A Comparative X-Ray Diffraction Study of Aqueous MnSO₄ and Crystals of MnSO₄ • 5 H₂O

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X-ray single crystal analysis of MnSO₄ • 5 H₂O shows that the manganese atoms are octahedrally coordinated by oxygen atoms, four of which belong to water molecules and two to sulphate groups. A model derived from the crystal structure was fitted to the X-ray scattering intensities from aqueous MnSO₄. Good agreement with experimental data is achieved using a model in which Mn(H₂O)₆·₆(OSO₄)₂⁻ interacts with about ten water molecules and each sulphate ion with about seven water molecules.

Analysis of X-ray [1—3] and neutron [4] diffraction data from concentrated aqueous salt solutions gives details about the environment of the ions and information about the geometry of the coordination polyhedra. This is particularly useful in the case of direct interaction between the anion and the cation, since information about their relative orientation cannot be obtained through other experimental techniques than diffraction; in the last several years contributions to the knowledge of complex-formation in solution have been provided by the analysis of halogen salt solutions [1, 3, 5] and recently by that of some sulphate salts, i.e. Fe₂(SO₄)₃ [6], CdSO₄ [7], In₂(SO₄)₃ [8] and Cr₂(SO₄)₃ [9].

Shapovalov and Radechenko [10] examined diffraction data of dilute MnSO₄ solutions; their analysis was, however, limited to the first hydration sphere and no mention was made of cation-anion interaction, although an indication for its presence is suggested by the values of equilibrium constants [11]. We therefore undertook a detailed analysis of the diffraction data of two concentrated MnSO₄ solutions, which is reported in this paper, together with the single crystal structure determination of MnSO₄ • 5 H₂O.

Experimental and Data Processing

MnSO₄ · H₂O (Merck reagent grade) was dissolved in water to give a 2 M (Sol. A) and a saturated (Sol. B) solution. Mn⁴⁺ and SO₄²⁻ contents were determined by titrations with standard EDTA [12] and with a cation exchange resin (Dowex 50 W-X8). The analytical results are given in Table 1.

X-ray scattering data were obtained at 20 ± 1°C on a θ — 2θ diffractometer using Mokz radiation (wavelength λ = 0.7107 Å). A divergent beam was diffracted at the horizontal surface of the sample and then monochromatized by reflection from a curved quartz crystal. The observed range of scattering angles (2θ) was from 3° to 134°, corresponding to the range 0.46 Å⁻¹ ≤ s ≤ 16.3 Å⁻¹, where s = (4π/λ) sin θ is the scattering variable. The measured intensities were corrected for background, polarization and absorption [13], and smoothed by fourth differences [14]. The Compton contribution was evaluated by a semiempirical method [15] in order to account for the monochromator discrimination. The corrected intensities were scaled to the independent scattering factor for the solution using both the analytical method [16] and visual comparison. The structure function was then constructed according to

\[
i(s) = \left( I_{e.u.} - \sum_{i=1}^{m} x_i f_i^2 \right) / \left( \sum_{i=1}^{m} x_i f_i \right)^2,
\]

Table 1. Composition of the examined solutions in moles/liter. d is the density and μ the linear absorption coefficient calculated for Mokz radiation.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Mn</th>
<th>SO₄</th>
<th>H₂O</th>
<th>d g · cm⁻³</th>
<th>μ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.00</td>
<td>2.00</td>
<td>53.635</td>
<td>1.2683</td>
<td>5.76</td>
</tr>
<tr>
<td>B</td>
<td>3.775</td>
<td>3.775</td>
<td>50.075</td>
<td>1.4722</td>
<td>9.76</td>
</tr>
</tbody>
</table>
where $f_i$ are the atomic scattering amplitudes corrected for anomalous dispersion, $x_i$ are the stoichiometric coefficients in a structural unit containing $m$ kinds of atoms and $I_{e.u.}$ is the intensity in electron units. The scattering factors were computed according to an analytical formula using the coefficients proposed by Hajdu [17] for H$_2$O and S, and by Cromer and Waber [18] for O; that of Mn was interpolated from the values given in the International Tables [19]. The experimental correlation function $G(r)$ was obtained from $i(s)$ by Fourier transformation according to

$$G(r) = 1 + (2\pi^2 q_0 r)^{-1} \int_{s_{\min}}^{s_{\max}} i(s) \sin(s r) \, ds,$$  

where $r$ is the interatomic distance, $s_{\min}$ and $s_{\max}$ are the lower and upper limits of the experimental data and $q_0$ is the bulk number density of the stoichiometric units.

