

The Crystal Structure of Hexakis(dimethylsulfoxide)zinc(II) Perchlorate and the Structure of the Hexakis(dimethylsulfoxide)-zinc(II) Ion in Dimethylsulfoxide Solution

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The compound $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ crystallizes in the trigonal space group $P31c$ (No. 159) with $a=12.006(3)$, $c=12.578(9)$ Å and $Z=2$. The X-ray investigation was based on 817 independent reflections collected with an automatic single-crystal diffractometer of the type CAD-4, using $\text{MoK}\alpha$ -radiation. The structure consists of discrete hexakis(dimethylsulfoxide)zinc(II) complex ions and perchlorate ions. The zinc atom coordinates six DMSO molecules through the oxygen atoms, forming an almost regular octahedron. A structural investigation of the hexakis(dimethylsulfoxide)zinc(II) ions has also been performed in dimethylsulfoxide solution, using a large-angle $\theta-\theta$ diffractometer for X-ray diffraction measurements on liquids. The average Zn–O bond length is 2.110 Å in the solid state and 2.127(5) Å in dimethylsulfoxide solution, the corresponding Zn–S distances are 3.135 Å and 3.147(3) Å, respectively.

The configuration of zinc(II) is usually either octahedral or tetrahedral.¹ With most unidentate ligands coordinating *via* oxygen octahedral complexes are formed. Many structural investigations of crystals containing the hexaaquazinc(II) ions, $\text{Zn}(\text{OH}_2)_6^{2+}$, have been reported.^{2–8} The structure of the hexaaquazinc(II) ion has also been determined in concentrated aqueous solutions.^{9,10} The average Zn–O bond length in this ion is 2.09 Å in both crystals and solutions. Also organic ligands coordinating *via* oxygen, such as pyridine *N*-oxide, form regular octahedral structures¹¹ with an average Zn–O bond length of 2.102 Å.

The solvation of the divalent d^{10} ions, zinc(II), cadmium(II) and mercury(II) in dimethylsulfoxide solution has previously been studied by means of calorimetry, large angle X-ray diffraction on solu-

tions and Raman and infrared spectroscopy.^{12,13} For cadmium(II) and mercury(II) the structures have been determined in both solid state and solution.^{13–15} For zinc(II), spectroscopic measurements show that the dimethylsulfoxide is coordinated *via* the oxygen atom.¹³ The preparation of the compound $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ has been described previously.¹⁶ Judging from the empirical formula, the zinc(II) ion probably coordinates six DMSO molecules in an octahedral configuration. The coordination geometry of the DMSO solvated zinc(II) ion in solution plays a fundamental part in the discussion of the thermodynamics of the complex formation of zinc(II) in DMSO solution.¹⁷

In an earlier paper,¹³ it was reported that the solubility of $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ in DMSO is only 0.29 M. This concentration is too low to allow a study of the solvate structure by means of X-ray diffraction measurements. It is, however, possible to prepare a supersaturated 0.70 M solution. With this solution the structure of the zinc(II) DMSO solvate can be determined.

EXPERIMENTAL

Preparation of crystals. The crystals were prepared and analyzed as described previously.¹⁶ They are slightly hygroscopic; single-crystals decompose in air to powder in two days. The crystals also react with organic compounds such as stopcock and silicon grease and different types of glue. Epoxy glues work satisfactorily, however. The density of the crystals was determined by the displacement method with benzene.

X-Ray data collection. Weissenberg photograms revealed the Laue class $\bar{3}m$ and the systematic

absences: $hh2\bar{h}l$; $l=2n+1$ indicating the space groups $P31c$ or $P31c$.

The intensity data were collected by an automatic single-crystal diffractometer of type CAD-4, at 246 ± 1 K, in order to avoid extensive decomposition of the crystal. Zr-filtrated $\text{MoK}\alpha$ -radiation ($\lambda=0.71300$ Å) was used. A hexagonal prismatic crystal with all edges ≈ 0.20 – 0.25 mm was used. The unit cell dimensions were obtained from the θ values of 25 reflections. Crystal data: $a=12.006(3)$, $c=12.578(9)$ Å, $V=1570.2(2)$ Å³, $Z=2$, $D_m=1.54(2)$, $D_x=1.55$ g cm⁻³, $\mu(\text{MoK}\alpha)=14.1$ cm⁻¹.

