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# The Molecular and Crystal Structure of Tris(1,2-ethanediol)-zinc(II) Sulfate: $[Zn(C_2H_6O_2)_3]SO_4$

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The crystal structure of $[Zn(C_2H_6O_2)_3]SO_4$ has been determined and refined using three-dimensional X-ray diffraction data. The unit cell is orthorhombic, $Ac2a(C_{2v}^{17})$, with $Z=4$ and the following cell parameters: $a=9.544(1)$ Å, $b=14.198(1)$ Å and $c=9.180(1)$ Å. The structure was solved by heavy-atom Patterson and Fourier methods. The refinement using full-matrix least-squares techniques was based on 1364 reflexions and converged at an $R$-value of 0.042. The structure consists of discrete $[Zn(C_2H_6O_2)_3]^{2+}$-cations and $SO_4^{2-}$-anions. Zn(II) is octahedrally surrounded by the six glycol oxygens, with a mean Zn—O distance of 2.091 Å. The sulfate ions connect the cations by means of hydrogen bond contacts thus forming a three-dimensional network.

This work forms part of a research program at this department, which aims at elucidating the coordination behaviour of glycol* towards different transition metal ions ($Mn^{2+}-Zn^{2+}$) especially with chloride [1,2] and sulfate as anions. This structure is the fourth in the series with sulfate as anion, the other three being $[Cu(C_2H_6O_2)_3]SO_4$,[3] $[Ni(C_2H_6O_2)_3]SO_4$ and $[Co(C_2H_6O_2)_3]SO_4$.[4]

## EXPERIMENTAL

*Crystal preparation and analyses.* The crystals were prepared by dissolving $ZnSO_4.7H_2O$ in glycol on a water-bath (molar ratio 1:3) and leaving the solution in a desiccator over sulfuric acid. After a few days colourless, thick tabular, hygroscopic crystals separated. The zinc content of the crystals was determined by titration with EDTA [5] to 18.2 (weight-%). Calculated for $[Zn(C_2H_6O_2)_3]SO_4$: 18.6. IR-spectra indicated that no water was present in the structure.

*Crystal data and space group.* Weissenberg and precession photographs revealed that the crystals were orthorhombic. The cell parameters measured from these photographs were refined using data obtained from a powder film, taken in a camera of Guinier-Hägg type using $CuK\alpha_1$-radiation and Si ($a=5.43054$ Å) as internal standard. The final cell parameters with estimated standard deviations are: $a=9.544(1)$ Å, $b=14.198(1)$ Å and $c=9.180(1)$ Å. The density of the crystals was determined by the flotation method using xylene and bromoform. The experimentally determined density is $1.84\pm0.01$ g cm$^{-3}$ and the calculated value with $Z=4$ is 1.856 g cm$^{-3}$. The systematic extinctions found (for $hkl$ when $k+l=2n+1$, for $0kl$ when $k$ and $l=2n+1$ and for $hk0$ when $h=2n+1$) are characteristic for the space groups $Ac2a(C_{2v}^{17}$; No. 41) and $Abma(D_{2h}^{18}$; No. 64). In standard setting these space groups are $Aba2$ and $Cmca$ respectively, but in order to label the axes so as to get $c<a<b$, which is consistent with international convention, $Aba2$ was transformed to $Ac2a$ by the matrix $100/00\bar{1}/010$ and $Cmca$ to $Abma$ by the matrix 001/100/010. The general eight-fold positions for $Ac2a$ become: $x,y,z$; $\bar{x},y,\bar{z}$ $1/2-x,y,$ $1/2+z$; $1/2+x,y,$ $1/2-z$, and $A$-centering. In $Abma$ a center of symmetry is added to these positions. As $Z=4$ in this structure both Zn and S must be in a fourfold position. The only way this can be achieved with a reasonable Zn-S distance is by choosing the acentric space group $Ac2a$. The correctness of this choice is further supported by the successful refinement and the lack of high correlation coefficients between any of the atoms.

*Intensity data.* A crystal with the dimensions $0.19\times0.19\times0.19$ mm was mounted in a capillary of Lindeman glass to protect it from moisture. Intensities for $hk0-hk7$ were measured on the automatic diffractometer PAILRED using graphite-monochromated $MoK\alpha$-radiation. During the seventh layer the crystal started to decompose and a new crystal with

* Throughout this paper 1,2-ethanediol will be referred to as glycol.

*Table 1a.* Atomic positional and vibrational parameters for $[Zn(C_2H_6O_2)_3]SO_4$. All parameters have been multiplied by $10^4$. The anisotropic temperature factors have been calculated according to the expression $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$. (Standard deviations are given in parentheses.)

