

The Molecular and Crystal Structure of Tris(1,2-ethanediol)-cobalt(II) Sulfate: $[\text{Co}(\text{C}_2\text{H}_6\text{O}_2)_3]\text{SO}_4$

BRITT-MARIE ANTTI

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

The crystal structure of $[\text{Co}(\text{C}_2\text{H}_6\text{O}_2)_3]\text{SO}_4$ has been determined and refined using three-dimensional X-ray diffraction data. The unit cell is monoclinic, $P2_1/c$, with $Z=4$ and cell dimensions $a=8.818(1)$ Å, $b=7.585(1)$ Å, $c=19.264(1)$ Å and $\beta=99.357(5)^\circ$. The structure was solved by heavy-atom Patterson and Fourier methods and refined by full-matrix least-squares techniques based on 3130 independent intensities. The final R -value was 0.038. The structure consists of discrete $[\text{Co}(\text{C}_2\text{H}_6\text{O}_2)_3]^{2+}$ -cations and SO_4^{2-} -anions. Co(II) is octahedrally surrounded by six glycol oxygens with the Co—O distances ranging between 2.054(2) and 2.108(2) Å. The sulfate ions connect these cations by means of hydrogen bonds.

This work forms part of a research program at this department which includes the investigation of the coordination changes in complexes between glycol* and a series of transition metal ions ($\text{Mn}^{2+} - \text{Zn}^{2+}$). Two series are considered, one with chloride as anion^{1,2} and the other with sulfate as anion. This paper presents the structure of $[\text{Co}(\text{C}_2\text{H}_6\text{O}_2)_3]\text{SO}_4$, which is the third in the sulfate series, the other two being $[\text{Cu}(\text{C}_2\text{H}_6\text{O}_2)_3]\text{SO}_4^3$ and $[\text{Ni}(\text{C}_2\text{H}_6\text{O}_2)_3]\text{SO}_4$. The nickel compound has only been characterized from Weissenberg film data and was found to be isostructural with $[\text{Cu}(\text{C}_2\text{H}_6\text{O}_2)_3]\text{SO}_4$.² No further X-ray data have been collected so far.

EXPERIMENTAL

Crystal preparation and analyses. Pink, tabular (100), crystals separated when solutions of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in glycol (molar ratio 1:3) were

kept in a desiccator over sulfuric acid for a few days. The cobalt content of the crystals was determined by titration with EDTA⁴ to be 17.24 (weight-%). Calculated for $[\text{Co}(\text{C}_2\text{H}_6\text{O}_2)_3]\text{SO}_4$: 17.27. IR-spectra confirmed the absence of water in the structure.

Crystal data and space group. Rotation and Weissenberg photographs (zero and first layers) taken from crystals mounted around their b - and c -axes revealed that the crystals were monoclinic. The unit cell parameters measured from these photographs were refined using data obtained from powder photographs taken with a camera of Guinier-Hägg type with $\text{CuK}\alpha$ -radiation and Si ($a=5.43054$ Å) as internal standard. (Copper foil was used to avoid fluorescence.) The cell parameters, with estimated standard deviations in parentheses, are $a=8.818(1)$ Å, $b=7.585(1)$ Å, $c=19.264(1)$ Å and $\beta=99.357(5)^\circ$. A density of 1.77 ± 0.01 g cm^{-3} was measured for $[\text{Co}(\text{C}_2\text{H}_6\text{O}_2)_3]\text{SO}_4$ with the flotation method using bromoform and xylene. The calculated value for four formula units was 1.78 g cm^{-3} . The systematic extinctions of intensities found for $h0l$ when $l=2n+1$ and for $0k0$ when $k=2n+1$ are characteristic for the space group $P2_1/c$ (No. 14).