The $\omega-2\theta$ scan technique was employed, with a scan interval $\Delta\omega=1.00+0.15 \tan \theta$. The background measurements were performed by increasing $\Delta\omega$ with 1/4 on both sides. 2141 independent reflections in the range $3^\circ \leq \theta \leq 32^\circ$ were measured. Among these, 7 strong reflections were deleted because they were too intense for the counter. Another 810, with $I < 3\sigma_c(I)$ were deleted as being too weak. The values of $\sigma_c(I)$ were based on counting statistics. Three reflections were selected as standard. The fluctuations in the intensities of the standard reflections were irregular and less than 8%. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects.

X-Ray data collection from solutions. The X-ray scattering of $\text{MoK}\alpha$ -radiation ($\lambda=0.71069$ Å) from the free surface of the DMSO solution was measured as described in previous papers.^{18,19} The solution was enclosed in an air-tight shield, with cylindrical beryllium windows for the X-rays. The scattered intensity was measured at discrete points between the θ values 1.0 and 62.5° , where 2θ is the scattering angle. Intervals of 0.1° for $1.0^\circ \leq \theta \leq 20.0^\circ$ and 0.25° for $20.0^\circ \leq \theta \leq 62.5^\circ$ were used. 40 000 counts were accumulated twice for each point, corresponding to a statistical error of 0.35%. All measurements were performed at 25 ± 1 °C.

Preparation of the solution. The DMSO solution investigated was prepared by dissolving $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ in DMSO at around 90°C . The solution was cooled to room temperature very slowly. The 0.70 M solution obtained was metastable and had to be handled with care. On shaking, solid $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ immediately precipitated. The absorption coefficient, μ , of the solution was 6.1 cm⁻¹.

Computer programs. The computer programs used for determining the crystal structure are the same as listed elsewhere.²⁰ All calculations of the structures in solution were made by the KURVLR and PUTSLR computer programs.²¹ All calculations were carried out on a UNIVAC 1100/80 computer at the Computer Center, University of Lund.

STRUCTURE DETERMINATION OF THE SOLID SOLVATE

In the space group $P31c$ (no. 159), the zinc ions were placed in $z=0.25$ (2(b)), which fixed the origin. The chlorine atoms were given z coordinates close to 0.00 and 0.75 in the special positions 2(a) and 2(b), respectively. This was in accordance with the Patterson map. From a difference Fourier map, the positions of the sulfur, oxygen and carbon atoms in the DMSO molecules could be identified. With these atoms isotropic, full-matrix least-squares refinements, minimizing $\Sigma w(|F_o| - |F_c|)^2$, gave $R=0.14$ ($R_w=0.18$).

The conventional R -value is defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, and the weighted as $R_w = ((\Sigma w|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$. A refinement in the space group $P31c$ was unsuccessful.

At this stage a difference Fourier map revealed the positions of three oxygen atoms in each perchlorate ion. The remaining oxygen, on the three-fold axis, could not be located, presumably due to a very high temperature coefficient. In the following calculations, a high, fixed value was therefore given to this coefficient. Reflections with $\theta > 23^\circ$ are all very weak and were therefore excluded in the final refinements. This resulted in $R=0.073$ and $R_w=0.089$ for the remaining 817 independent reflections. A total of 92 parameters, including two scale factors, were varied in the final refinements. In the last cycle the shifts in the parameters were less than

Table 1. Final fractional atomic positional parameters with estimated standard deviations in parentheses.

Atom	x	y	z
Zn	1/3	2/3	1/4
O1	0.1699(12)	0.6293(12)	0.1584(10)
S1	0.1518(4)	0.7406(4)	0.1313(4)
C1	0.0728(25)	0.6995(22)	0.0043(16)
C2	0.0204(19)	0.7261(22)	0.2137(15)
O2	0.2198(12)	0.5045(13)	0.3443(10)
S2	0.0890(5)	0.4722(5)	0.3815(4)
C3	0.0806(23)	0.4209(24)	0.5164(17)
C4	0.9815(19)	0.3237(24)	0.3240(19)
Cl1	0	0	0.0019(14)
Cl2	2/3	1/3	0.2639(10)
O11	0.1145(26)	0.0121(23)	0.0481(15)
O12	0	0	0.897(7)
O21	0.6653(25)	0.2166(27)	0.2217(19)
O22	2/3	1/3	0.369(7)

Table 2. Final anisotropic thermal parameters (\AA^2) with estimated standard deviations in parentheses. The temperature factor expression used is $\exp[-\beta_{11}h^2 - \dots - 2\beta_{12}hk - \dots]$. The isotropic temperature coefficients are given in \AA^2 .