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Zn | 0 | 1500 | 0 | 41(0.5) | 21(0.2) | 52(0.7) | 0 | 4(0.6) | 0 |
| O(1) | 1381(3) | 363(3) | 88(5) | 39(2) | 28(1) | 129(6) | 4(2) | 11(3) | 1(3) |
| O(2) | 1573(3) | 2502(3) | −384(4) | 49(3) | 24(1) | 71(4) | −4(2) | −1(3) | 5(2) |
| O(3) | 39(4) | 1585(3) | 2271(4) | 58(2) | 34(2) | 61(3) | 13(2) | 3(3) | 10(2) |
| C(1) | 725(5) | 4497(4) | 4686(7) | 60(4) | 26(2) | 104(7) | 5(2) | 11(4) | −4(3) |
| C(2) | 3236(6) | 2700(4) | 3089(6) | 82(5) | 39(3) | 80(6) | 20(3) | −33(4) | −5(3) |
| C(3) | 3687(6) | 1879(5) | 2214(6) | 90(6) | 46(3) | 79(6) | 23(4) | −28(5) | −12(3) |
| S | 0 | 4708(1) | 0 | 36(1) | 20(0.5) | 49(2) | 0 | −3(1) | 0 |
| O(4) | 901(3) | 4114(3) | 921(4) | 66(3) | 29(1) | 57(3) | 8(2) | −19(3) | 6(2) |
| O(5) | 923(3) | 311(3) | 4109(5) | 50(3) | 39(2) | 106(5) | −3(2) | 2(3) | 31(3) |

the dimensions $0.20 \times 0.22 \times 0.37$ mm was used to collect the intensities for $hk7-hk12$. Altogether 2552 intensities were measured from the first crystal and 1215 from the second. The intensities were measured by omega-scan. The half scan interval for $hk0$ reflexions was 1.2° for $\theta > 20°$ and 1.7° for $\theta < 20°$ and it was gradually increased to 1.3 and 1.9° ,respectively, for $hk7$ reflexions (first crystal). For the second crystal the intervals were 1.4 and 2.0° for $hk7$ reflexions, the latter being gradually increased to 2.3° for $hk12$ reflexions. Reflexions for which the total number of counts during one scan interval did not exceed 10 000 were remeasured. Background intensities were measured 40 s before and after each scan and the scan speed used was 1°/min.

After Lp- and absorption corrections [$\mu$(MoK$\alpha$) = 22.17 cm$^{-1}$] had been applied to all intensities in the two data materials the $hkl$ and $\bar{h}kl$ reflexions were averaged by taking the arithmetic mean value of their respective $F^2$-values. The intensity data at this stage consisted of two separate sets; I($hk0-hk7$) with 1132 independent intensities and II($hk7-hk12$) with 565 independent intensities. Since the first crystal had started to decompose during the seventh layer and there were large differences between the two $hk7$ layers, that of data I was deleted, leaving 1019 intensities. At the end of the refinements, structure factors for all the unobserved reflexions were calculated and they all had amplitudes lower than the corresponding threshold values. The computer programs used were the same as those described in an earlier paper by the author.[4]

*Table 1b.* Atomic positional coordinates for the hydrogen atoms. The fractional coordinates have been multiplied by $10^3$. An overall temperature factor $B = 4$ Å$^2$ was used throughout the refinement. (Standard deviations are given in parentheses.)

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| H(1) | 288(8) | 44(6) | 475(9) |
| H(2) | 154(8) | 291(6) | −6(9) |
| H(3) | 22(9) | 119(6) | 222(11) |
| H(4) | 85(8) | 439(6) | 371(10) |
| H(5) | 125(9) | 393(6) | 500(9) |
| H(6) | 382(7) | 327(6) | 288(9) |
| H(7) | 235(8) | 283(6) | 311(8) |
| H(8) | 387(8) | 217(6) | 129(9) |
| H(9) | 286(7) | 131(6) | 230(8) |

## STRUCTURE DETERMINATION AND REFINEMENT

Data I was used to calculate a three-dimensional Patterson synthesis. Both Zn and S were found in the special fourfold position 0,$y$,0. From subsequent three-dimensional Fourier and difference Fourier syntheses the rest of the non-hydrogen atoms could be located. Least-squares refinements with individual scale factors and the positional coordinates and isotropic thermal factors for all atoms as parameters yielded an $R$-value of 0.069.

