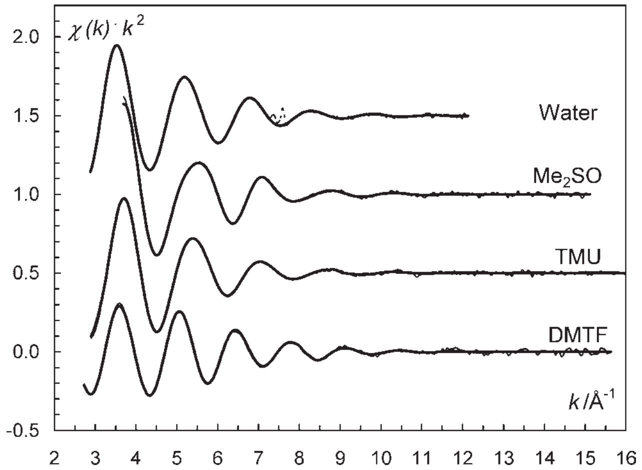

Figure 4. Experimental EXAFS data (solid lines) fitted with a model (Table 3) formed by ab initio-calculated scattering paths from the FEFF program (dashed lines).

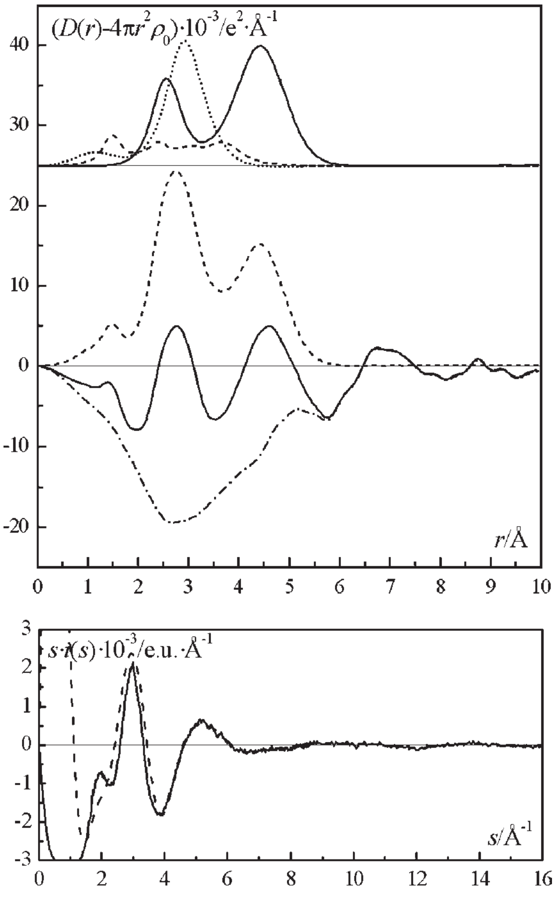

Figure 5. (Top) LAXS radial distribution curves for a 1.00 mol$\cdot$dm^{-3} aqueous solution of lead(II) perchlorate. Upper part: Separate model contributions (offset: 25) of the hydrated lead(II) ion (solid line), the perchlorate ion (dashed line) and aqueous bulk (dotted line). (Middle) Experimental RDF: $D(r) - 4pr^2\rho_o$ (solid line); sum of model contributions (dashed line); difference (dash-dotted line). (Bottom) Reduced LAXS intensity functions $s\cdot i(s)$ (solid line); model $s\cdot i_{calc}(s)$ (dashed line).

The wide Pb−O bond distance distribution and the absence of multiple scattering contributions indicates that the hydrated lead(II) ion is hemidirected.

The RDFs from the LAXS experiments on the aqueous lead(II) perchlorate solutions reveal three peaks at 1.45, 2.65, and 4.5 Å, see Figures 5 and Supporting Information, Figure S2. The peak at 1.45 Å corresponds to the Cl−O bond distance in the perchlorate ion. The fairly broad peak at 2.65 Å has two contributions. The main contribution is the Pb−O bond distance in the first hydration shell, and the other contribution is the intramolecular O$\cdots$O distance in the aqueous bulk. The broad peak at 4.5 Å corresponds to the second hydration shell, Pb$\cdots$O$_{II}$. The shoulder around 3.0 Å corresponds to the O$\cdots$O distances within the aqueous bulk, O$_w\cdots$O$_w$, between the water molecules in the first and second hydration sphere, O$_I\cdots$O$_{II}$, and from O$_w\cdots$O$_p$ distances between water molecules hydrogen bound to the perchlorate ion. The Pb−O bond distance has been refined to 2.527(7) and 2.536(5) Å, and the Pb$\cdots$O$_{II}$ distance to 4.41(4) and 4.461(9) Å in the 1.0 and 1.9 mol dm^{-3} aqueous solutions, respectively. The temperature factors of the Pb−O bond distances are unusually large for a hydrated divalent metal ion, b = 0.019(2) and 0.024(2) Å^2. These values are about twice as large as those found for hydrated divalent transition metal ions.[55] This is evidence that the Pb−O bond and the Pb$\cdots$O$_{II}$ distances in the hydrated lead(II) ion have a very wide bond distance distribution, and that no O$\cdots$O distances from the inner coordination core were observed, which they normally are in regular octahedral hydrates.[55] The structure of the hydrated perchlorate ion is identical to the one reported in previous studies of perchlorate salts in aqueous solution, with a Cl−O bond distance of 1.453(2) Å.[56]