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.0051(1)	0.0051(2)	0.005(2)	0.0026(1)	0	0
O1	0.0097(13)	0.0097(13)	0.0081(10)	0.0055(11)	-0.0012(9)	0.0000(9)
S1	0.0073(4)	0.0079(5)	0.0069(3)	0.0039(4)	-0.0002(3)	0.0037(6)
C1	0.0183(32)	0.0162(26)	0.0074(16)	0.0115(25)	-0.0039(18)	0.0010(17)
C2	0.0111(22)	0.0139(26)	0.0084(15)	0.0085(20)	0.0024(14)	-0.0011(16)
O2	0.0114(15)	0.0104(14)	0.0068(9)	0.0067(13)	0.0000(9)	0.0007(9)
S2	0.0100(6)	0.0120(6)	0.0087(4)	0.0058(5)	0.0031(4)	0.0038(4)
C3	0.0165(30)	0.0189(33)	0.0064(13)	0.0125(28)	0.0054(16)	0.0047(17)
C4	0.0079(20)	0.0166(31)	0.0114(20)	0.0046(21)	-0.0013(16)	-0.0016(19)
Cl1	0.0097(5)	0.0097(5)	0.0185(10)	0.0048(2)	0	0
Cl2	0.0082(4)	0.0082(4)	0.0118(8)	0.0041(2)	0	0
O11	11.4(6)					
O12	25.0					
O21	12.6(8)					
O22	25.0					

1% of the e.s.d.'s. The weighting scheme was $w = 1/\sigma_c^2 + 0.040|F_o|^2 + 3.00$ which, according to a weight analysis, gave a satisfactory error distribution. The largest remaining peak found in the final difference Fourier map was 1.35 e \AA^{-3} . This peak was close to the position of the sulfur atom, the distance being 0.85 \AA . Definite H atom positions could not be ascertained. The scattering factors used in the calculations were taken from International Tables for X-Ray Crystallography, Vol. IV. The final refined parameter values are given in Tables 1 and 2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure consists of hexakis(dimethylsulfoxide)zinc(II) cations, $\text{Zn}(\text{DMSO})_6^{2+}$, with a three-fold axis, and of perchlorate ions, ClO_4^- . A stereoscopic view of the molecular geometry of the DMSO solvated zinc(II) ion is given in Fig. 1, and a stereoscopic view of the unit cell in Fig. 2. Some intramolecular distances and angles are listed in Table 3.

The $\text{Zn}(\text{DMSO})_6^{2+}$ complex. Each zinc(II) ion coordinates six DMSO molecules through the

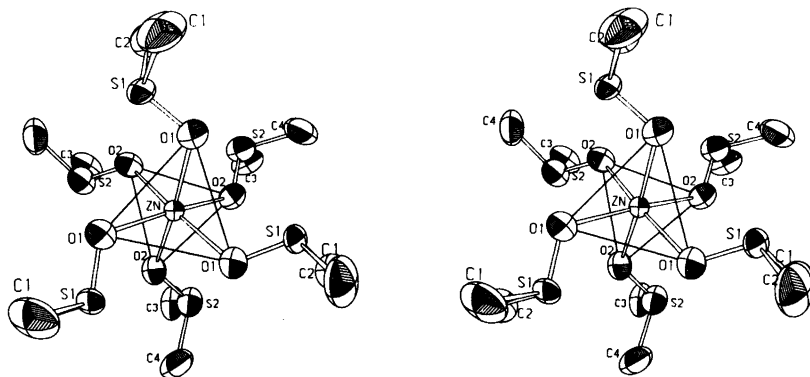


Fig. 1. A stereoscopic view of the $\text{Zn}(\text{DMSO})_6^{2+}$ cation. All atoms are represented by 50% probability ellipsoids.

Table 3. Some intramolecular atomic distances (Å) and angles (degrees) in $\text{Zn}(\text{DMSO})_6(\text{ClO}_4)_2(\text{s})$. Estimated standard deviations are given in parentheses.