Before calculating the final correlation function, the structure function $i(s)$ was corrected for residual systematic errors by means of a procedure described by Levy, Danford and Narten [15]. The method is based on removal of spurious peaks of the $G(r)$ curve in the low $r$ region, where they clearly do not correspond to any interatomic distance; the peak due to S–O distance was also removed according to a procedure previously described [20].

**Single crystal**

Crystals suitable for X-ray analysis were obtained by evaporation of a concentrated water solution of MnSO$_4$·H$_2$O (Merek reagent grade). A crystal of dimensions $0.13 \times 0.17 \times 0.30$ mm was sealed in a Lindemann glass capillary and used for X-ray data collection. Preliminary cell dimensions were obtained from Weissenberg photographs and were refined together with orientation matrix by a procedure previously described [20]. The structure was solved by conventional Patterson and Fourier techniques; positional and isotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares methods using reflections with $I \geq 2.5 \sigma(I)$; the quantity minimized was $\Sigma w(\Delta F)^2$, where $w=1/\sigma^2$. After three cycles the $R$ factor was 0.066; anisotropic temperature factors further lowered the $R$ factor to 0.043. In a difference map calculated at this stage, the highest peaks were between 0.5 and 0.7 el $\text{Å}^{-3}$ and could all be identified as possible positions for hydrogen atoms. With the H atoms held fixed in the Fourier positions ($B = 3.5$ Å$^2$), the least squares refinement was continued until all parameter shifts were smaller than the corresponding standard deviations. Final positional parameters are given in Table 2. Anisotropic temperature factors together with observed and calculated structure factors are available from the authors.

**Table 2. Positional parameters (×10$^4$) with estimated standard deviations in parentheses. Coordinates of hydrogen atoms are deduced from 3D difference synthesis.**

<table>
<thead>
<tr>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
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<tbody>
<tr>
<td>MN(1)</td>
<td>0000 (0)</td>
<td>0000 (0)</td>
</tr>
<tr>
<td>MN(2)</td>
<td>5000 (0)</td>
<td>5000 (0)</td>
</tr>
<tr>
<td>S</td>
<td>0345 (1)</td>
<td>2886 (1)</td>
</tr>
<tr>
<td>O(1)</td>
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<tr>
<td>O(4)</td>
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<tr>
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<tr>
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<tr>
<td>H(59)</td>
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<tr>
<td>H(62)</td>
<td>360</td>
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<tr>
<td>H(69)</td>
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<td>H(74)</td>
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<tr>
<td>H(83)</td>
<td>866</td>
<td>374</td>
</tr>
<tr>
<td>H(84)</td>
<td>821</td>
<td>387</td>
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<tr>
<td>H(91)</td>
<td>635</td>
<td>143</td>
</tr>
<tr>
<td>H(92)</td>
<td>384</td>
<td>162</td>
</tr>
</tbody>
</table>

Atomic scattering factors were taken from [19].

**Crystal data**: MnSO$_4$·5H$_2$O $M = 241.12$ triclinic $a = 6.36(1)$; $b = 10.77(1)$; $c = 6.16(1)$ Å; $\alpha = 80.3(1)^{\circ}$; $\beta = 110.1(1)^{\circ}$; $\gamma = 106.0(1)^{\circ}$; $U = 382.1$ Å$^3$; $D_m(\text{flotation}) = 2.07$; $Z = 2$; $D_e = 2.095$ g/cm$^{-3}$; $F(000) = 246$; space group P1 (from structure analysis); $\mu = 19.96$ cm$^{-1}$. A total of 1408 independent reflections were measured up to $2\theta \leq 52^\circ$. The final $R$ factor is 0.034 for the 1334 refined reflections and 0.036 for the 1408 measured ones.
Analysis of the Results

a) Solutions

The experimental structure functions $s_i(s)$ and the resulting correlation functions $G(r)$ are plotted in Figs. 1 and 2 respectively. In the experimental $G(r)$ four peaks are present, with their maxima centered at about 2.2, 2.8, 3.5 and 4.2 Å.