The mean number of water molecules bound to the lead(II) ion cannot be unambiguously determined from these measurements. Using the ionic radius of the lead(II) ion derived in this paper, Table 5, the expected holodirected Pb−O bond distance in six- and eight-coordination is 2.50 and 2.62 Å, respectively, while the hemidirected Pb−O bond distance in six-coordination is 2.55 Å. These distances were calculated from the corresponding radii of lead(II), $r_{Pb(II)}$ = 1.16, 1.28, and 1.21 Å, respectively, and r_{Owater} = 1.34 Å.[51] The experimental results together with the mean bond distance and the width of the bond distance distribution indicate that the hydrated lead(II) ion in aqueous solution is six-coordinate in hemidirected fashion. The structure parameters from the LAXS and EXAFS measurements are summarized in Tables 6 and 7.

Dimethylsulfoxide Solvated Lead(II) Ion. The fitting of the EXAFS data of the dmso solvated lead(II) ion in solution (Figure 4) resulted in a similar pattern as found for the hydrated lead(II) ion in aqueous solution with a broad bond distance distribution and no multiple scattering from the inner-coordination core of the solvate. The three-leg Pb−O−S scattering path gives, as expected, a significant contribution to the EXAFS signal. The refinements yielded Pb−O and S−O bond distances of 2.517(10) and 1.543(8) Å, respectively, and a Pb−O−S bond angle of 131.7(9)° corresponding to a Pb$\cdots$S distance of 3.723(16) Å. The Debye−Waller factor of the Pb−O bond distance, σ^2, is very large, 0.020(2) Å^2, while it is in normal range for the S−O bond, 0.003(1) Å^2. The fit of the EXAFS data are

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(55) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157–1204, and references therein;. Johansson, G. *Adv. Inorg. Chem.* **1992**, *39*, 159–232, and references therein.

(56) Lindqvist-Reis, P.; Muñoz-Páez, A.; Díaz-Moreno, S.; Pattanaik, S.; Persson, I.; Sandström, M. *Inorg. Chem.* **1998**, *37*, 6675–6683.

Table 6. Mean Bond Distances, *d*/Å, Number of Distances, *N*, Temperature Coefficients, *b*/Å^2, and the Root-Mean-Square Variation, *l*/Å, in the LAXS Studies of the Solvated Lead(II) Ion in aqueous, dmso, dmf, dma, dmpu, and dmtf Solution at Room Temperature

species	interaction	*N*	*d*	*b*	*l*
Lead(II) Perchlorate in Water, 1.0 mol·dm^{-3}					
$Pb(OH_2)_6^{2+}$	Pb−O	6	2.527(7)	0.0193(6)	0.196
	$Pb\cdots O_{II}$	12	4.42(4)	0.072(4)	0.38
ClO_4^- (aq)	Cl−O	4	1.453(4)	0.0020(2)	0.063
	(Cl-)O···O	4	3.040	0.0075	0.12
	Cl-(O)···O	4	3.700	0.0250	0.22
Water bulk	O···O	2	2.889(5)	0.0187(8)	0.19
Lead(II) Perchlorate in Water, 1.9 mol·dm^{-3}					
$Pb(OH_2)_6^{2+}$	Pb−O	6	2.536(5)	0.0241(8)	0.22
	$Pb\cdots O_{II}$	12	4.461(9)	0.059(2)	0.34
ClO_4^- (aq)	Cl−O	4	1.453(4)	0.0020(2)	0.063
	(Cl−)O···O	4	3.04(2)	0.007(3)	0.12
	Cl−(O)···O	4	3.70(2)	0.025(3)	0.22
Water bulk	O···O	2	2.887(5)	0.0186(9)	0.19
Lead(II) Nitrate in Dimethylsulfoxide (dmso), 1.03 mol·dm^{-3}					
$Pb(dmso)_6^{2+}$	Pb−O	6	2.522(7)	0.0189(10)	0.19
	Pb···S	6	3.733(5)	0.0436(15)	0.30
NO_3^- (dmso)	N−O	3	1.243(5)	0.0015(4)	0.055
Lead(II) Trifluoromethanesulfonate in *N*,*N*′-dimethylformamide (dmf), 0.736 mol·dm^{-3}					
$Pb(dmf)_6^{2+}$	Pb−O	6	2.558(5)	0.0269(7)	0.23
	Pb···C	6	3.488(6)	0.0170(8)	0.18
Lead(II) trifluoromethanesulfonate in N,N′-dimethylacetamide (dma), 0.814 mol·dm^{-3}					
$Pb(dma)_6^{2+}$	Pb−O	6	2.480(5)	0.0136(4)	0.16
	Pb···C	6	3.646(5)	0.0148(5)	0.17
Lead(II) Trifluoromethanesulfonate in *N*,*N*′-dimethylpropyleneurea (dmpu), 0.30 mol·dm^{-3}					
$Pb(dmpu)_6^{2+}$	Pb−O	6	2.488(10)	0.0146(7)	0.17
	Pb···C	6	3.52(5)	0.046(7)	0.30
Lead(II) Trifluoromethanesulfonate in *N*,*N*-dimethylthioformamide (dmtf), 1.02 mol·dm^{-3}					
$Pb(dmtf)_6^{2+}$	Pb−S	5	2.891(4)	0.0192(3)	0.20
	Pb···C	5	3.647(15)	0.025(2)	0.22
DMTF bulk	S···S	0.5	4.03(22)	0.021(3)	0.20