Zn—O1	2.121(13)	O1—Zn—O1	93.3(5)
Zn—O2	2.098(13)	O2—Zn—O2	91.2(5)
		O1—Zn—O2	85.2(5)
Zn—S1	3.115(4)	O1—Zn—O2	90.4(5)
Zn—S2	3.154(5)	O1—Zn—O2	176.1(5)
S1—O1	1.496(13)	Zn—O1—S1	117.8(7)
S1—C1	1.796(22)	Zn—O2—S2	122.0(8)
S1—C2	1.820(20)		
S2—O2	1.492(13)	O1—S1—C1	104.5(9)
S2—C3	1.790(23)	O1—S1—C2	106.9(9)
S2—C4	1.750(24)	C1—S1—C2	99.6(10)
C11—O11	1.43(3)	O2—S2—C3	104.9(10)
C11—O12	1.31(9)	O2—S2—C4	106.3(9)
C12—O21	1.48(3)	C3—S2—C4	98.9(12)
C12—O22	1.32(9)		
		O11—C11—O11	104.7(12)
		O11—C1—O12	113.9(10)
		O12—C12—O12	109.4(11)
		O12—C12—O22	109.5(11)

oxygen atoms. The resulting coordination polyhedron around the zinc(II) ion is a slightly distorted octahedron with an average Zn—O bond length of 2.110 Å, Table 3. The sulfur atoms also form a somewhat irregular octahedron around zinc, with an average Zn—S distance of 3.135 Å. The slight distortion of the octahedron around zinc is shown by a torsion angle of 57.3° along the three-fold axis and a distance of 0.017 Å between the zinc atom and the centre of gravity of the oxygen octahedron.

The average S—O and S—C distances within the pyramidal DMSO molecule are 1.494 and 1.790 Å, respectively, which agree well with distances found for other solvates where DMSO is coordinated *via* oxygen.²² The S—O bond is slightly longer and consequently weaker than in crystalline

DMSO.²³ This is also indicated by the Raman and infrared spectra¹³ which show a lowering of the S—O stretch frequency on the coordination of DMSO *via* oxygen. The S—C bond is, on the other hand, shorter, and consequently stronger, in the coordinated DMSO. Consistent with this, the S—C stretching frequency is higher in coordinated than in free DMSO.¹³

The average Zn—O—S angle is 120°, Table 3, a value found for the M—O—S angle in many DMSO solvates. It is obvious that the hybridization around the oxygen atom in DMSO determines this angle. The angles within the coordinated DMSO molecules are much the same as in other DMSO complexes^{14,15,24,25} and in free DMSO.²³

The ClO₄⁻ ion. The four oxygen positions 011,

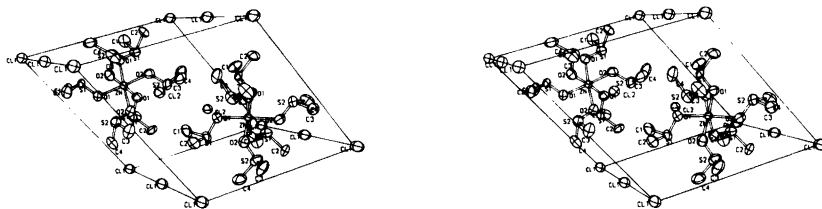


Fig. 2. A stereoscopic view of the trigonal unit cell.

012, 021 and 022 belong to the two perchlorate ions. Two of these, 011 and 021, are situated around a three-fold axis and fairly well-defined. The bond lengths Cl—O for these oxygens are 1.43 and 1.48 Å (Table 3), *i.e.* close to the bond lengths generally found in perchlorates, 1.42–1.43 Å.²⁶ The other two oxygen positions 012 and 022 are on the three-fold axis. Disordered perchlorate ions are also found, *e.g.*, in the structure of $\text{AgClO}_4 \cdot 2\text{DMSO}$,²⁴ $[\text{Cd}(\text{DMSO})_6](\text{ClO}_4)_2$,¹⁴ $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$,¹⁵ $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$.²⁵ A survey of such structures is given in Ref. 24.

STRUCTURE DETERMINATION IN SOLUTION

Data reduction and correction. The measured intensities were corrected for the background and normalized to a stoichiometric unit of volume, V , corresponding to the average volume per zinc(II) ion in the solution. The normalization was done by comparing the high angle region of the corrected intensities with the sum of the independent coherent scattering and the fraction of the incoherent scattering reaching the counter. No corrections for the absorption were applied.