Subsequently an overall scale factor was used in the refinement and data was further reduced by omitting those reflexions for which $\Delta I/I \geq 0.5$[1] which left 891 independent intensities (sin $\theta_{max} = 0.66$). When anisotropic thermal factors for all atoms were introduced, the $R$-value decreased to 0.044. From a difference Fourier synthesis reasonable positions for the nine hydrogen atoms were found and their positional

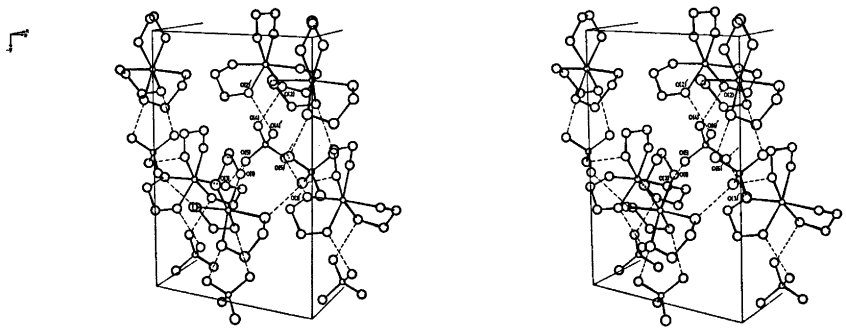

*Fig. 1.* A stereoscopic view of the molecular packing in $[Zn(C_2H_6O_2)_3]SO_4$. Hydrogen bonds are indicated with dashed lines. For the sake of clarity only one unique repeating unit in the [100]-direction has been illustrated.

coordinates refined. The data sets were then brought together and the refinement continued until convergence at an $R$-value of 0.043. As the space group is polar and the calculated structure amplitudes include the effect of anomalous scattering, two orientations of the structure had to be considered. In this case it was sufficient to change $k$ to $-k$ in order to change the orientation and the decrease in the conventional $R$-factor from 0.0432 to 0.0418 ($R_w$: 0.0508→ 0.0491) is significant with more than 99 % certainty.[6] The scattering curves used for $Zn^{2+}$, S, O, and C were those proposed by Cromer and Waber [7] and the dispersion correction terms ($\Delta f'$ and $\Delta f''$) for $Zn^{2+}$ and S were selected from Cromer and Lieberman's [8] calculations. For the hydrogen atoms the scattering curve proposed by Stewart *et al.*[9] was used. The weights were calculated according to the relation suggested by Cruickshank [10]

$w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$ using the constants $a = 250$, $c = -0.02$ and $d = 0.0003$. The final weighted $R$-value

$$R_w = [\sum w_i(|F_o| - |F_c|)^2 / \sum w_i|F_o|^2]^{\frac{1}{2}} = 0.047.$$

The isotropic temperature factors for the hydrogen atoms were included as parameters for some additional cycles of refinement. Due to the fact that the data set is comprised from two different materials being scaled together, there was no physical significance in the values obtained and they are not published.

In a final difference Fourier synthesis nothing abnormal could be detected. The highest peaks were in the vicinity of Zn and S and there were some additional peaks at the oxygen atoms which possibly could arise from small errors in the scattering factors. The final atomic positional and vibrational parameters are listed in Table 1. The observed and calculated struc-

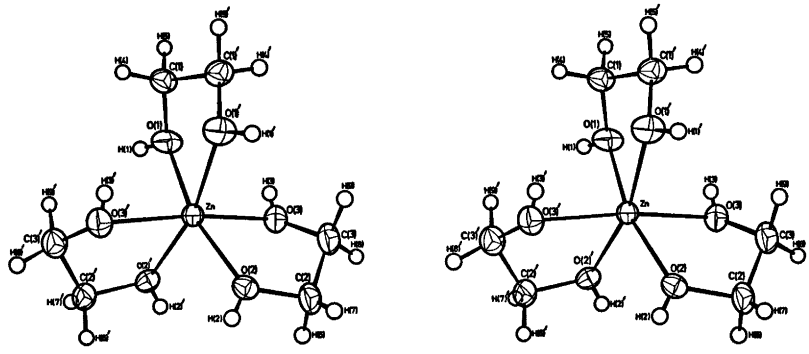

*Fig. 2.* A stereoscopic illustration of the $[Zn(C_2H_6O_2)_3]^{2+}$-ion. Thermal ellipsoids are scaled to enclose 50 % probability.

