

Crystal structure of *cis*-tetraaqua-dichloridocobalt(II) sulfolane disolvate

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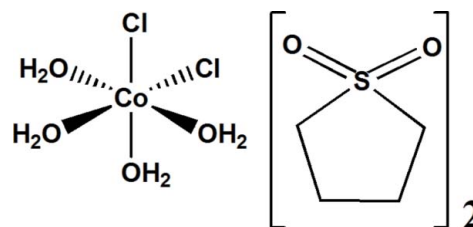
In the title compound, $[\text{CoCl}_2(\text{H}_2\text{O})_4] \cdot 2\text{C}_4\text{H}_8\text{SO}_2$, the Co^{II} cation is located on the twofold rotation axis and is coordinated by four water molecules and two adjacent chloride ligands in a slightly distorted octahedral coordination environment. The *cisoid* angles are in the range 83.27 (5)–99.66 (2)°. The three *transoid* angles deviate significantly from the ideal linear angle. The crystal packing can be described as a linear arrangement of complex units along *c* formed by bifurcated $\text{O}—\text{H} \cdots \text{Cl}$ hydrogen bonds between two water molecules from one complex unit towards one chloride ligand of the neighbouring complex. Two solvent molecules per complex are attached to this infinite chain *via* $\text{O}—\text{H} \cdots \text{O}$ hydrogen bonds in which water molecules act as the hydrogen-bond donor and sulfolane O atoms as the hydrogen-bond acceptor sites.

Keywords: crystal structure; cobalt(II) complex; sulfolane solvate.

CCDC reference: 1040554

1. Related literature

For structures where the Co^{II} atom exhibits an octahedral geometry and is coordinated by water molecules, see: Waizumi *et al.* (1990); Sarangarajan *et al.* (2008). For potential applications of organic–inorganic hybrid compounds, see: Al-Ktaifani & Rukiah (2011). For related structures, see: Bouacida *et al.* (2005, 2013); Sahbani *et al.* (2014).



2. Experimental

2.1. Crystal data

$[\text{CoCl}_2(\text{H}_2\text{O})_4] \cdot 2\text{C}_4\text{H}_8\text{O}_2\text{S}$
 $M_r = 442.22$
 Monoclinic, $C2/c$
 $a = 20.062(2) \text{ \AA}$
 $b = 9.4284(10) \text{ \AA}$
 $c = 10.5882(13) \text{ \AA}$
 $\beta = 118.734(5)^\circ$

$V = 1756.2(3) \text{ \AA}^3$
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.55 \text{ mm}^{-1}$
 $T = 295 \text{ K}$
 $0.21 \times 0.15 \times 0.09 \text{ mm}$

2.2. Data collection

Bruker APEXII diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2002)
 $T_{\text{min}} = 0.649$, $T_{\text{max}} = 0.748$

20238 measured reflections
 5090 independent reflections
 3409 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.061$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.129$
 $S = 1.01$
 5090 reflections
 108 parameters
 4 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.90 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.44 \text{ e \AA}^{-3}$

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
$\text{O1W}—\text{H1W} \cdots \text{Cl1}^{\text{i}}$	0.77 (3)	2.44 (3)	3.1885 (15)	165 (3)
$\text{O1W}—\text{H2W} \cdots \text{O11}$	0.81 (2)	1.99 (2)	2.782 (2)	165 (2)
$\text{O2W}—\text{H3W} \cdots \text{Cl1}^{\text{ii}}$	0.83 (2)	2.41 (2)	3.2289 (16)	171 (2)
$\text{O2W}—\text{H4W} \cdots \text{O12}$	0.79 (3)	2.05 (3)	2.835 (2)	174 (3)

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $x, -y + 1, z + \frac{1}{2}$.

Data collection: APEX2 (Bruker, 2011); cell refinement: SAINT (Bruker, 2011); data reduction: SAINT; program(s) used to solve structure: SIR2002 (Burla *et al.*, 2005); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and DIAMOND (Brandenburg & Berndt, 2001); software used to prepare material for publication: WinGX (Farrugia, 2012).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: IM2458).