Intensity data. A crystal with dimensions $0.08 \times 0.25 \times 0.14$ mm was chosen for the measurements. As it was hygroscopic, it was mounted in a capillary of Lindeman glass with its b -axis parallel to the rotation axis. 4227 diffracted intensities from $h0l-h10l$ were measured with the automatic linear diffractometer PAILRED using graphite-monochromated $\text{MoK}\alpha$ -radiation. The intensities were measured by omega-scan and the half scan interval for $h0l$ reflexions was 1.0° for $\theta > 18^\circ$ and 1.9° for $\theta \leq 18^\circ$. For $h1l$ reflexions the corresponding values were 1.0 and 2.0° and these values were then used for the remaining layers. Reflexions for which the total number of counts during one scan interval did not exceed 4000 were measured twice. Background intensities were measured for 40 s before and after each scan and the scan speed was $1^\circ/\text{min}$. 3130 independent intensities ($\sin \theta_{\text{max}} = 0.58$), which were significantly above back-

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

Table 1. Computer programs used for the crystallographic calculations.

Name	Program function	Authors
PIRUM	Indexing and refinement of cell parameters from powder data.	P.-E. Werner, Stockholm, Sweden. ¹¹
TAPESUSY	Primary reduction of PAILRED diffractometer data.	O. Mårtensson and B. Hedman, Umeå, Sweden.
ABSOT ^a	Lorentz, polarization and absorption corrections for data collected using Weissenberg geometry. Preparative calculations for isotropic extinction correction in subsequent least-squares program.	P. Coppens, L. Leiserowitz and D. Rabinovich; modified by J. O. Thomas, Uppsala, Sweden.
UPALS ^a	Full-matrix least-squares refinement of atomic positional and thermal parameters, scale factors, and isotropic or anisotropic extinction parameters according to P. Coppens and W. C. Hamilton. ¹³	J.-O. Lundgren, Uppsala, Sweden. ¹² The program is based on LALS, a revised version of UCLALS1 by P. K. Gantzel, R. A. Sparks and K. N. Trueblood.
DRF ^a	Fourier summations including routines for structure factor calculations.	A. Zalkin, Berkeley, USA; modified by R. Liminga, J.-O. Lundgren, Uppsala and O. Lindgren, Göteborg, Sweden.
DISTAN ^a	Calculation of distances and angles, with corresponding standard deviations.	A. Zalkin, Berkeley, USA; modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
PLANE ^a	Calculation of least-squares planes using the method suggested by D. Blow ¹⁴ and calculation of the distance from a point to a plane and dihedral angles between planes.	C.-I. Brändén, Uppsala; modified by J.-O. Lundgren, Uppsala, Sweden.
SFIG	Calculation of structure factors for possible reflexions in a preset part of the reflexion sphere.	R. Liminga, Uppsala, Sweden.
ORTEP	Thermal ellipsoid plot program for stereoscopic illustrations of crystal structures.	C. K. Johnson, Oak Ridge, USA. ¹⁵
LAYOUT	Editing of structure factor tables.	O. Mårtensson, Umeå, Sweden.

^a These programs have been modified for a CDC 3300 computer by B. Hedman, Umeå, Sweden.

ground at the 95 % level, *i.e.* had $\Delta I/I \leq 0.5$,¹ were used in the refinements. L_p and absorption corrections were made. The linear absorption coefficient was 15.94 cm^{-1} and the transmission factor varied from 0.79 to 0.88. When the refinements were terminated, structure factors for all the unobserved intensities were calculated. They all had amplitudes lower than or equal to the corresponding threshold value.

The data programs used in the course of this structure determination are listed in Table 1. All calculations were performed on a CDC 3300 computer.