Table 7. Number of Distances, *N*, Mean Bond Distances, *R*/Å, Maximum of Bond Distance Distribution, R_m/Å, Debye-Waller Factor Coefficients, σ^2/Å^2, and the Third Cumulant Factor, C_3/ Å^3, $C_3 = \beta\cdot\sigma^3$, in the EXAFS Studies of the Solvated Lead(II) Ion in aqueous, dmso, dmpu, tmu and dmtf Solution at Ambient Room Temperature

species	interaction	*N*	R/R_m	σ^2	C_3
Lead(II) Perchlorate in Water, 1.0 mol·dm^{-3}					
$Pb(OH_2)_6^{2+}$	Pb−O	6	2.541(6)/2.520	0.0268(8)	1.3×10^{-4}
Lead(II) Perchlorate in Water, 1.9 mol·dm^{-3}					
$Pb(OH_2)_6^{2+}$	Pb−O	6	2.543(5)/2.520	0.0236(8)	3.3×10^{-4}
Lead(II) Nitrate in Dimethylsulfoxide (dmso), 1.03 mol·dm^{-3}					
$Pb(dmso)_6^{2+}$	Pb−O	6	2.517(5)/2.494	0.0197(10)	3.3×10^{-4}
	S−O	6	1.543(3)	0.0029(6)	0.0
Lead(II) Trifluoromethanesulfonate in 1,1,3,3-Tetramethylurea (tmu), 0.300 mol·dm^{-3}					
$Pb(tmu)_6^{2+}$	Pb−O	6	2.517(7)/2.502	0.0094(10)	1.3×10^{-4}
	C−O	6	1.288(5)	0.0010(4)	0.0
Lead(II) Trifluoromethanesulfonate in *N*,*N*-dimethylthioformamide (dmtf), 1.02 mol·dm^{-3}					
$Pb(dmtf)_6^{2+}$	Pb−S	5	2.908(4)/2.889	0.0192(3)	2.1×10^{-4}
	S−C	5	1.665(5)	0.0055(4)	0.0

given in Figure 4, and including the individual contributions in Supporting Information, Figure S1b.

The RDF from the LAXS experiment on the dmso solution of lead(II) nitrate reveals three peaks at 1.65, 2.5, and 3.8 Å, respectively (Figure 6). The peak at 1.65 Å corresponds mainly to intramolecular distances in dmso. The latter peaks, refined to 2.522(7) and 3.733(9) Å, respectively, correspond to the Pb−O bond and Pb···S distances

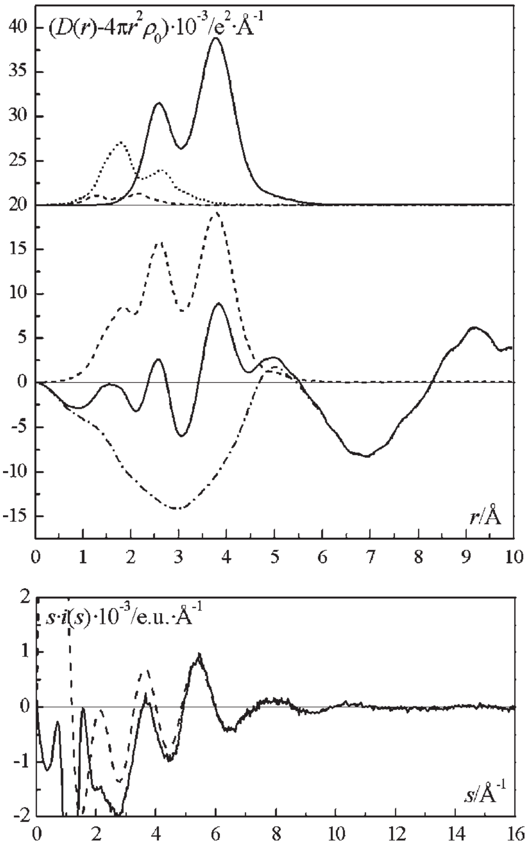

Figure 6. (Top) LAXS radial distribution curves for a 1.03 mol·dm^{-3} dimethylsulfoxide solution of lead(II) nitrate. Upper part: Separate model contributions (offset: 20) of the dimethylsulfoxide solvated lead(II) ion (solid line), the nitrate ion (dashed line) and dimethylsulfoxide molecule (dotted line). (Middle) Experimental RDF: $D(r) - 4\pi r^2\rho_o$ (solid line); sum of model contributions (dashed line); difference (dash-dotted line). (Bottom) Reduced LAXS intensity functions $s \cdot i(s)$ (solid line); model $s \cdot i_{calc}(s)$ (dashed line).

in the dmso solvated lead(II) ion, giving a Pb−O−S angle of 132.1(1.1)°. No contribution from inner-core O···O distance was possible to detect.