The dominant peak at 2.2 Å, a value comparable with Mn-O distance in the crystal structure, is to be ascribed mainly to Mn-O nearest neighbours interactions; a partial contribution to this peak comes also from the O-O interactions within the sulphate group, which fall at 2.4 Å.

The peak at 2.8 Å is to be ascribed to O-O nearest neighbours interactions between hydrogen-bonded water molecules, which are present both in the bulk and in the cation hydration shells; further contributions to this peak come from interactions among oxygen atoms of the sulphate ion and anionic hydration water molecules.

The large peak at 4.2 Å should mainly result from the interactions between Mn$^{2+}$ and water molecules in the second coordination shell (Mn-(OH$_2$)$_{11}$) and partially from the trans water molecules within the cation hydration complex. This peak contains also the contributions from SO$_4^-$-H$_2$O interactions (distances between sulphur atom and H$_2$O molecules).

The peak at 3.5 Å, which is well defined in the saturated solution but less evident in the 2M one, should derive from Mn-S contacts within the expected Mn(H$_2$O)$_6$-(OSO$_3$)$_{2-2z}$ complexes. Its value is very close to the Mn-S distance in the crystal structure and falls within the range (3.20—3.50 Å) found for cation-sulphur interaction in the previously investigated solutions [6—9].

b) The crystal structure

The main features of the crystal structure of MnSO$_4$·5H$_2$O agree with those of MgSO$_4$·5H$_2$O [21] and CuSO$_4$·5H$_2$O [22]. The two non-equivalent manganese atoms in the unit cell, Mn(1) and Mn(2), have very similar surroundings. Each of them is octahedrally coordinated by oxygen atoms, four of which belong to water molecules and two to sulphate groups. SO$_4^-$ tetrahedra share two corners...
with adjacent MnO(6) octahedra giving rise to polymeric chains, which run along [1 1 0]; a view of the chains down c axis is shown in Figure 3. The values of bond distances and angles are given in Table 3. Within the MnO(6) octahedra the two MnO_SO distances (average value 2.190 Å) are longer than Mn-O_H2O ones (average value 2.145 Å), as also found in MgSO4 • 5H2O.

In the SO4 group, which has a very regular tetrahedral geometry, S-O distances are in the range 1.46—1.48 Å, but no significant difference exists between distances involving the two free oxygen atoms and those bonded to the manganese ions. The bonding angles at the bridging oxygens, that is Mn(l)—0(1) Mn(l)—0(W5) Mn(l)—0(W6) Mn(2)—0(2) Mn(2)—0(W7) Mn(2)—0(W8) S—0(1) S—0(2) S—0(3) S—0(4) O(1)—Mn(1)—O(W5) O(1)—Mn(1)—O(W6) O(W5)—Mn(1)—O(W6) O(2)—Mn(2)—O(W7) O(2)—Mn(2)—O(W8) O(W7)—Mn(2)—O(W8) O(1)—S—O(2) O(1)—S—O(3) O(1)—S—O(4) O(2)—S—O(3) O(2)—S—O(4) O(3)—S—O(4) Table 3. Bond distances and angles with standard deviations in parentheses.

Table 4. Distances and angles in hydrogen bonding. The e.s.d.'s are 0.06, 0.07, 0.09 Å and 6° respectively.

\[
\begin{array}{cccc}
O—H & H···O & O···O & O···OH \\
O(W5)—H(54)···O(4) & 0.90 & 1.92 & 2.82 & 178° \\
O(W5)—H(59)···O(W9) & 0.76 & 2.00 & 2.74 & 166° \\
O(W6)—H(62)···O(2) & 0.90 & 2.15 & 2.89 & 173° \\
O(W6)—H(69)···O(W9) & 1.01 & 1.80 & 2.80 & 170° \\
O(W7)—H(73)···O(3) & 0.92 & 1.83 & 2.72 & 164° \\
O(W7)—H(74)···O(4) & 0.89 & 1.95 & 2.79 & 157° \\
O(W8)—H(83)···O(3) & 0.83 & 1.92 & 2.73 & 165° \\
O(W9)—H(91)···O(1) & 1.02 & 1.93 & 2.85 & 160° \\
O(W9)—H(92)···O(2) & 0.90 & 2.09 & 3.11 & 150° \\
\end{array}
\]

\[a \quad x, y, z; \quad b \quad 1 + x, y, z; \quad c \quad 1 - x, - y, 1 - z; \quad d \quad x, y, z - 1; \quad e \quad 1 + x, y, z - 1.\]
Refinement of the Structural Model in Solution