STRUCTURE DETERMINATION AND REFINEMENT

From a three-dimensional Patterson vector map the positions for the cobalt and sulfur atoms were found. A Fourier synthesis was calculated, based on these positions, and from this all the remaining non-hydrogen atoms were located. All atoms lie in general four-fold positions. The structure was refined by full-matrix least-squares techniques. When the positional

Table 2a. Atomic positional and thermal parameters for $[\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_3]\text{SO}_4$. All parameters have been multiplied by 10^4 . The anisotropic temperature factors have been calculated according to the formula $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. (Standard deviations are given in parentheses.)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	2351(0.4)	1229(0.5)	3706(0.2)	53(0.4)	66(0.5)	12(0.1)	5(0.4)	3(0.1)	1(0.2)
O(1)	3090(2)	2946(3)	3007(1)	82(3)	158(5)	13(0.5)	-19(3)	1(1)	12(1)
O(2)	4580(2)	1812(3)	4235(1)	64(2)	93(4)	19(0.6)	10(2)	-0.2(1)	5(1)
O(3)	1485(2)	3218(3)	4276(1)	75(3)	89(3)	16(0.5)	13(2)	6(1)	-4(1)
O(4)	74(2)	1275(3)	3166(1)	64(2)	132(4)	18(0.6)	-8(3)	1(1)	-2(1)
O(5)	2892(2)	-1123(3)	3241(1)	86(3)	106(4)	18(0.6)	8(3)	11(1)	-7(1)
O(6)	1800(3)	-600(3)	4436(1)	122(3)	77(3)	14(0.5)	-2(3)	10(1)	-1(1)
C(1)	4692(4)	3389(5)	3166(2)	78(4)	126(6)	20(1)	21(4)	9(1)	6(2)
C(2)	5087(3)	3420(4)	3953(2)	76(4)	82(5)	22(1)	-14(3)	-0.1(1)	-4(2)
C(3)	-170(4)	3236(5)	4117(2)	70(4)	118(6)	26(1)	18(4)	14(2)	-6(2)
C(4)	-599(4)	2887(5)	3344(2)	70(4)	142(6)	24(1)	25(4)	-3(2)	9(2)
C(5)	2065(4)	-2531(4)	3508(2)	89(4)	80(5)	21(1)	1(3)	5(1)	-12(2)
C(6)	2225(4)	-2365(4)	4295(2)	148(5)	69(5)	19(1)	1(4)	12(2)	-3(2)
S	2775(1)	3267(1)	1141(0.3)	56(1)	83(1)	12(0.2)	-14(1)	4(0.3)	5(0.3)
O(7)	1832(3)	3586(4)	1696(1)	88(3)	193(6)	17(1)	41(3)	13(1)	18(1)
O(8)	2913(2)	4947(3)	760(1)	94(3)	93(4)	19(1)	-27(3)	0.5(1)	13(1)
O(9)	4298(2)	2668(3)	1478(1)	63(3)	137(5)	32(1)	13(3)	5(1)	16(2)
O(10)	2041(3)	1947(4)	649(1)	188(5)	143(5)	18(1)	-91(4)	3(1)	-2(1)

Table 2b. Atomic positional and thermal parameters for the hydrogen atoms. The fractional coordinates have been multiplied by 10^3 . (Standard deviations are given in parentheses.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	273(4)	307(6)	262(2)	3.4(8)
H(2)	480(4)	633(6)	75(2)	3.4(8)
H(3)	172(4)	327(6)	469(2)	3.8(9)
H(4)	52(4)	554(6)	180(2)	4.0(9)
H(5)	361(5)	869(7)	326(2)	4.7(10)
H(6)	212(5)	964(6)	485(2)	4.0(10)
H(7)	466(3)	747(4)	203(1)	1.3(6)
H(8)	483(4)	445(6)	291(2)	3.3(8)
H(9)	389(4)	858(5)	91(2)	2.2(7)
H(10)	451(4)	422(6)	419(2)	3.6(9)
H(11)	64(5)	729(6)	60(2)	4.0(9)
H(12)	62(5)	939(7)	72(2)	5.2(11)
H(13)	30(4)	872(5)	194(2)	2.2(7)
H(14)	171(4)	786(6)	181(2)	3.2(8)
H(15)	247(4)	629(5)	338(2)	2.5(7)
H(16)	96(4)	763(5)	323(2)	2.0(7)
H(17)	160(3)	679(5)	450(2)	2.0(7)
H(18)	325(4)	738(6)	455(2)	3.5(9)