The results from the EXAFS and LAXS studies of the dmso solvated lead(II) ion in dmso solution with somewhat shorter Pb−O bond distances than in water but with the same very broad bond distance distribution, absence of PbO_6 inner-core multiple scattering in EXAFS, and no detectable O···O distances within the solvate complex in LAXS all support a six-coordinate hemidirected configuration. On the other hand, the reported crystal structures of dmso solvated lead(II) ions[25] display all an unusual configuration with perchlorate ions very weakly bound either completing a distorted six-coordinate holodirected complex or showing near exemplary five-coordinate hemidirectionality, see Introduction. Perchlorate ions are clearly not bound to lead(II) in dmso solution. It is not possible to unambiguously determine whether the dmso solvated lead(II) ion has holo or hemidirected configuration, even though there are more indications of a hemidirected complex, with a broad bond distance distribution and no detachable PbO_6 inner-core multiple scattering, than of holodirection, with a shorter mean Pb−O bond distance than in the hydrate in aqueous solution. The structure parameters from the LAXS and EXAFS measurements are summarized in Tables 6 and 7.

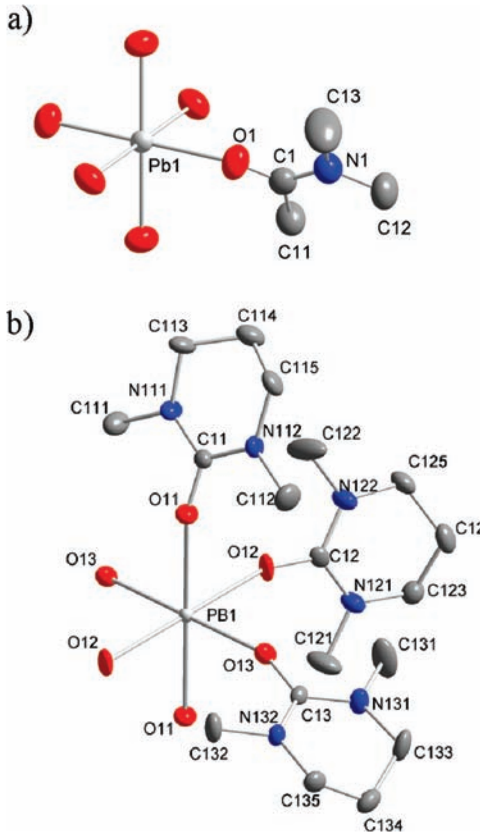

Figure 7. (a) Structure of the regular $[Pb(OCN(CH_3)_2CH_3)_6]^{2+}$ ion in **5**. The atoms are shown as the 50% probability ellipsoids. Hydrogen atoms and symmetry-related dma molecules have been omitted for clarity. (b) Structure of the regular $[Pb(OCN_2(CH_3)_2(CH_2)_3)_6]^{2+}$ ion in **6**. The atoms are shown as the 50% probability ellipsoids. Hydrogen atoms and symmetry-related dmpu molecules have been omitted for clarity.

Crystal Structure of Hexakis(*N*,*N*-dimethylacetamide)-lead(II) Perchlorate, 5. Hexakis(*N*,*N*-dimethylacetamide)-lead(II) perchlorate crystallizes in the trigonal space group $P\overline{3}$ (No. 147), $Z = 1$; the unit cell and refinement parameters are listed in Table 3. The unit cell contains a lead(II) ion on a 6-fold axis coordinating one crystallographically unique dma ligand and one unique perchlorate ion, altogether describing the $[Pb(dma)_6]^{2+}$ complex, Figure 7a, and the perchlorate counterions. This compound has a regular octahedral holodirected geometry around the lead(II) ion which is located in the center of this octahedron with a Pb−O bond length of 2.519(3) Å and angles of 90.0(1) and 180.0(1)°. The Pb−O−C angle is 137.7(3)°, which is smaller than in dma solution, see below. All atoms, except for the hydrogen atoms of the methyl groups, of the dma ligand molecule lie in the same plane. The distance from the center of the lead(II) ion to the center of the perchlorate ion is 7.3 Å.

***N*,*N*-Dimethylformamide and *N*,*N*-Dimethylacetamide Solvated Lead(II) Ions in Solution.** The RDFs from the LAXS experiments on dmf and dma solutions of lead(II) trifluoromethanesulfonate reveals three peaks at 1.45, 2.5, and 3.7 Å, Figures 8, 9 and Supporting Information, Figure S3. The peak at 1.5 Å corresponds to intramolecular distances in the trifluoromethanesulfonate ion and the solvents, the one at 2.5 Å to the Pb−O bond distances in the dmf and dma solvated lead(II) ions, and the one at about 3.5 Å to the Pb···C distance. The Pb−O bond