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supporting information

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Crystal structure of *cis*-tetraaquadichloridocobalt(II) sulfolane disolvate

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S1. Comment

Organic-inorganic hybrid salts have received considerable attention because of their potential applications in analytical, material and supramolecular chemistry (Al-Ktaifani *et al.*, 2011; Bouacida *et al.* 2005, 2013; Sahbani *et al.*, 2014). In this work, we report the preparation and the structural investigation of $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2] \times 2 \text{C}_4\text{H}_8\text{SO}_2$. Since the central cobalt the Co^{II} cation is located on the twofold rotation axis the asymmetric unit of (I) consists of one one half of the complex unit and one molecule of sulfolane (Figure 1).

The structure of the compound consists of discrete tetraaquadichlorocobalt(II) complexes stacked in chains parallel to the *c* axis. The Co^{II} cation is coordinated by four water molecules and two adjacent chloride ligands in a slightly distorted octahedral geometry. The two Co—Cl distances are 2.510 (6) Å and the Co—O distances are between 2.165 (3) and 2.243 (3) Å in good agreement with that found in mineral compound $\text{CoCl}_2\text{O}_4\text{H}_8$ (Waizumi *et al.*, 1990) and in the coordination compound $[\text{CoCl}_2(\text{H}_2\text{O})_4]\text{C}_4\text{H}_6\text{N}_2\text{O}_2$ (Sarangarajan *et al.*, 2008). Cisoid angles around Co atom are in the range of 83.27 (5)° to 99.66 (2)°. In the organic molecule, the S atom is tetrahedrally coordinated by two O and two C atoms. The three bonds C—C are in the range 1.516 (2)–1.531 (3) Å. In the crystal, molecules are linked by O—H⋯O and O—H⋯Cl hydrogen bonds forming chains along [001] (Figure 2). The crystal packing can be described as a linear arrangement of complex units along *c* formed by bifurcated O—H⋯Cl hydrogen bonds between two water molecules from one complex unit towards one chloride ligand of the neighboring complex. Two solvent molecules per complex are attached to this infinite chain via O—H⋯O hydrogen bonds in which water molecules act as the hydrogen bond donor and sulfolane oxygen atoms as the hydrogen bond acceptor sites.

S2. Experimental

A solution of $\text{CoCl}_2 \times 2 \text{H}_2\text{O}$ (34 mg, 0.2 mmol) in water (10 ml) was added dropwise to a solution of sulfolane (24 mg, 0.2 mmol) in water (10 ml). The mixture was then refluxed with stirring for 3 h and the resulting solution was left to stand at room temperature. After several days, blue crystals were obtained and dried under vacuum (yield: 55%).

S3. Refinement

All non-H atoms were refined with anisotropic displacement parameters. Approximate positions for all H atoms were first obtained from the difference electron density map. However, the H atoms were situated into idealized positions and the H-atoms have been refined within the riding atom approximation with C—H = 0.93 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ except for H atoms of water molecules, which were refined isotropically using the following restraints: O—H = 0.84 (2) Å, H⋯H = 1.45 (2) Å and $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{O})$.

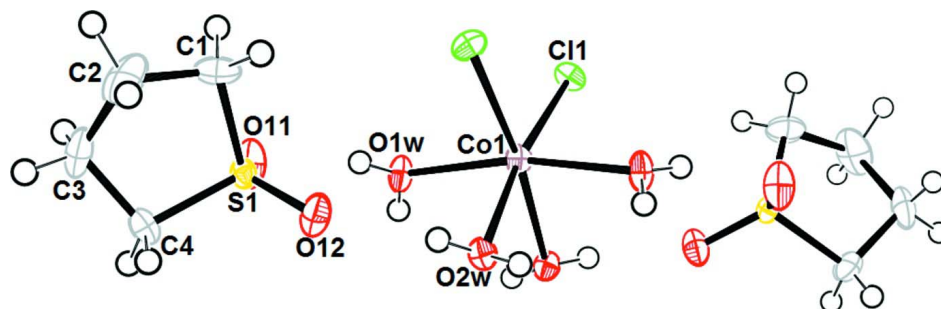


Figure 1

Molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level. Only the asymmetric unit is labelled. H atoms are represented as small spheres of arbitrary radii.