coordinates and the anisotropic temperature factors for all atoms were used as parameters, the refinement converged at an *R*-value of 0.049 ($R = [\sum |F_o| - |F_c|] / \sum |F_o|$). At this stage a difference electron density map was calculated, and, from this, probable positions for the hydrogen atoms were located. When their atomic positional and isotropic thermal factors were included as parameters, the refinement finally gave an *R*-value of 0.038. The weights were calculated by the method suggested by Cruickshank,⁵ $w = 1/(\alpha + |F_o| + c|F_o|^2 + d|F_o|^3)$ with $\alpha = 400$, $c = 0.03$ and $d = 0.001$. The final $R_w = [\sum w_i(|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2} = 0.034$. The scattering curves used for Co^{2+} , S, O, and C were those proposed by Cromer and Waber.⁶ The anomalous dispersion corrections for Co^{2+}

and S were selected from Cromer and Liebermans' calculations, and both $\Delta f'$ and $\Delta f''$ were taken into account. For the hydrogen atoms, the scattering curve given by Stewart *et al.*⁸ was used. A final difference electron density map was almost flat (the highest peak corresponded to $0.44 \text{ e } \text{\AA}^{-3}$).

The final atomic positional and thermal parameters are given in Tables 2a and b. The corresponding observed and calculated structure amplitudes can be obtained from the author, on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure consists of discrete $[\text{Co}(\text{C}_2\text{H}_4\text{O}_2)_3]^{2+}$ -cations and SO_4^{2-} -anions. These are mutually related in the way shown in Fig. 1, and are connected by means of hydrogen bonds between sulfate and glycol oxygens.

The coordination around Co(II). In the cation, Co(II) coordinates the six glycol oxygens with a slightly distorted octahedral arrangement with O(1) at the significantly shortest distance (2.054 Å); O(3), O(5) and O(6) at a mean distance of 2.086 Å, and O(2) and O(4) at the significantly longest distance (mean value 2.107 Å) to Co(II). The deviation of the four nearest ligands from the calculated least-squares plane around Co(II) is $-0.073(3)$, $0.073(3)$, $0.083(3)$, $-0.100(3)$ Å for O(1), O(3), O(5), and O(6), respectively, the atoms on which the calculation is based. Co(II) is situated 0.009(1) Å above the plane

The ligands. The glycol ligands, which act as bidentate ligands, all have *gauche* conformation with dihedral angles between connected O-C-C planes of 51.3, 55.9, and 51.8°, respectively, for ligands I, II, and III (for the labeling of ligands see Table 3). These values are

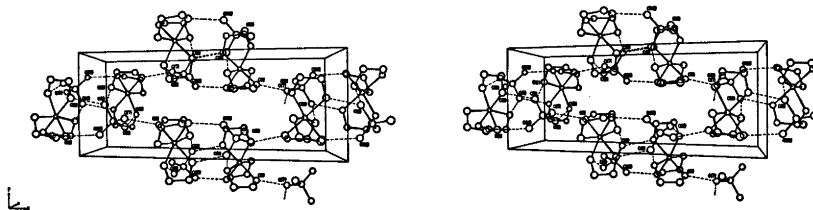


Fig. 1. A stereoscopic view of the molecular packing in $[\text{Co}(\text{C}_2\text{H}_4\text{O}_2)_3]\text{SO}_4$. Hydrogen bonds are marked with dashed lines.

Table 3. Dimensions of the $[\text{Co}(\text{C}_2\text{H}_4\text{O}_2)_3]^{2+}$ -ion. (Standard deviations are given in parentheses.) The labelling of atoms is in accordance to Fig. 2.

