Structures of Solvated Cations of Palladium(II) and Platinum(II) in Dimethyl Sulfoxide, Acetonitrile and Aqueous Solution Studied by EXAFS and LAXS

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X-Ray absorption edge and EXAFS spectra of the solvated cations of platinum(II) in water, dimethyl sulfoxide and acetonitrile and of palladium(II) in dimethyl sulfoxide have been recorded and analyzed. The cations are four-coordinated. Pt–O in $Pt(H_2O)_4^{2+}$ is 2.01(1) Å and Pt–N in $Pt(CH_3CN)_4^{2+}$ is 2.00(1) Å. The dimethyl sulfoxide solvated cations of both platinum and palladium contain two sulfur- and two oxygen-bonded ligands with Pt–O 2.07(2), Pt–S 2.21(2), Pd–O 2.04(2), and Pd–S 2.23(2) Å, probably in a square-planar *cis*-arrangement, as in the solid state. Large-angle X-ray scattering (LAXS) studies of the platinum(II) dimethyl sulfoxide solvated cation in a solution of the triflate salt gave Pt–O 2.07(1) and Pt–S 2.20(1) Å and in a solution of the tetrafluoroborate salt Pt–O 2.07(2) and Pt–S 2.21(5) Å, in good agreement with the EXAFS results. Neither technique gave any support for axially bound solvent molecules in addition to the four in the assumed square coordination plane.

Although $Pt(H_2O)_4^{2+}$ and $Pd(H_2O)_4^{2+}$ are known in solution,[1–3] attempts to prepare crystalline compounds containing those complexes have been unsuccessful so far.[4,5] Only a few crystallographic studies of compounds containing platinum(II) or palladium(II) complexes with one water molecule coordinated directly to the metal ion seem to have been published.[6–8] NMR studies of aqueous solutions of $Pt^{2+}(aq)$ and $Pd^{2+}(aq)$ show that those cations coordinate four aqua ligands with observable exchange rates.[9–12] Their electronic spectra[13] and substitutional behavior[2,3,14–18] are compatible with a square-planar coordination geometry. Information on the Pt–O bonding distance as well as the possible presence of axially coordinated, weakly bound solvent molecules is still lacking. It was therefore considered to be of interest to apply the X-ray absorption edge and EXAFS (extended X-ray absorption fine structure) techniques to solutions of a square-planar tetraaqua cation to obtain such information. The LAXS (large-angle X-ray scattering) technique requires too high concentrations and long exposure times to be applicable to the solutions of the hydrated cations available.

Solutions of the dimethyl sulfoxide solvates of both palladium(II) and platinum(II) were prepared previously.[19–21] IR and NMR spectra indicate that those solvates probably contain two oxygen- and two sulfur-bonded ligands in a *cis* arrangement.[19–21] Recent crystallographic studies[22,23] of $[Pd(Me_2SO)_4](BF_4)_2{\cdot}Me_2SO$ and $[Pt(Me_2SO)_4](CF_3SO_3)_2$, as well as a proton-NMR study of the solvent exchange on $Pt(Me_2SO)_4^{2+}$, confirm this structure.[24] Also, in this case it appeared to be of interest to obtain more direct information on the structures in solution of those solvated cations. Therefore, two different LAXS studies and one EXAFS study on $Pt(Me_2SO)_4^{2+}$ were performed, as well as one EXAFS study on $Pd(Me_2SO)_4^{2+}$. The LAXS technique is more sensitive than EXAFS to longer and less well-defined distances, and is therefore more suitable for detecting the presence of any loosely bound axial solvent molecules in the solvated cations.

Finally, the present study also contains an EXAFS study of the acetonitrile solvate of platinum(II), which does not seem to have been characterized so far.