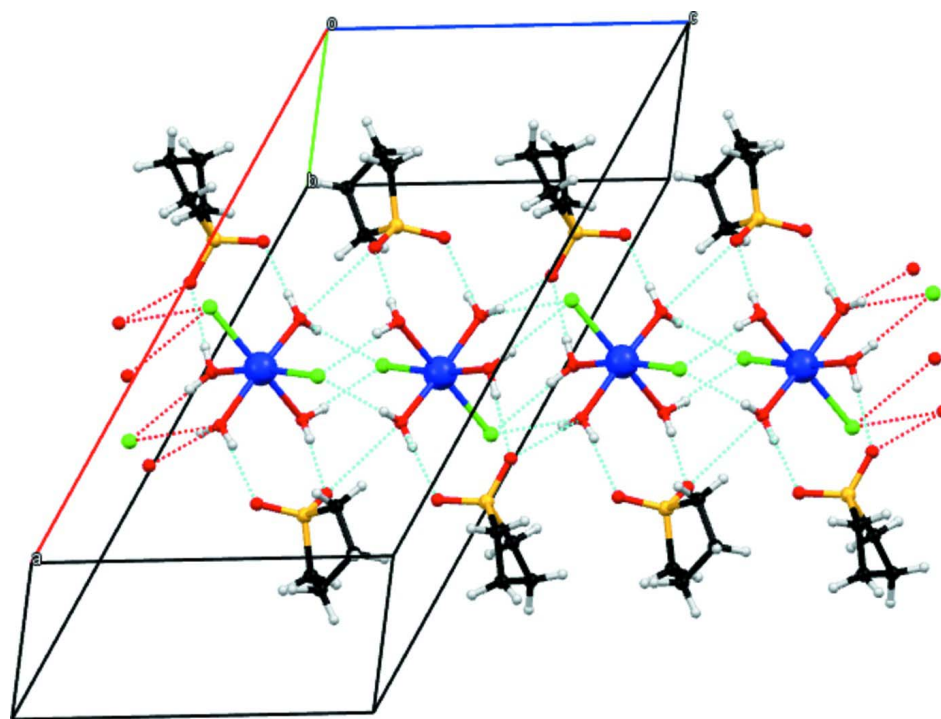


Figure 2

Packing diagram of (I) showing the infinite chains of complex units and solvent molecule along the *c* axis.

cis-Tetraaquadichloridocobalt(II) sulfolane disolvate

Crystal data

$[\text{CoCl}_2(\text{H}_2\text{O})_4] \cdot 2\text{C}_4\text{H}_8\text{O}_2\text{S}$

$M_r = 442.22$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 20.062 (2) \text{ \AA}$

$b = 9.4284 (10) \text{ \AA}$

$c = 10.5882 (13) \text{ \AA}$

$\beta = 118.734 (5)^\circ$

$V = 1756.2 (3) \text{ \AA}^3$

$Z = 4$

$F(000) = 916$

$D_x = 1.673 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5148 reflections