Atoms	d (Å)	Atoms	Angle (°)	Atoms	Angle (°)
Co—O(1)	2.054(2)	O(1)—Co—O(2)	79.3(1)	O(3)—Co—O(4)	81.2(1)
Co—O(2)	2.108(2)	O(1)—Co—O(3)	93.9(1)	O(3)—Co—O(5)	167.2(1)
Co—O(3)	2.082(2)	O(1)—Co—O(4)	92.6(1)	O(3)—Co—O(6)	88.9(1)
Co—O(4)	2.106(2)	O(1)—Co—O(5)	98.2(1)	O(4)—Co—O(5)	93.9(1)
Co—O(5)	2.087(2)	O(1)—Co—O(6)	175.0(1)	O(4)—Co—O(6)	92.0(1)
Co—O(6)	2.088(2)	O(2)—Co—O(3)	89.2(1)	O(5)—Co—O(6)	79.4(1)
		O(2)—Co—O(4)	167.0(1)		
		O(2)—Co—O(5)	97.3(1)		
		O(2)—Co—O(6)	96.6(1)		

Ligand	Atoms	$d_{\text{O-C}}$ (Å)	$d_{\text{C-C}}$ (Å)	$\angle_{\text{O-C-C}}$ (°)	$\angle_{\text{Co-O-C}}$ (°)
I	Co < O(1)—C(1) O(2)—C(2) O(3)—C(3)	1.435(4)	1.500(5)	106.2(2)	114.5(2)
		1.436(4)		109.5(3)	108.6(2)
		1.442(4)		107.0(3)	109.9(2)
II	Co < O(4)—C(4) O(5)—C(5)	1.426(4)	1.500(5)	110.0(3)	107.2(2)
		1.435(4)		109.3(3)	108.5(2)
III	Co < O(6)—C(6)	1.429(4)	1.503(5)	106.6(3)	113.5(2)

Atoms	d (Å)	Atoms	d (Å)	Atoms	d (Å)
O(1)—H(1)	0.77(4)	C(1)—H(7)	1.01(3)	C(4)—H(13)	0.91(4)
O(2)—H(2)	0.66(4)	C(1)—H(8)	0.96(4)	C(4)—H(14)	0.97(4)
O(3)—H(3)	0.79(4)	C(2)—H(9)	0.90(3)	C(5)—H(15)	1.01(4)
O(4)—H(4)	0.77(4)	C(2)—H(10)	0.95(4)	C(5)—H(16)	1.04(3)
O(5)—H(5)	0.64(4)	C(3)—H(11)	1.03(4)	C(6)—H(17)	0.97(3)
O(6)—H(6)	0.82(4)	C(3)—H(12)	1.03(5)	C(6)—H(18)	0.97(4)

in good agreement with those previously determined for metal-glycol complexes where glycol functions as a bidentate ligand.¹⁻³

In the five-membered Co—O₂—C₂ rings, the intramolecular distances show no significant deviations from other published values. The intra-ring angles show the same trend for all three rings; when the Co—O—C angle is larger than or almost equal to the tetrahedral angle the corresponding O—C—C angle is smaller than that value or *vice versa*. The O—H and C—H distances are normal for X-ray data and the angles around oxygen and carbon involving hydrogen atoms agree fairly well with the tetrahedral angle, they range between 98 and 128°. A list of distances and angles is presented in Table 3.

Conformational analysis. Using the terminology discussed by Raymond *et al.*³ for tris-(ethylenediamine)-metal complexes and looking down the molecular three-fold axis, which almost parallels the crystallographic *c*-axis, the $[\text{Co}(\text{C}_2\text{H}_4\text{O}_2)_3]^{2+}$ -ions have the $\Lambda\delta\delta\delta (= \Delta\lambda\lambda\lambda)$ conformation (Fig. 2). As the structure is centrosymmetric both enantiomorphs Λ and Δ will be present in equal amounts. In $[\text{Cu}(\text{C}_2\text{H}_4\text{O}_2)_3]\text{SO}_4^3$ at least one of the glycol ligands has a $\Lambda\lambda (= \Delta\delta)$ conformation which was explained in terms of shorter hydrogen bond distances to sulfate oxygens from that ligand, compared to the other two. In this structure the hydrogen bond distances are all of about the same order of magnitude [2.614(3)–2.683(4) Å] as would be expected