Experimental

Materials. Palladium sponge (Specpure), platinum foil (0.025 mm), $Pt(NH_3)_2Cl_2$, K_2PtCl_4 (all from Johnson and Matthey), $HClO_4$ (Baker p.a.), fuming HNO_3 (Merck p.a.). CF_3SO_3H (Fluka purum), NaOH (Merck titrisol), $AgClO_4$ (G. F. Smith reagent quality), $KHCO_3$ and KNO_3 (Merck p.a.), dimethyl sulfoxide and acetonitrile (Merck

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Table 1. Concentrations, densities and linear absorption coefficients, $\mu(MoK\alpha)$, for the solutions studied by LAXS.

Anion	C_{Pt}/M	c_{Me_2SO}/M	C_{anion}/M	C_{H_2O}/M	ϱ/g cm^{-3}	$\mu(MoK\alpha)$/cm^{-1}
$CF_3SO_3^-$	0.55	12.64	1.84	<0.001	1.36	17.23
BF_4^-	0.57[a]	12.64[a]	2.53[a]	0–1[b]	1.35[a]	17.76

[a]At the end of the experiment. [b]1 M at the end of the experiment.

Uvasol) were used as purchased. Dimethyl sulfoxide (Merck spectral grade) was distilled under reduced pressure over calcium hydride, and dried over 4 Å molecular sieves before use.

$Pt(H_2O)_4(ClO_4)_2$ solution. A ca. 9 mM platinum(II) stock solution in 1.00 M $HClO_4$ was prepared as described elsewhere.[1] The solution was concentrated to 88.6 mM platinum and 4.8 M perchloric acid by cautious addition of 7.51 g $KHCO_3$ to 150 ml stock solution under nitrogen followed by centrifugation and separation of the $KClO_4$ precipitate and evaporation (rotating vacuum evaporator) at 40°C to 13 ml. The perchloric acid concentration was reduced to ca. 1.5 M by cautious addition of 3.07 g $KHCO_3$. The precipitate was separated, and the solution was flushed with nitrogen and kept cold.

$Pt(OH)_2{\cdot}xH_2O$. 140 ml 1.00 M NaOH was added to 140 ml of a stirred 9.8 mM $Pt(H_2O)_4(ClO_4)_2$ stock solution.[1] The resulting solution was rapidly titrated to pH 7.1 (Orion pH electrode) with 0.100 M NaOH. The light yellow–green precipitate of $Pt(OH)_2{\cdot}xH_2O$, described previously,[1,25] was allowed to settle for a few minutes. It was separated from the solution on a Millipore filter (HVLP 02500) and was washed quickly on the filter with 4×1 ml ice-cold water under suction. The precipitate ages quickly and must be used directly after preparation.[1]

$Pt(Me_2SO)_4(CF_3SO_3)_2$. The platinum hydroxide precipitate was dissolved on the filter by addition of 1.25 ml of a cooled solution obtained by mixing 2 ml Me_2SO and 1 ml CF_3SO_3H, and stirring with nitrogen. The first yellow–brown, and after a few minutes bright yellow, solution was passed through the filter together with 5 ml Me_2SO. Residual water was removed by distillation at ca. 65°C under reduced pressure in a microdistillation apparatus to a volume of ca. 2 ml. The distillation was restarted after addition of 5 ml Me_2SO. The procedure was repeated twice to a final volume of ca. 3 ml, giving a concentration of $Pt(Me_2SO)_4(CF_3SO_3)_2$ of 0.51 M. The solution is very light yellow. Crystals of the salt were precipitated by evaporating and cooling this solution as described elsewhere.[23]