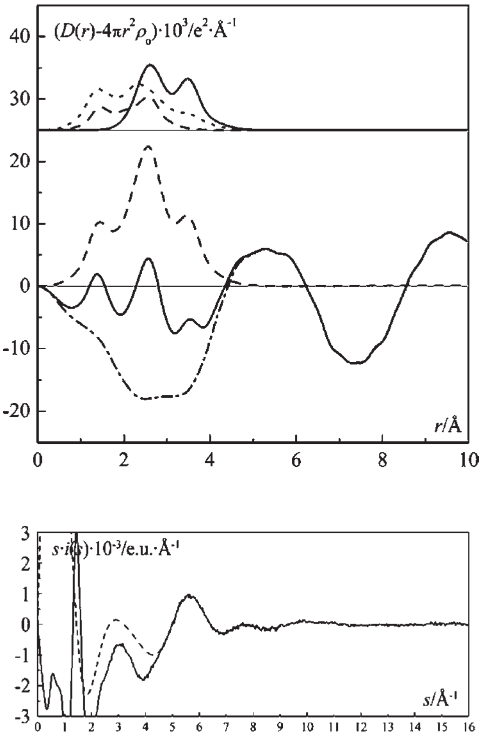

Figure 8. (Top) LAXS radial distribution curves for a 0.736 mol·dm^{-3} *N,N*-dimethylformamide solution of lead(II) trifluoromethanesulfonate. Upper part: Separate model contributions (offset: 25) of the *N,N*-dimethylformamide solvated lead(II) ion (solid line), the trifluoromethanesulfonate ion (dashed line), and *N,N*-dimethylformamide molecule (dotted line). (Middle) Experimental RDF: $D(r) - 4\pi r^2\rho_o$ (solid line); sum of model contributions (dashed line); difference (dash-dotted line). (Bottom) Reduced LAXS intensity functions $s\cdot i(s)$ (solid line); model $s\cdot i_{calc}(s)$ (dashed line).

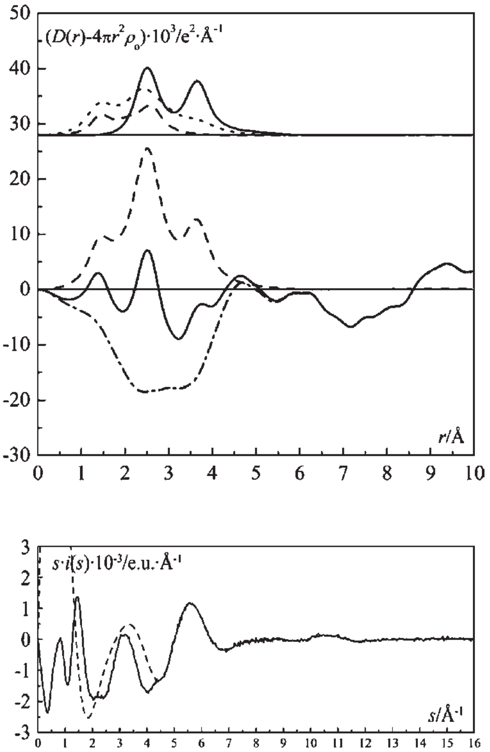

Figure 9. (Top) LAXS radial distribution curves for a 0.814 mol·dm^{-3} *N,N*-dimethylacetamide solution of lead(II) trifluoromethanesulfonate. Upper part: Separate model contributions (offset: 28) of the *N,N*-dimethylacetamide solvated lead(II) ion (solid line), the trifluoromethanesulfonate ion (dashed line) and *N,N*-dimethylacetamide molecule (dotted line). (Middle) Experimental RDF: $D(r) - 4\pi r^2\rho_o$ (solid line); sum of model contributions (dashed line); difference (dash-dotted line). (Bottom) Reduced LAXS intensity functions $s\cdot i(s)$ (solid line); model $s\cdot i_{calc}(s)$ (dashed line).

distance in dmf and dma were refined to 2.56(1) and 2.48(1) Å, and the Pb···C distances to 3.49(1) and 3.65(1) Å, respectively, giving Pb−O−C bond angles of 128.1(8) and 151(1)°, respectively. The longer mean Pb−O bond distance and the larger temperature coefficient in dmf strongly indicate that the dmf solvated lead(II) ion is hemidirected; the mean Pb−O bond distance in the hemidirected dmf solvated lead(II) ion in solid $[C_8H_{18}N_2][Pb(OCHN(CH_3)_2)_6][Pb_5I_{14}]$ is 2.536 Å.[19] On the other hand, the dma solvated lead(II) ion seems to be holodirected as also found in the solid state. The methyl group on the amide carbon in dma causes significant spatial demands upon coordination forcing the dma solvated lead(II) ion to be holodirected and the Pb−O−C bond angle to be much wider than in dmf. The fact that the M−O−C angles are wider for dma than dmf complexes are generally observed in solid metal ion solvate complexes of dmf and dma.[2] The structure parameters from the LAXS measurements are summarized in Table 6.