*Table 2.* Dimensions of the $[Zn(C_2H_6O_2)_3]^{2+}$-ion. For the labelling of atoms, see Fig. 2. (Standard deviations are given in parentheses.)

| Ligand | Atoms | $d_{Zn-O}$(Å) | $d_{O-C}$(Å) | $d_{C-C}$(Å) | $\angle_{O-C-C}$(°) | $\angle_{Zn-O-C}$(°) |
|---|---|---|---|---|---|---|
| I | Zn(O(1)–C(1))(O(1)′–C(1)′) | 2.086(4) | 1.428(6) | 1.499(10) | 107.8(4) | 112.3(3) |
| II, II′ | Zn(O(2)–C(2))(O(3)–C(3)) | 2.099(4)<br>2.089(3) | 1.441(7)<br>1.436(7) | 1.480(9) | 109.7(5)<br>108.2(5) | 112.7(3)<br>109.2(3) |

| Atoms | Angle(°) | Atoms | Angle (°) |
|---|---|---|---|
| O(1)–Zn–O(1)′ | 78.6(2) | O(2)–Zn–O(2)′ | 94.6(2) |
| O(1)–Zn–O(2)′ | 94.6(1) | O(2)–Zn–O(3)′ | 96.7(2) |
| O(1)–Zn–O(2) | 166.1(2) | O(2)–Zn–O(3) | 78.8(2) |
| O(1)–Zn–O(3) | 89.7(2) | O(3)–Zn–O(3)′ | 173.4(2) |
| O(1)–Zn–O(3)′ | 95.4(2) | | |

| Atoms | $d$ (Å) | Atoms | Angle (°) | Atoms | Angle (°) |
|---|---|---|---|---|---|
| O(1)–H(1) | 0.78(8) | Zn–O(1)–H(1) | 117(6) | O(3)–C(3)–H(8) | 104(5) |
| O(2)–H(2) | 0.65(8) | Zn–O(2)–H(2) | 119(7) | O(3)–C(3)–H(9) | 111(4) |
| O(3)–H(3) | 0.59(8) | Zn–O(3)–H(3) | 83(9) | C(1)′–C(1)–H(4) | 120(5) |
| C(1)–H(4) | 0.91(9) | C(1)–O(1)–H(1) | 114(6) | C(1)′–C(1)–H(5) | 111(5) |
| C(1)–H(5) | 0.99(8) | C(2)–O(2)–H(2) | 106(7) | C(3)–C(2)–H(6) | 112(4) |
| C(2)–H(6) | 1.00(8) | C(3)–O(3)–H(3) | 124(9) | C(3)–C(2)–H(7) | 118(5) |
| C(2)–H(7) | 0.86(8) | O(1)–C(1)–H(4) | 109(5) | C(2)–C(3)–H(8) | 102(5) |
| C(3)–H(8) | 0.96(8) | O(1)–C(1)–H(5) | 114(5) | C(2)–C(3)–H(9) | 106(4) |
| C(3)–H(9) | 1.15(8) | O(2)–C(2)–H(6) | 106(4) | H(4)–C(1)–H(5) | 95(7) |
| | | O(2)–C(2)–H(7) | 98(5) | H(6)–C(2)–H(7) | 112(7) |
| | | | | H(8)–C(3)–H(9) | 124(6) |

ture amplitudes can be obtained from the author on request.

## DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure is built up from discrete $[Zn(C_2H_6O_2)_3]^{2+}$-cations and $SO_4^{2-}$-anions. The $SO_4^{2-}$-ions connect the cations by means of hydrogen bonds forming a three-dimensional network as shown in Fig. 1.

*The coordination around Zn(II).* The six coordinated glycol oxygens form an almost regular octahedron around Zn(II); there are no significant differences between the Zn–O distances which range between 2.086(4) and 2.099(4) Å. This is consistent with what would be expected for an ion with a closed $d$-shell and six equivalent ligands. The mean Zn–O distance of 2.091 Å agrees well with the Zn–O distances measured in five different octahedral hexaquozinc complexes, where the weighted mean value of $Zn-OH_2$ is $2.099 \pm 0.020$ Å.[11]

The angular distribution in the octahedron around Zn is not so ideal as in the hexaquo complexes. As glycol acts as a bidentate ligand (see below) the dimensions of the glycol molecules will determine the O–Zn–O angles, which in all the complexes investigated so far fall considerably below 90° (Fig. 2 and Table 2)