Concentrated solutions of the solvated platinum(II) cation in dimethyl sulfoxide with $CF_3SO_3^-$ and BF_4^- as counter-ions for the LAXS studies were prepared from solutions of $Pt(H_2O)_4(ClO_4)_2$ via $Pt(OH)_2{\cdot}xH_2O$ as described above and elsewhere[23] by dissolution of the hydroxide in CF_3SO_3H or HBF_4. The solutions were dried over 4 Å molecular sieves before use. Their water content after drying was less than 1 mM as checked by ^1H-NMR. The platinum concentrations of the two solutions were calculated from UV spectra. The solutions were diluted with 1.0 M aqueous hydrochloric acid to $C_{Pt} \approx 0.1$ mM, $[Me_2SO] \approx 2.5$ mM and $[Cl^-] \approx 1.0$ M. After ca. 1 h, all platinum is present as $PtCl_3(Me_2SO)^-$.[15,26] The platinum(II) concentrations were calculated by comparison of spectra for these solutions with spectra of standard solutions, prepared from a 6.0 mM stock solution of $Pt(H_2O)_4^{2+}$, 1.0 M hydrochloric acid and dimethyl sulfoxide to give corresponding concentrations of $PtCl_3(Me_2SO)^-$. The acid concentration was determined by titration with standard NaOH, and Me_2SO concentrations were calculated from the densities, using known total concentrations of platinum (II) and acid. Concentrations, densities and linear absorptions of the concentrated solutions studied by LAXS are given in Table 1. The water content of the two solutions was also checked by ^1H-NMR after X-ray exposure, which lasted for about 15 days. The trifluoromethanesulfonate solution, which had been kept in a closed glass vessel, was still dry with a water concentration of less than 1 mM. The tetrafluoroborate solution, which had been kept in an open vessel in a radiation shield where the opening for X-rays was covered by Mylar film, had increased its water content to about 1 M during the LAXS experiment.

$Pt(CH_3CN)_4(CF_3SO_3)_2$ solution. The platinum(II) hydroxide on the filter was dissolved in 1.0 ml of a solution obtained by mixing 2 ml CH_3CN and 1 ml CF_3SO_3H. The precipitate dissolved within 2 min under N_2 flushing to a light yellow solution, which passed through the filter together with 4 ml acetonitrile. After heating to 40°C for 10 min the color changed to bright orange. The solution was distilled at 40°C under reduced pressure to ca. 3 ml. Then 7 ml acetonitrile was added and the distillation repeated twice to a final volume of 2.8 ml and a concentration of $[Pt(CH_3CN)_4](CF_3SO_3)_2$ of 0.47 M. Attempts to obtain crystals of the salt from this solution were not successful.

$K_2Pt(NO_3)_4{\cdot}1/2\ H_2O$ and $K_2Pd(NO_3)_4$. The platinum complex was prepared as described elsewhere.[5] The palladium compound was obtained by adding 3.88 g KNO_3 to 173 ml of a solution prepared by dissolving 2.655 g palladium sponge in fuming nitric as described previously,[2] and reducing the volume to 250 ml. The dark-red solution was

Table 2. Model compounds used for determination of empirical Pt/Pd–X back-scattering amplitude and phase functions.

Compound	Distance	d/Å	Ref.
$K_2Pt(NO_3)_4 \cdot 1/2H_2O$	Pt–O	2.010(5)	5
$Pt(NH_3)_2Cl_2$	Pt–N	2.06[a]	46
$[Pt(Me_2SO)_4](CF_2SO_3)_2$	Pt–O	2.06(1)	23
	Pt–S	2.21(1)	23
$K_2Pd(NO_3)_4$	Pd–O	2.000(5)	47
PdS	Pd–S	2.33	40

[a]Pt–N for $[Pt(NH_3)_4][PtCl_4]$.[46]

evaporated under a heating lamp for 2 h to dryness. The resulting yellow–orange precipitate of $K_2Pd(NO_3)_4$, which also contains some KNO_3, was ground in a mortar and dried to remove residual acid.

$Pd(Me_2SO)_4(NO_3)_2$ solution. A ca. 0.6 M solution for the EXAFS experiments was obtained by dissolving 450 mg $K_2Pd(NO_3)_4$ in 1.75 ml Me_2SO. The resulting solution is bright red.

PdS. A precipitate was obtained by bubbling H_2S through a ca. 50 mM solution of $[Pd(H_2O)_4](ClO_4)_2$ in 1.00 M perchloric acid prepared as described elsewhere.[2]

Sample preparation for EXAFS studies. The solid samples were ground to fine powders, mixed well with BN (Alfa Thiokol), pressed into uniform pellets and sealed between Mylar tape for the recording of data. The solutions were contained in cells with a 1 mm thick Teflon spacer and with Mylar windows.