Crystal Structure of Hexakis(*N,N'*-dimethylpropyleneurea)lead(II) Trifluoromethanesulfonate, 6. The crystallographic data of **6**, obtained from measurements on two different X-ray diffractometers at two different temperatures, ambient room temperature ($\mathbf{6_{RT}}$) and 100 K (**6**), are given in Table 3. The structure consists of discrete hexakis(dmpu)lead(II) cations and trifluoromethanesulfonate anions. The lead(II) ion is surrounded by six oxygen atoms from the dmpu molecules in octahedral geometry, Figure 7b. The triclinic crystal symmetry, $P\overline{1}$ (No. 2), present at 100 K shows two crystallographically independent lead(II) ions coordinating six dmpu molecules each, in an octahedral fashion. The average Pb−O bond distance is 2.501 Å, range 2.438−2.536 Å, Table 4. The low symmetry allows one of the lead(II) complexes to obtain six independent bond distances, whereas the other, lying on a point of symmetry, is restricted to three. The CF_3 group of one of the trifluoromethanesulfonate ions was refined for partial occupancy at two positions, 46 and 54%, respectively. The average Pb−O−C angle is 154.2°, with a larger spread for the non-symmetry restricted complex, 147.9−161.9° as compared to 152.6−157.7° for the other lead(II) complex. At room temperature, $\mathbf{6_{RT}}$ refines to a low *R* value ($R_1 = 0.051$) at much higher crystal symmetry, the hexagonal space group $P\overline{3}$ (No. 147). This results in equidistant Pb−O bonds, 2.520 Å, and a regular octahedral configuration around lead(II). The cause of the higher symmetry at higher temperature is certainly due to the fact that the orientation of the lead(II) complexes becomes random thereby increasing the mean symmetry even though the symmetry of the individual complexes remains equally low as observed at 100 K. This phenomenon has been observed for several other complexes reported previously.[57] Without any possibilities to form standard hydrogen bonds in the room temperature measurement, the trifluoromethanesulfonate counterions are distributed within two voids each on a 3-fold axis and encompassing approximately 173 Å^3. The refined trifluoromethanesulfonate ion was constructed

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(57) Persson, I.; D'Angelo, P.; De Panfilis, S.; Sandström, M.; Eriksson, L. *Chem.—Eur. J.* **2008**, *14*, 3056–3066.

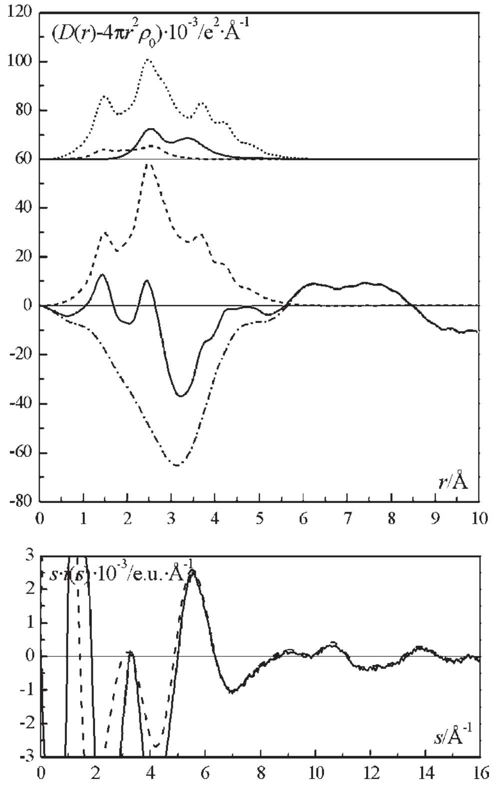

Figure 10. (Top) LAXS radial distribution curves for a 0.300 mol·dm^{-3} *N,N′*-dimethylpropyleneurea solution of lead(II) trifluoromethanesulfonate. Upper part: Separate model contributions (offset: 60) of the *N,N′*-dimethylpropyleneurea solvated lead(II) ion (solid line), the trifluoromethanesulfonate ion (dashed line) and *N,N′*-dimethylpropyleneurea molecule (dotted line). (Middle) Experimental RDF: $D(r) - 4\pi r^2\rho_o$ (solid line); sum of model contributions (dashed line); difference (dash-dotted line). (Bottom) Reduced LAXS intensity functions $s\cdot i(s)$ (solid line); model $s\cdot i_{calc}(s)$ (dashed line).

using mean bond distances found in Cambridge Structural Database and multiple restraints. A separate refinement using the Squeeze command in PLATON, where the contribution of disordered solvents and similar molecules distributed in cavities are neglected, resulted in an appreciably better refinement, $R_1 = 0.033$.[58]

***N,N′*-Dimethylpropyleneurea and 1,1,3,3-Tetramethylurea Solvated Lead(II) Ions in Solution.** The RDF from the LAXS experiments on a dmpu solution of lead(II) trifluoromethanesulfonate reveals two peaks at 1.5 and 2.5 Å, see Figure 10. The peak at 1.5 Å corresponds to intramolecular distances in the trifluoromethanesulfonate ion and the dmpu molecule. The peak at 2.5 Å, refined to 2.49(2) Å, corresponds to the Pb—O bond distance in the dmpu solvated lead(II) ion. The weak shoulder at 3.5 Å corresponds to O···O distances within the octahedral PbO_6 core and to the Pb···C distance. The latter was refined to 3.52(5) Å, giving a Pb—O—C angle of 136(2)°. This angle is much smaller than observed in the solid state showing the larger flexibility of the complex in solution. The basic structure of the holodirected $[Pb(dmpu)_6]^{2+}$ solvate ion in the solid trifluoromethanesulfonate salt is maintained in dmpu solution with a regular octahedral configuration around lead(II).