RHF scattering factors, f , were used²⁷ for the neutral atoms and zinc(II). For hydrogen, the spherical form factors proposed by Stewart *et al.* were employed.²⁸ No absorption corrections were necessary. Anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, were applied to all atoms.²⁷ The incoherent scattering factors, I_{incoh} , were taken from the same sources as before.²⁹ Corrections for the Breit-Dirac factor in the form appropriate for a radiation counter, $(\lambda'/\lambda)^3$, where $\lambda' = \lambda + \Delta\lambda$ and

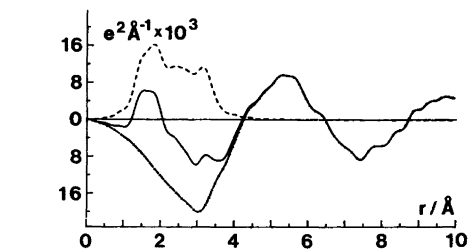


Fig. 3. The function $D(r) - 4\pi r^2 \rho_0$ (solid line) compared with sums of calculated peak shapes of the refined model (dashed line). The parameter values used are given in Table 4 and in the text. The difference is shown by the dashed-dotted lines.

$\Delta\lambda = \frac{h}{mc}(1 - \cos 2\theta)$, were applied.²⁷ The reduced intensity curves, $i(s)$, and the electronic radial distribution functions, $D(r)$, with $M = \text{Zn}$, were calculated as described previously.¹³ Small spurious peaks below 1.5 Å in the $[D(r)_{\text{obs}} - D(r)_{\text{calc}}]$ function which could not be related to interatomic distances, were removed by a Fourier transformation procedure.³ The calculation of intramolecular intensity contributions to the reduced intensity curve and the electronic radial distribution function were carried out as described previously.^{21,30}

RESULTS

Intensity curve and radial distribution (RDF). The electronic radial distribution function (RDF), $D(r) - 4\pi r^2 \rho_0$, is given in Fig. 3. The peak found at about 3.2 Å in the radial distribution function (RDF) fits with the zinc–sulfur distance, found in the solid state of $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$, Table 3.

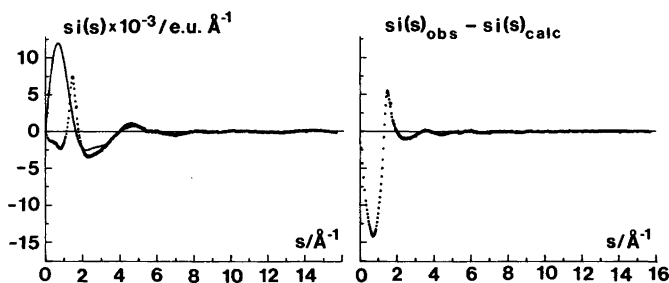


Fig. 4. Reduced intensities, $i(s)$, multiplied with s , for 0.7 M $\text{Zn}(\text{DMSO})_6^{2+}$ solution (left). Experimental values are denoted by dots (the six first are obtained by extrapolation) and values calculated for the refined model by a solid line. The difference between experimental and calculated values, $si_{\text{obs}}(s) - si_{\text{calc}}(s)$, is also shown (right).

The expected zinc–oxygen distance at about 2.1 Å could not be seen in the RDF, however.

The intramolecular DMSO distances should occur at about 1.48(S–O), 1.81(S–C), 2.66(O–C) and 2.77 Å(C–C). The peak at 1.6–1.7 Å, Fig. 4 is due to the S–O and S–C distances. Expected Cl–O and O–O distances within the tetrahedral ClO_4^- ion are 1.43 and 2.33 Å, respectively.²⁶ The broad peaks at 5–6 and 9–10 Å are certainly due to interactions between DMSO molecules.³¹

The sum of all calculated intramolecular reduced intensity contributions, $i_{\text{calc}}(s)$, is compared with experimental $i_{\text{obs}}(s)$ curves in Fig. 4, after multiplication by s .

Least-squares refinements. This procedure was carried out as described previously.¹³ The model finally selected consisted of the following parts.

1. In the $\text{Zn}(\text{DMSO})_6^{2+}$ complex, the distances Zn–O and Zn–S, d , the coefficients b of their temperature factors $\exp(-bs^2)$, and the number of distances, n , were refined. Also the contribution from the O–O interactions was introduced, assuming an octahedral arrangement around the zinc atom.

2. Intramolecular DMSO bond distances and temperature factor coefficients were taken from a study of liquid DMSO.³¹ These distances agree very well with the values found in solid and gaseous

Table 4. Least-squares refinement of the 0.70 M zinc(II) perchlorate DMSO solution. The refined parameters d =distance (Å), b =temperature factor coefficient (Å²) and n =number of distances per metal atom are obtained in the range $5.50 \leq s \leq 15.25$ of the reduced intensity curve. Estimated standard deviations are given in parentheses for refined parameters.