Collection and analysis of EXAFS data. X-Ray absorption data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL), using the unfocussed eight-pole wiggler beam line 4-1 and a Si(220) double-crystal monochromator. The spectra were measured as transmission data with an average of 2–7 scans collected per sample. All spectra were calibrated with the internal calibration method[27] assigning the palladium K and platinum L_{III} edge inflection points of palladium sponge and platinum foil as 24 349 and 11 563 eV, respectively. The data reduction was performed using standard procedures for pre-edge subtraction, spline fit and subtraction, normalization and Fourier filtering.[28,29] The background-corrected normalized data were converted to k-space by assuming a threshold energy, E_0, of 24 360 and 11 575 eV, respectively. The photoelectron vector k is defined as $k = [2m_e(E-E_0)/h^2]^{1/2}$, where m_e is the electron mass and $2\pi h$ is Planck's constant.

EXAFS data analysis was performed by the curve-fitting technique using empirical phase and amplitude functions from compounds of known structure.[28] Empirical Pd–X and Pt–X back-scattering functions were obtained from the model compounds listed in Table 2, and the compositions of the solutions investigated are given in Table 3. All curve-fitting was based on least-squares minimization using k^3-weighted data. Fourier filtering was used to isolate the first back-scattering shell. Filter limits are given in Table 4. For each system, fittings were performed for this individual filtered shell as well as for the unfiltered data. The distance and the corresponding Debye–Waller factor, $\Delta\sigma^2$, in each shell were allowed to vary. Variation of the number of distances, n, resulted in values between 4.1 and 4.7, and the F-values decreased only slightly. Since the coordination numbers are known from previous studies using other techniques, fixed n-values of 4 were used in the final calculations. EXAFS data analysis and least-squares refinements were performed using the XFPAKG program package.[30]

X-Ray scattering experiments and data treatment. The X-ray scattering from the free surfaces of the solutions was measured in a large-angle Θ–Θ diffractometer[31] of the Seifert GSD type. To avoid contact with the atmosphere and evaporation, the trifluoromethanesulfonate solution was enclosed in a cylindrical thin-walled glass container, which was half-filled as in the calibration experiment.[32] The tetrafluoroborate solution was kept in an open Teflon vessel and enclosed in a radiation shield covered with Mylar film. In both cases Mo$K\alpha$ radiation (λ = 0.7107 Å) was used. The scattered intensities were determined at discrete angles in the interval $4 < \Theta < 60°$, separated by 0.0335 in s, defined as $s = 4\pi\lambda^{-1}\sin\Theta$, where the scattering angle is 2Θ. Since the trifluoromethanesulfonate solution was kept in a closed glass container, an extrapolation of the intensity data for $\Theta < 4°$ was necessary because of the upward liquid meniscus on the container walls. A statistical counting error of 0.35 % was achieved by accumulating 40 000 counts twice at each sampling point. The fraction of incoherent

Table 3. Composition of solutions investigated with EXAFS.

Metal	Solvent	Anion	C_{Pt}/M	$C_{solvent}$/M	C_{anion}/M	C_{H^+}/M
Pt	H_2O	ClO_4^-	0.088	55	2.7	2.5
Pt	CH_3CN	ClO_4^-	0.47	19	1.34	0.4
Pt	Me_2SO	$CF_3SO_3^-$	0.6	13	1.62	0.6
Pd	Me_2SO	NO_3^-	2.4	13	2.4	1.2[a]

[a]Potassium ion concentration.

scattering contributing to the intensities was estimated as described elsewhere.[33]

The data reduction procedure and corrections are described elsewhere.[32–34] The experimental intensities were normalized to a stoichiometric unit of volume containing one platinum atom. The scattering factors, corrections for anomalous dispersion and values for incoherent scattering were taken from Refs. 35–37. Spurious peaks in the experimental distribution function below 1.4 Å for the trifluoromethanesulfonate solution, and below 1.7 Å for the tetrafluoroborate one, which could not be related to interatomic distances within the Me_2SO molecule or within the anion, were removed using a Fourier transformation procedure.[31] All calculations were performed by means of the computer programs KURVLR[38] and STEPLR.[39]