The EXAFS data of a 1,1,3,3-tetramethylurea solution of lead(II) trifluoromethanesulfonate (Figure 4) were modeled with Pb—O and C—O bond distances, refined to 2.52(2) and 1.29(1) Å, respectively, and a Pb—O—C bond angle refined to 129(2)°, which corresponds to a Pb···C distance of 3.43 Å. The Debye—Waller coefficient of the Pb—O distance is less than half compared to those observed for the hydrated and dmso solvated lead(II) ions, Table 4, supporting a holodirected complex. Very weak contributions from multiple scattering within the PbO_6 core were detected. The 1,1,3,3-tetramethylurea solvated lead(II) ion seems to have the same holodirected octahedral configuration as the other solvent molecules which are regarded as space-demanding upon coordination in this study, dmpu and dma. The fit of the EXAFS data are given in Figures 4 and Supporting Information, Figure S1c, the latter including the individual contributions, and the structure parameters from the LAXS and EXAFS measurements are summarized in Tables 6 and 7.

***N,N*-dimethylthioformamide Solvated Lead(II) Ion.** The EXAFS data of the dmtf solvated lead(II) ion in solution were modeled with Pb—S and C—S bond distances, refined to 2.908(8) and 1.665(10) Å, respectively, and the Pb—S—C angle was refined to 108(2)°, corresponding to a Pb···C distance of 3.86 Å; the obtained Pb—S—C angle is typical for metal complexes with dmtf.[59] The value of the Debye—Waller coefficient of the Pb—S distance is similar to that observed for the dmso solvated lead(II) ion, Table 6, supporting a hemidirected complex. The fit of the EXAFS data are given in Figures 4 and Supporting Information, Figure S1d, the latter including the individual contributions.

The RDF from the LAXS experiments on the dmtf solution of lead(II) trifluoromethanesulfonate reveals three peaks at 1.5, 2.9, and 3.8 Å, see Figure 11. The peak at 1.5 Å is related to intramolecular distances in the trifluoromethanesulfonate ion and the dmtf molecule. The peak at 2.9 Å corresponds to the Pb—S bond distance in the dmtf solvated lead(II) ion. The Pb—S and Pb···C distances have been refined to 2.891(5) and 3.833(9) Å, respectively, giving a Pb—O—S angle at 107°. A S···S distance at 4.03 Å was introduced to model the solvent—solvent interactions in dmtf as described elsewhere.[32] The structure parameters from the LAXS measurements are summarized in Table 6.

The revealed Pb—S bond distance by both EXAFS and LAXS, 2.90 Å, supports a hemidirected five-coordination of the dmtf solvated lead(II) ion in solution, $r_{Pb} = 1.12$ Å, Table 5, and $r_{Sdmtf} = 1.75$ Å,[52] as it has been applied in the model refined for both EXAFS and LAXS data. Furthermore, in respect of such a low coordination number the geometry around lead(II) ion in dmtf solution is expected be hemidirected.[9] The structure of this solvate has only been investigated in solution by means of LAXS and EXAFS techniques, since attempts to obtain crystals with both perchlorate and trifluoromethanesulfonate as counterion were unsuccessful, another but far more unreliable indication of a hemidirected system.

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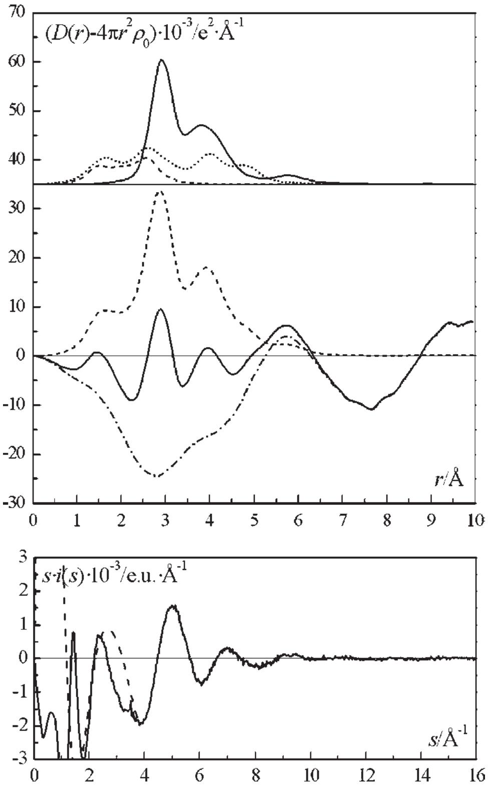

Figure 11. (Top) LAXS radial distribution curves for a 1.02 mol·dm^{-3} *N,N*-dimethylthioformamaide solution of lead(II) trifluoromethanesulfonate. Upper part: Separate model contributions (offset: 35) of the *N,N*-dimethylthioformamide solvated lead(II) ion (solid line), the trifluoromethanesulfonate ion (dashed line), and *N,N*-dimethylthioformamaide molecule (dotted line). (Middle) Experimental RDF: $D(r) - 4\pi r^2\rho_o$ (solid line); sum of model contributions (dashed line); difference (dash-dotted line). (Bottom) Reduced LAXS intensity functions $s\cdot i(s)$ (solid line); model $s\cdot i_{calc}(s)$ (dashed line).