Complex	Interaction	Parameter	
$\text{Zn}(\text{DMSO})_6^{2+}$	Zn–O	d	2.127(5)
		b	0.0148(9)
	Zn–S	d	3.147(3)
		b	0.0158(6)
	Zn–O and Zn–S	n	6.0(1)
ClO_4^-	Cl–O	d	1.425
		b	0.0010
		n	4
DMSO	S–O	d	1.496
	S–C	d	1.805
	S–O and S–C	b	0.0017

state.^{23,32} In this way, all DMSO molecules, bonded as well as non-bonded, were accounted for.

3. The same parameters as before were used for the perchlorate ion.¹³

The parameter values from the refinements in the range $5.50 \leq s \leq 15.25 \text{ \AA}^{-1}$ are summarized in Table 4. The standard deviations given are those calculated in the least-squares procedure.

DISCUSSION

The zinc(II) ion coordinates six DMSO molecules through the oxygen atoms in an octahedral configuration. A zinc(II) solvate of the same type is formed with pyridine-N-oxide.¹¹ In the solid solvates, the Zn–O distances are 2.110 and 2.102 Å, respectively. The Zn–O distance of 2.127 Å found in the zinc(II) solvate in DMSO solution is very close to the values found in the solid.

Zinc(II) is a hard acceptor preferring hard donor atoms like oxygen. The bonds formed are of a mainly electrostatic character. Among the important oxygen ligands coordinated is water. In all crystalline zinc(II) hydrates investigated, six water molecules are octahedrally coordinated.^{2–8} The average Zn–O distance ranges from 2.078 to 2.107 Å, with an overall average of 2.092 Å. This value is very close to the distances found in the hexahydrated zinc(II) ion in aqueous solution, 2.08 and 2.092 Å.^{9,10}

The Zn–O distances in the hexahydrates are significantly shorter than in the DMSO and pyridine-N-oxide hexasolvates. Water is thus more strongly bonded than organic solvents coordinating *via* oxygen. The oxygen in solvents such as DMSO and pyridine N-oxide thus acts as a less hard donor than the water oxygen.

From the average bond lengths of the zinc(II) hydrates and solvates, the ionic radius of the zinc (II) ion in octahedral configuration can be derived. The radii of oxygen are taken as 1.35 Å in the organic solvates where oxygen is two-coordinated and as 1.36 Å in the hydrates where oxygen is three-coordinated.³³ From the solid hexasolvates a value of $r(\text{Zn}^{2+})=0.76 \text{ \AA}$ is calculated and from the DMSO hexasolvate in solution $r(\text{Zn}^{2+})=0.78 \text{ \AA}$. From the hydrates in solid phase and solution $r(\text{Zn}^{2+})=0.73 \text{ \AA}$ is found. The value calculated from oxide and fluoride structures by Shannon and Prewitt,³³ 0.745 Å, is very close to the value derived from the present measurements.

The enthalpy change of the transfer $^{12}\text{Zn}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{DMSO})$, $\Delta H_{\text{tr}}^\circ = -60 \text{ kJ mol}^{-1}$, indicates that the solvation of the zinc(II) ion is favoured in DMSO relative to water, in spite of the fact that the Zn—O bonds are shorter and consequently stronger in water than in DMSO. An obvious explanation of this apparent contradiction is that more energy has to be spent in water to break the solvent structure. This difference must evidently be $>60 \text{ kJ}$, the value of $\Delta H_{\text{tr}}^\circ$. It should be noted that for mercury(II), the bond distances Hg—O are about the same,¹³ 2.40 Å, in aqueous and DMSO solution, while the value of $\Delta H_{\text{tr}}^\circ = -76 \text{ kJ mol}^{-1}$.

Acknowledgements. My thanks are due to Dr. Åke Oskarsson for his continuous readiness to help during the crystallographic part of this work. I am also most indebted to Professor Oliver Lindqvist and Mr. Åke Iverfeldt who recorded the data of the zinc(II) perchlorate in DMSO solution on the X-ray diffractometer for liquids of the Department of Inorganic Chemistry, University of Göteborg. Professor Sten Ahrland is gratefully thanked for his stimulating and continuous interest in this investigation.

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Received May 5, 1981.