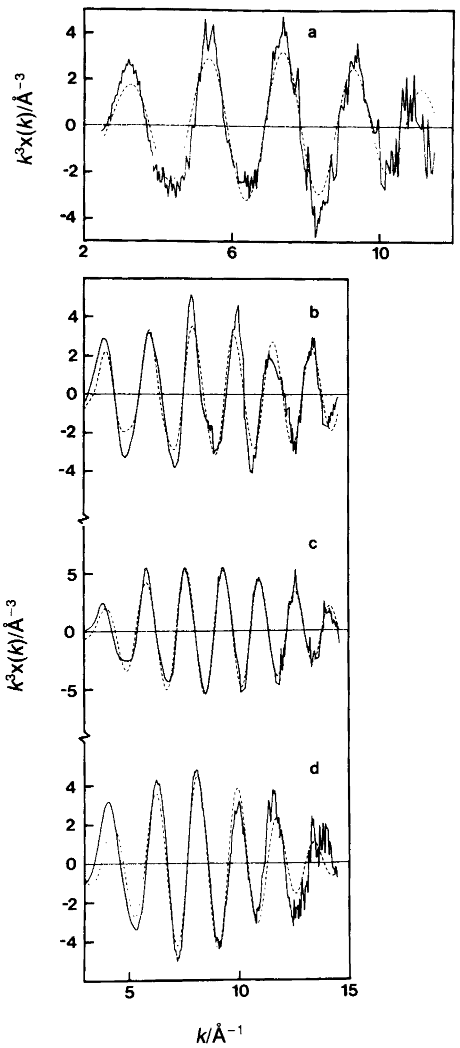

Fig. 1. Curve fitting of unfiltered EXAFS data of the tetraaquaplatinum(II) (a), tetraacetonitrileplatinum(II) (b), tetrakis(dimethyl sulfoxide)platinum(II) (c) and tetrakis(dimethyl sulfoxide)palladium(II) (d) complexes. Experimental data are denoted with solid lines, calculated models with dashed lines.

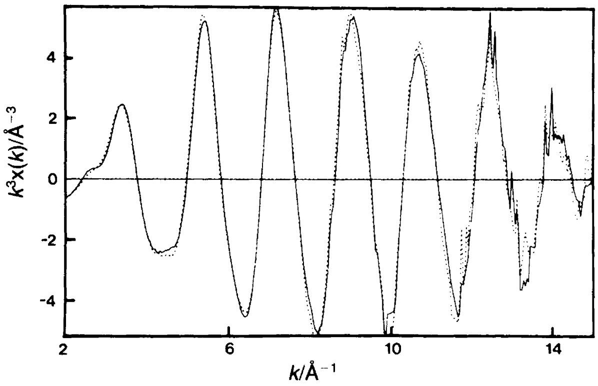

Fig. 2. Comparison of EXAFS data for the tetrakis(dimethyl sulfoxide)platinum(II) cation in the solid state (solid line) and in dimethyl sulfoxide solution (dotted line).

Results and discussion

The reference compounds for the EXAFS experiments listed in Table 2 have well-defined metal–ligand distances except for PdS, which has a spread in four Pd–S distances between 2.26 and 2.43 Å with an average of 2.33 Å.[40] This leads to a relatively broad shape of the Pd–S peak from PdS, which means that the number of distances in the unknown structure may be less precise. The availability of the crystalline compound $[Pt(Me_2SO)_4](CF_3SO_3)_2$ as a reference compound is especially valuable for the accurate structural characterization of the dimethyl sulfoxide solvated cation.