Relationship between Bond Distance Distribution and Gap Size. The gap for excess electron density is much smaller in **2** than in **1**, Figures 1 and 2. The bond distance distribution seems to be related to the volume of an electron density sufficiently large to hinder bond formation, the gap size in the coordination sphere, with increasing bond distance distribution with increasing gap size, 0.8−0.9 Å in **1**, while it is only 0.3 Å in **2** with a much smaller gap size than in **1**, Figures 2a and 3a. On the other hand, holodirected complexes have a much more narrow Pb−O bond length distribution, less than 0.07 Å, as shown in Tables 4 and Supporting Information, Figure S1. The wide bond distance distribution in the hemidirected complexes is well explained by the recent proposed MO theory where the metal−ligand bonds form antibonding covalent interactions.[6−9] On the other hand, with symmetric electron distribution as in the holodirected complexes, the bond distance distribution is comparable to metal complexes in general with the same type of configuration.

Conclusions

The coordination chemistry of lead(II) is unusually diverse as the formation of antibonding lead 6s/ligand np molecular orbital metal ligand interactions cause a more or less extensive unsymmetric electron distribution around the lead(II) ion depending on how strong these covalent antibonding features are. This causes a coordination sphere with room for excess electron density and wide bond distance distribution, which lead to the formation of hemidirected complexes. On the other hand, if these antibonding interactions are weak, and possible attractive or repulsive forces exist between the space-demanding ligands, the electron distribution around lead(II) will be symmetric, and the complexes will have a normal bond distance distribution and relative high symmetry, holodirected complexes as observed for *N,N*-dimethylacetamide, *N,N*-dimethylpropyleneurea, and 1,1,3,3-tetramethylurea. The regular octahedral configuration of these complexes may also be favored by the ligand−ligand intermolecular interactions.[4,7] For the solvent molecules with cone angles larger than about 65°, Table 1, as defined in the Introduction, all solvents used in this study are forming holodirected complexes, while the solvent molecules with a smaller cone angle all are hemidirected. Holodirected complexes are also observed for lead(II) complexes with a coordination number of nine or higher.[2,3] Under these conditions the energy gain by forming low-symmetric complexes is not sufficient to counter-balance the energy obtained by formation of highly symmetric complexes. In the attempts to obtain suitable crystals for the crystallographic studies it was more difficult for hemidirected complexes to form than for the holodirected ones with higher symmetry. Furthermore, the melting points of the hemidirected complexes are lower than for the holodirected ones. The solvate complexes of lead(II) of water and *N,N*-dimethylformamide, with small cone angles, 28 and 45°, respectively, are hemidirected in both solution and the solid state. Contrary to many other metal ions, lead(II) normally crystallizes from aqueous solutions without or with only a limited number of water molecules not forming a complete hydration shell as found in $[Pb_2(H_2O)_2(ClO_4)_4]_n$ (**1**) and $[Pb(H_2O)(CF_3SO_3)_2]_n$ (**2**). The dmso solvated lead(II) ion seems to be hemidirected in dmso solution, while in the solid state weak bonds from perchlorate ions fill the coordination sphere to form holodirected complexes. As indicated for the aqueous and dmso systems different coordination chemistry may be present in the solid state and solution. It is possible that the cone angle of dmso, 54°, is close to the break point for hemi and holodirected complexes of lead(II), and that hemidirected complexes are favored in solution, while holodirected complexes are favored in the solid state supported by increasing lattice energies of complexes with higher symmetry. The mean Pb−O bond distances, for holodirected solvates formed in solution, 2.48(1) (dma − cone angle 68°), 2.52(1) (tmu −81°), and 2.49(2) Å (dmpu −84°) are slightly shorter than in the case of hemidirected lead(II) solvates in water (2.54(1) Å), dmso (2.52(1) Å) and dmf (2.56(1) Å). The *N,N*-dimethylthioformamide solvated lead(II) ion in solution with Pb−S bond distances of 2.910(5) and 2.891(5) Å as observed by EXAFS and LAXS, respectively, supports five-coordination in a hemidirected fashion.[9] Lead(II) complexes with sulfur donor ligands display a similar configurational picture as the complexes with oxygen donor ligands. A vast majority of the lead(II) complexes with sulfur donor ligands are four- and five-coordinate with large bond distance distribution and a clear hemidirected configuration, Supporting Information, Table S1b. The few 6-coordinate complexes have large bond distance distribution and S−Pb−S angles very different from 90°, Supporting Information, Table S1b, making gaps in the coordination sphere showing the typical signs of hemidirected configuration. The structure of the only complex with a space-demanding sulfur donor ligand reported so far, hexakis(*N*,*N*′-dicyclohexylthiourea)lead(II), has a very narrow bond distance distribution and was classified as holodirected even though its octahedral geometry is distorted. DFT calculations indicate that the sulfide ion in the mineral galena, PbS, forms weaker antibonding lead-ligand interactions giving its highly symmetric structure in the solid state.[5−8] This, however, does not follow the general trend, and the highly symmetric structure of galena is most certainly the result of strong lattice energies.

Acknowledgment. We gratefully acknowledge the Swedish Research Council and the Visby program through the Swedish Institute for financial support to K.L. and A.P. Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource (SSRL), which is acknowledged for the allocation of beamtime and laboratory facilities. SSRL is a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Services. The SSRL Structural Molecular Biology Program is supported by the Department of Energy, Office of Biological and Environmental Research, and by the National Institute of Health, National Center for Research Resources, Biomedical Technology Program.

Supporting Information Available: Further details are given in Tables S1−S3 and Figures S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.