In order to get more detailed information than that given by the experimental $G(r)$, the analysis based on the refinement of a model structure function was used [23–24]. The contribution of discrete interactions to the structure function is accounted for by using the Debye formula modified to give a Gaussian like distribution of interatomic distances while a uniform distribution of distances is described by the formula proposed by Narten and Levy [25]. Least squares refinement of the model parameters were performed by the PUTSLR program [26] connected with the generalized least-squares LETA-GROP program [27]; the minimized function was

$$U = \sum (v_{\text{obs}}(s) - v_{\text{calc}}(s))^2$$

The starting model was built up assuming octahedral geometry around the cation with an apex filled by an oxygen atom of $SO_4^-$ group; the structural parameters including the relative position of $SO_4^-$ tetrahedron and MnO(6) octahedron were taken from the single crystal structure. A second hydration shell around the cation was also considered by introducing two waters around each of the coordinated water molecules; an hydration sphere was also assumed around the oxygen atoms of the sulphate groups.

According to this model the following parameters were considered as independent and refined in the least-squares procedure:

a) The distance $r_{\text{Mn}-(H_2O)_n}$ and two mean square deviations $\sigma_{\text{Mn}-(H_2O)_n}$ and $\sigma_{(H_2O)_n-(H_2O)_n}$ within the manganese $\text{Mn(H}_2\text{O)}_{6-z}(\text{SO}_4)_z$ octahedron.

b) The $r_{O_s-O_s}$ distance and their pertinent $\sigma_{O_s-O_s}$ in the $SO_4^-$ group.

c) One mean square deviation $\sigma$ for all the discrete interactions and the value of the $z$ parameter within the complex $\text{Mn(H}_2\text{O)}_{6-z}(\text{SO}_4)_z$; all the values of the interactions, namely $\text{Mn(1)-S, Mn(1)-O(2), Mn(1)-O(3), Mn(1)-O(4)}$ and $(\text{H}_2\text{O})_{6-z}(\text{SO}_4)_z$ were held fixed and given the values found in the single crystal structure.

d) The $r_{(H_2O)_{n-1}-(H_2O)_{n}}$, its mean square deviation $\sigma_{(H_2O)_{n-1}-(H_2O)_{n}}$ and the number of interactions $n_{(H_2O)_{n-1}-(H_2O)_{n}}$ in the second hydration shell of the cation, where no fixed orientation of the external water molecules was assumed; therefore also $r_{\text{Mn}-(H_2O)_n}$ and its mean square deviation $\sigma_{\text{Mn}-(H_2O)_n}$ were considered as independent parameters.

e) The number of $n_{S-H_2O}$ interactions together with $r_{O_s-H_2O}$ and $r_{S-H_2O}$ distances and their mean square deviations $\sigma_{O_s-H_2O}$ and $\sigma_{S-H_2O}$.

f) $r_{\text{eff}}$ and $\sigma_{\text{eff}}$, pertinent to $\text{Mn-H}_2\text{O, S-H}_2\text{O, O-H}_2\text{O and H}_2\text{O-H}_2\text{O}$ contacts, which are the terms of higher weight in a uniform distribution of distances.

The structure and correlation functions obtained from the best fit are compared with the experimental data in Figs. 1 and 2. The agreement is very satisfactory and supports the consistency of the proposed model with the experimental data; minor differences can be attributed to the fact that the complex

Table 5. Values of the most significant parameters [$r =$ distance (Å); $\sigma =$ mean square deviations (Å); $n =$ number of interactions] used in the final calculation of the synthetic structure function. $z$ is the average aggregation number of sulphate bonded to $\text{Mn}^{++}$.