The calculated bond distances and relative mean square deviations, and the assumed numbers of distances in the solvated cations are given in Table 4. The fits of the unfiltered experimental data of $Pt(H_2O)_4^{2+}$, $Pt(CH_3CN)_4^{2+}$, $Pt(Me_2SO)_4^{2+}$ and $Pd(Me_2SO)_4^{2+}$ solutions are shown in Fig. 1. The EXAFS of the $Pt(Me_2SO)_4^{2+}$ complex in dimethyl sulfoxide solution and solid state are compared in Fig. 2.

As expected from earlier NMR[9,11,12] and UV/visible[13] spectra, $Pt^{2+}(aq)$ is surrounded by four water molecules. The Pt–O bond distance of 2.01(1) Å is very similar to Pt–O bond distances observed *trans* to oxygen in other platinum complexes in solid compounds. For instance, nitrato, squarato and oxalato complexes all have Pt–O bond distances in the interval 1.99–2.01 Å.[5,41,42] This distance is somewhat shorter than the Pt–O distances of 2.052(8) and 2.099(5) Å *trans* to nitrogen observed for the monoaqua complexes *cis*-$[Pt(NH_3)_2(OH_2)(C_5H_7N_3O)]^{2+}$ and $PtL(H_2O)SO_4 \cdot H_2O$ [L = 1,1-bis(aminomethyl)cyclohexane], respectively, indicating a larger ground-state *trans*-influence for nitrogen than for oxygen.

The acetonitrile solvated platinum(II) cation is also four-coordinated. The Pt–N distance of 2.00(1) Å is shorter than Pt–N distances in ammine complexes *trans* to other ammine ligands, which usually are ca. 2.06 Å.[43] This is due to a smaller ionic radius of the nitrile nitrogen and to a possibility of back-bonding from filled metal d-orbitals to empty

Table 4. Bond distances, *d*, and relative square deviations, $\Delta\sigma^2$, and number of distances, *n*, calculated from the EXAFS experiments,[a] with estimated errors.

Complex	Distance	*k*-Range	Filtered data				Unfiltered data			
			d/Å	$\Delta\sigma^2/10^{-3}$Å^{2b}	n	F^c	d/Å	$\Delta\sigma^2/10^{-3}$Å^{2b}	n	F^c
$Pt(H_2O)_4^{2+}$	Pt–O	2.5–11.5	2.01(1)	1.8	4.0	0.28	2.01(1)	2.2	4.0	0.92
$Pt(CH_3CN)_4^{2+}$	Pt–N	2.5–14.5	2.00(1)	−0.4	4.0	0.35	2.00(1)	−0.7	4.0	0.82
$Pt(Me_2SO)_4^{2+}$	Pt–O	2.5–14.5	2.07(2)	−1.5	2.0	0.30	2.07(2)	−0.7	2.0	0.61
	Pt–S		2.21(2)	0.5	2.0		2.21(2)	−0.4	2.0	
$Pd(Me_2SO)_4^{2+}$	Pt–O	3.0–14.5	2.04(2)	−1.0	2.0	0.18	2.04(2)	−1.1	2.0	0.98
	Pt–S		2.23(2)	−0.1	2.0		2.23(2)	−0.1	2.0	

[a]The number of distances, *n*, was not refined in the final curve fitting analyses. [b]The Debye–Waller factor $\Delta\sigma^2$ is defined as $\sigma^2_{sample} - \sigma^2_{ref}$, where σ^2_{ref} = 0.0025 for the absorber–scatterer interaction in all model compounds. The estimated error in this quantity is ca. (0.2–0.3) × 10^{-3} Å^2. [c]Goodness of fit $F = \{\Sigma[k^3(\chi_{obs}-\chi_{calc})]^2/\mathrm{NPTS}\}^{1/2}$, where χ_{obs} and χ_{calc} refer to measured and simulated EXAFS, and NPTS denotes number of points.

π*-orbitals of the acetonitrile, which might shorten the bond. There seems to be only one previous structure determination of a complex where acetonitrile is coordinated to platinum, viz. *cis*-$Pt(CH_3CN)_2Cl_2$ in the solid state.[44] The Pt–N bond distance *trans* to chloride is 1.98(1) Å, slightly shorter than the distance observed here, *trans* to acetonitrile. Although the difference is small, it might reflect an expected larger ground-state *trans*-influence of acetonitrile compared to chloride.