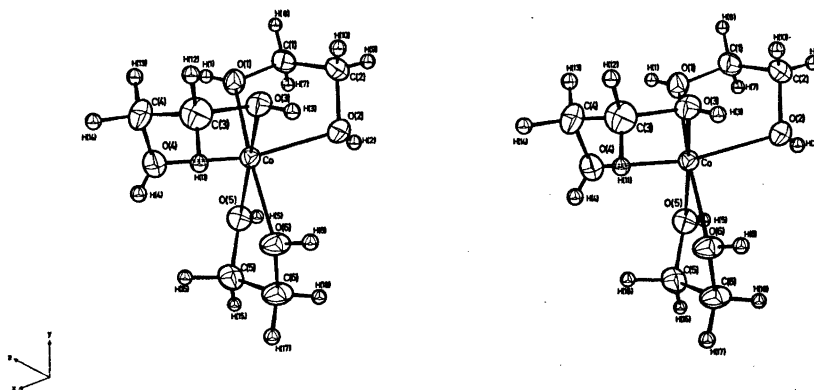


Fig. 2. A stereoscopic illustration of the $[\text{Co}(\text{C}_2\text{H}_4\text{O}_2)_3]^{2+}$ -ion looking down $[101]$ and showing the coordination around $\text{Co}(\text{II})$. Thermal ellipsoids are scaled to enclose 50 % probability.

from the conformational analysis. These values agree well with those found in $[\text{Co}(\text{H}_2\text{O})_6]\text{SO}_4$,¹⁰ where the $\text{O}\cdots\text{O}$ distances range between 2.65(3) and 2.93(3) Å. The $\Delta\delta$ -conformation of the glycol ligands in $[\text{Co}(\text{C}_2\text{H}_4\text{O}_2)_3]\text{SO}_4$, which means that the C—C bonds almost parallel $[001]$, could be a reason for the elongation of the unit cell in the c -direction.

The sulfate ion and the hydrogen bond contacts. The sulfate group, like the rest of the molecule, seems to be essentially strain-free. The largest deviation from the tetrahedral angle is 1.3° . The S—O distances could be divided into two groups which differ slightly in length. O(7) and O(8) have a mean distance of 1.481 Å to the

sulfur atom and show two hydrogen bonds each, while O(9) and O(10) having one hydrogen bond contact each are at a mean distance of 1.461 Å from the sulfur atom. As is indicated in Table 4, none of the hydrogen bonds deviate significantly from linearity.

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Table 4. Dimensions of the sulfate group and hydrogen bond contacts in $[\text{Co}(\text{C}_2\text{H}_4\text{O}_2)_3]\text{SO}_4$. (Standard deviations are given in parentheses.)

Atoms	d (Å)	Atoms	Angle ($^\circ$)
S—O(7)	1.477(2)	O(7)—S—O(8)	108.5(1)
S—O(8)	1.485(2)	O(7)—S—O(9)	108.2(1)
S—O(9)	1.465(2)	O(7)—S—O(10)	110.0(2)
S—O(10)	1.456(3)	O(8)—S—O(9)	110.0(1)
		O(8)—S—O(10)	109.4(1)
		O(9)—S—O(10)	110.7(2)

Atoms	$d_{\text{O-H}}$ (Å)	$d_{\text{H}\cdots\text{O}}$ (Å)	$d_{\text{O}\cdots\text{O}}$ (Å)	$\angle_{\text{O-H}\cdots\text{O}}$ ($^\circ$)
O(1)—H(1) \cdots O(7)	0.77(4)	1.87(4)	2.633(3)	174(5)
O(2)—H(2) \cdots O(8)	0.66(4)	1.97(4)	2.623(3)	177(4)
O(3)—H(3) \cdots O(10)	0.79(4)	1.83(4)	2.614(3)	170(5)
O(4)—H(4) \cdots O(7)	0.77(4)	1.91(4)	2.683(4)	175(4)
O(5)—H(5) \cdots O(9)	0.64(4)	1.99(4)	2.615(3)	165(6)
O(6)—H(6) \cdots O(8)	0.82(4)	1.81(4)	2.628(3)	176(4)

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