| Cation | $r_{\text{Mn}-(H_2O)}$ | $\sigma_{\text{Mn}-(H_2O)}$ | $r_{(H_2O)_{n-1}-(H_2O)_{n}}$ | $\sigma_{(H_2O)_{n-1}-(H_2O)_{n}}$ | $n_{(H_2O)_{n-1}-(H_2O)_{n}}$ | $r_{\text{Mn}-(H_2O)}$ | $\sigma_{\text{Mn}-(H_2O)}$ | $r_{(H_2O)_{n-1}-(H_2O)_{n}}$ | $\sigma_{(H_2O)_{n-1}-(H_2O)_{n}}$ | $n_{(H_2O)_{n-1}-(H_2O)_{n}}$ | $r_{\text{Mn}-(H_2O)}$ | $\sigma_{\text{Mn}-(H_2O)}$ | $r_{(H_2O)_{n-1}-(H_2O)_{n}}$ | $\sigma_{(H_2O)_{n-1}-(H_2O)_{n}}$ | $n_{(H_2O)_{n-1}-(H_2O)_{n}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sol A | 2.195 (3) | 0.104 (5) | 2.779 (5) | 0.04 (1) | 4.17 (1) | 0.31 (1) | 10.4 (4) |
| Sol B | 2.218 (3) | 0.117 (5) | 2.736 (6) | 0.03 (2) | 4.22 (1) | 0.29 (1) | 9.8 (3) |

<table>
<thead>
<tr>
<th>Anion</th>
<th>$r_{O_s-O_s}$</th>
<th>$\sigma_{O_s-O_s}$</th>
<th>$r_{O-H_2O}$</th>
<th>$\sigma_{O-H_2O}$</th>
<th>$r_{S-H_2O}$</th>
<th>$\sigma_{S-H_2O}$</th>
<th>$\lambda_{S-H_2O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol A</td>
<td>2.44 (1)</td>
<td>0.14 (1)</td>
<td>2.890 (8)</td>
<td>0.07 (1)</td>
<td>3.90 (2)</td>
<td>0.19 (1)</td>
<td>7.4 (5)</td>
</tr>
<tr>
<td>Sol B</td>
<td>2.44 (1)</td>
<td>0.14 (1)</td>
<td>2.90 (1)</td>
<td>0.09 (1)</td>
<td>3.91 (2)</td>
<td>0.22 (1)</td>
<td>7.4 (4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex</th>
<th>$z$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol A</td>
<td>0.75 (6)</td>
<td>0.10 (1)</td>
</tr>
<tr>
<td>Sol B</td>
<td>0.92 (8)</td>
<td>0.13 (2)</td>
</tr>
</tbody>
</table>
geometry found in the crystal has been rigidly maintained in solution, where small variation of the Mn-O-S angle and of the relative orientation of the sulphate group and MnO$_6$ octahedron can be expected. The final values of the most significant parameters are given in Table 5.

**Conclusion**

From the final values of the structural parameters the following conclusions can be drawn:

The parameters referring to the manganese ion confirm its octahedral coordination by six oxygen atoms, with a value for the Mn-O distance, 2.20 Å, very close to that found in the crystal structures of MnSO$_4$ \cdot 5H$_2$O and of Mn(NO$_3$)$_2$ \cdot 4H$_2$O [28]. The same value was also found in the solutions of MnSO$_4$ [10] and Mn(ClO$_4$)$_2$ [29].

The hypothesis of the presence of a second hydration shell around the Mn$^{2+}$ ion should be accepted, with a network of hydrogen bonding among inner and outer water molecules. The possibility of a second hydration shell around the cation was taken into account neither by Ohtaky in the case of Mn(ClO$_4$)$_2$ [29] solution nor by Shaplow and Radchenko for MnSO$_4$ [10].

As for the average number of SO$_4^{2-}$ groups directly bonded to the cation, the least squares refinement gives final values of $Z = 0.75(6)$ and $0.92(8)$ for 2M and 3.775M solutions, respectively; these values are in good agreement with those calculated from the stability constants [30], if these are assumed to be valid in the range of concentrations used in the present analysis.

From the final value of the O$_5$-O$_3$ distance it is possible to calculate the value of S-O by assuming a tetrahedral geometry for SO$_4^{2-}$; its value, 1.50 Å, is in good agreement with that found both in crystal structures and in the previously investigated solutions; the agreement is good also for the values found for the parameters which refer to the hydration of the SO$_4^{2-}$ group.

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