The almost identical EXAFS observed for the dimethyl sulfoxide solvated platinum(II) ion in solution and the solid state shown in Fig. 2 strongly indicates that the coordination around platinum is very similar in solution and crystal. In the LAXS experiments a similar pattern of peaks and shoulders is observed in the radial distribution functions (RDFs) for the tetrafluoroborate and trifluoromethanesulfonate solutions, as shown by Fig. 3. The peak around 1.6 Å and the shoulder (weak for the BF_4^- solution and marked in the case of the $CF_3SO_3^-$ solution) around 2.6 Å in the RDFs correspond to intramolecular distances in dimethyl sulfoxide, *d*(S–O) = 1.50 Å, *d*(S–C) = 1.81 Å, *d*(O–C) = 2.66 Å and *d*(C–C) = 2.77 Å,[45] and in the anions, *d*(B–F) = 1.31 Å and *d*(F–F) = 2.15 Å in BF_4^-,[22] and *d*(C–F) = 1.31 Å, *d*(S–C) = 1.81 Å, *d*(S–F) = 2.60 Å, *d*(S–O) = 1.43 Å, and *d*(C–O) = 2.48 Å in $CF_3SO_3^-$.[23] The two remaining peaks in the RDFs at 2.2 and 3.1 Å originate from the dimethyl sulfoxide solvated platinum(II) ion. The line-shapes of these peaks indicate that each peak may contain contributions from at least two slightly different atom–atom correlations.

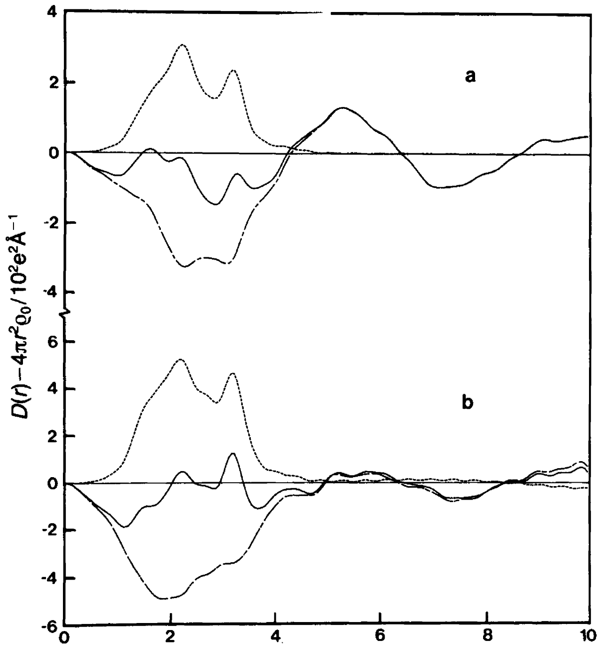

Fig. 3. LAXS results. Experimental differential radial distribution functions, $D(r)-4\pi r^2\varrho_0$, for the platinum(II) solutions with BF_4^-(a) and $CF_3SO_3^-$(b) as counter-ions (solid lines). The dotted lines represent calculated distribution functions with parameters from Table 5. Dashed lines represent differences between experimental and calculated functions.

The crystal structure[23] of $[Pt(Me_2SO)_4](CF_3SO_3)_2$ was used as a starting model for the refinement of the LAXS data for the solvated platinum(II) cation in dimethyl sulfoxide. In the solid state, the metal coordinates two sulfur- and two oxygen-bonded ligands in a slightly distorted square-planar *cis*-arrangement with Pt–S 2.208(3) and 2.205(4), and Pt–O 2.051(9) and 2.040(10) Å. The average Pt–O and Pt–C distances in the sulfur-coordinated Me_2SO are 3.12 and 3.28 Å, respectively, and the Pt–S distance in oxygen-bound Me_2SO is 3.155 Å. In solution, no discrete Pt–C distances can be observed, owing to lower scattering and larger thermal motions of the carbon atoms compared to sulfur.