*The ligands.* The glycol molecules have *gauche* conformation with dihedral angles between connected O–C–C planes of 50.7 and 48.2° for ligands I and II(II′), respectively. (For the

labelling of ligands, see Table 2). Because of the twofold rotation axis, ligand I possesses $C_2$-symmetry and ligands II and II′ are symmetry-related. As a consequence the carbon atoms in ligand I are situated at equal distances above and below the Zn – O – O plane, 0.330(7) Å, while ligand II shows more unsymmetric behaviour, C(2) being 0.118(6) Å above the Zn – O – O plane and C(3) 0.403(7) Å below it. In the three puckered five-membered $Zn-O_2-C_2$ rings the angles around the oxygen and carbon atoms do not differ significantly from the tetrahedral angle of 109.5° (Table 2). The C – C and C – O distances as well as the O – H and C – H distances in the five-membered rings all agree well with earlier reported values for this kind of complex.[1–4]

*Conformational analysis of the* $[Zn(C_2H_6O_2)_3]^{2+}$ *ion.* In the $[Zn(C_2H_6O_2)_3]^{2+}$-ion none of the ligands have their C – C bond parallel to the molecular three-fold axis (Fig. 2). Using the terminology derived for tris(ethylenediamine)-metal complexes and discussed by Raymond *et al.*,[12] and later by Hawkins,[13] the conformation for the $[Zn(C_2H_6O_2)_3]^{2+}$-ion thus becomes $\Lambda\lambda\lambda\lambda(-\Delta\delta\delta\delta)$. As the point group is *m2m*, both enantiomorphs $\Lambda$ and $\Delta$ will be present in equal amounts.

In $[Cu(C_2H_6O_2)_3]SO_4$,[3] where one of the ligands has a $\Lambda\lambda$-conformation, this was explained by the fact that this ligand showed shorter hydrogen bond distances to sulfate oxygens than the other two. This is not consistent with the conditions found in this structure, where ligand I shows two hydrogen bond distances of 2.726(5) Å, while the corresponding values for ligand II (II′) are 2.613(6) and 2.661(5) Å, *i.e.* significantly shorter although all three ligands have $\Lambda\lambda$-conformation. In the compound $[Zn(H_2O)]_6$-$SO_4[(NH_4)_2SO_4]$ (Tutton's salt),[14] where the Zn – O distances are comparable to those found in this structure (mean value = 2.105 ± 0.025 Å), the hydrogen bond distances between water oxygens and sulfate oxygens vary between 2.71 and 2.85 Å. A comparison between these values and those found in $[Zn(C_2H_6O_2)_3]SO_4$ reveals that ligand I shows quite normal hydrogen bond distances, while ligand II (II′) is involved in significantly shorter hydrogen bond contacts. Evidently there must be some additional factors besides hydrogen bond contacts that influence the ring conformation, probably molecular packing conditions.

*The sulfate group and hydrogen bond contacts.* There are no significant differences between the S – O distances which show a mean value of 1.474 Å. The O – S – O angles are in good agreement with the expected value of 109.5°; the largest deviation being 1.9°. The sulfate ions function as connecting groups between the $[Zn(C_2H_6O_2)_3]^{2+}$-cations by means of hydrogen bond contacts. O(4) has one hydrogen bond contact to O(2) with an O···O distance of 2.661(5) Å, and O(5) has hydrogen bond contacts to O(1) and O(3) with the corresponding O···O distances of 2.726(5) and 2.613(6) Å. A complete list of distances and angles within the sulfate ion is presented in Table 3. The bond O(3) – H(3)···O(5) is far from linear, while the other two do not differ significantly from 180°.

*Table 3.* Dimensions of the sulfate group and hydrogen bond contacts in $[Zn(C_2H_6O_2)_3]SO_4$.

| Atoms | $d$(Å) | Atoms | Angle(°) |
|---|---|---|---|
| S – O(4) | 1.471(3) | O(4) – S – O(4)′ | 110.1(3) |
| S – O(5) | 1.476(4) | O(4) – S – O(5) | 107.6(2) |
| | | O(4) – S – O(5)′ | 111.3(2) |
| | | O(5) – S – O(5)′ | 109.0(3) |

| Atoms | $d_{O-H}$(Å) | $d_{H\cdots O}$(Å) | $d_{O\cdots O}$(Å) | $\angle_{O-H\cdots O}$(°) |
|---|---|---|---|---|
| O(1) – H(1)···O(5) | 0.78(8) | 1.96(8) | 2.726(5) | 166(9) |
| O(2) – H(2)···O(4) | 0.65(8) | 2.02(8) | 2.661(5) | 165(9) |
| O(3) – H(3)···O(5) | 0.59(8) | 2.24(9) | 2.613(6) | 124(11) |

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