Introduction of a model containing these data gave a good fit to the LAXS intensity functions and experimental RDFs as shown by Figs. 3 and 4. There is still a small peak in the difference function in the RDFs around 2.4 Å as shown by Fig. 3. Introduction of an additional Pt–S distance of 2.4 Å to a hypothetical fifth axially coordinated Me_2SO molecule gives only a minor improvement of the fit

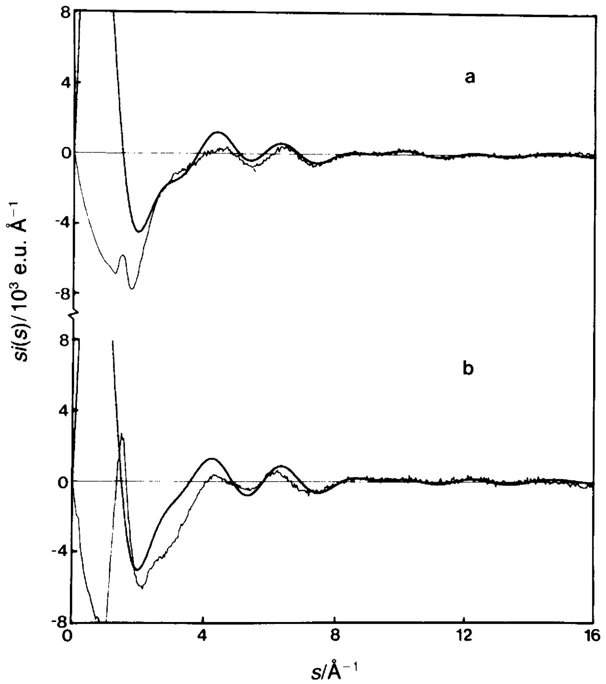

Fig. 4. Reduced LAXS intensity functions, $i(s)$, multiplied by the scattering variables, s, for the tetrakis(dimethyl sulfoxide)-platinum(II) cation with $CF_3SO_3^-$(a) and BF_4^-(b) as counter-ions. Calculated functions are denoted with solid lines.

Table 5. Interatomic distances, *d*, temperature factor coefficients, *b*, and number of distances, *n*, for the dimethyl sulfoxide solvated platinum(II) ion in solution with trifluoromethanesulfonate and tetrafluoroborate as counter-ions.[a]

Distance	d/Å	b/Å^2	n
Trifluoromethanesulfonate solution			
Pt–S[b]	2.23(1)	0.0039(7)	2.0
Pt–S[c]	3.21(1)	0.007(2)	2.0
Pt–O[b]	2.07(1)	0.0037(7)	2.0
Pt–O[c]	3.09(4)	0.006(3)	2.0
Pt–C[c]	3.29(3)	0.009(4)	4.0
Tetrafluoroborate solution			
Pt–S[b]	2.21(1)	0.0018(8)	2.0
Pt–S[c]	3.13(2)	0.008(2)	2.0
Pt–O[b]	2.07(3)	0.003(1)	2.0
Pt–O[c]	3.09(6)	0.007(5)	2.0
Pt–C[c]	3.26(3)	0.003(3)	4.0

[a]Refined parameters are given with e.s.d.s in parenthesis. [b]Denotes atoms coordinated to platinum. [c]Non-bonding distances.

for the tetrafluoroborate solution, and no improvement at all for the trifluoromethanesulfonate solution. Thus, the LAXS data also indicate that the structure of $Pt(Me_2SO)_4^{2+}$ in solution is very similar to that in the solid state. Neither the LAXS nor the EXAFS experiments give any support for a solution structure with additional solvent molecules coordinated in axial positions. The refined parameters, which are in close agreement with those for solid $[Pt(Me_2SO)_2](CF_3SO_3)_2$, are summarized in Table 5.

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