$\theta = 2.5\text{--}35.1^\circ$

$\mu = 1.55 \text{ mm}^{-1}$

$T = 295 \text{ K}$

Prism, blue

$0.21 \times 0.15 \times 0.09 \text{ mm}$

Data collection

Bruker APEXII diffractometer	20238 measured reflections
Radiation source: sealed tube	5090 independent reflections
Graphite monochromator	3409 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.061$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$\theta_{\text{max}} = 39.0^\circ$, $\theta_{\text{min}} = 2.3^\circ$
$T_{\text{min}} = 0.649$, $T_{\text{max}} = 0.748$	$h = -34 \rightarrow 35$
	$k = -16 \rightarrow 16$
	$l = -18 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.043$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.129$	$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
5090 reflections	$(\Delta/\sigma)_{\text{max}} = 0.007$
108 parameters	$\Delta\rho_{\text{max}} = 0.90 \text{ e } \text{\AA}^{-3}$
4 restraints	$\Delta\rho_{\text{min}} = -1.44 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.5	0.47467 (3)	0.25	0.01473 (8)
S1	0.76287 (2)	0.53220 (4)	0.58938 (4)	0.01334 (9)
Cl1	0.43290 (2)	0.30294 (4)	0.04608 (4)	0.01647 (9)
O1W	0.59916 (7)	0.49821 (15)	0.22088 (14)	0.0177 (2)
H1W	0.5953 (15)	0.556 (2)	0.168 (2)	0.027*
H2W	0.6412 (11)	0.483 (3)	0.288 (2)	0.027*
O2W	0.54617 (7)	0.65037 (13)	0.41295 (13)	0.0155 (2)
H3W	0.5200 (12)	0.669 (3)	0.452 (2)	0.023*
H4W	0.5887 (12)	0.631 (3)	0.467 (3)	0.023*
C3	0.90875 (11)	0.5145 (2)	0.7520 (3)	0.0298 (5)
H3A	0.955	0.5538	0.8296	0.036*
H3B	0.9206	0.4724	0.6815	0.036*
C4	0.84886 (10)	0.6288 (2)	0.6830 (2)	0.0240 (4)
H4A	0.8584	0.686	0.6172	0.029*
H4B	0.8475	0.69	0.7554	0.029*

C1	0.79391 (13)	0.3742 (2)	0.6942 (2)	0.0293 (4)
H1A	0.7618	0.3529	0.737	0.035*
H1B	0.7924	0.2945	0.635	0.035*
C2	0.87487 (14)	0.4035 (3)	0.8102 (3)	0.0386 (6)
H2A	0.9047	0.317	0.8342	0.046*
H2B	0.8752	0.4386	0.8966	0.046*
O12	0.70254 (8)	0.60180 (16)	0.60336 (16)	0.0245 (3)
O11	0.74827 (8)	0.50189 (17)	0.44424 (16)	0.0273 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01483 (14)	0.01815 (15)	0.01223 (15)	0	0.00731 (12)	0
S1	0.01081 (15)	0.01611 (17)	0.01057 (17)	-0.00112 (12)	0.00313 (13)	0.00104 (12)
Cl1	0.02063 (18)	0.01729 (17)	0.01137 (16)	-0.00469 (13)	0.00760 (14)	-0.00251 (13)
O1W	0.0121 (5)	0.0302 (7)	0.0117 (5)	0.0022 (4)	0.0064 (4)	0.0051 (5)
O2W	0.0149 (5)	0.0186 (5)	0.0130 (5)	-0.0020 (4)	0.0067 (4)	-0.0022 (4)
C3	0.0136 (7)	0.0444 (12)	0.0283 (11)	0.0051 (7)	0.0074 (7)	-0.0038 (9)
C4	0.0173 (7)	0.0219 (8)	0.0277 (9)	-0.0067 (6)	0.0068 (7)	-0.0036 (7)
C1	0.0397 (12)	0.0158 (8)	0.0332 (11)	0.0009 (7)	0.0182 (10)	0.0080 (7)
C2	0.0326 (11)	0.0517 (14)	0.0278 (11)	0.0189 (10)	0.0115 (9)	0.0219 (10)
O12	0.0160 (6)	0.0326 (7)	0.0230 (7)	0.0034 (5)	0.0079 (5)	-0.0044 (5)
O11	0.0188 (6)	0.0506 (9)	0.0112 (6)	-0.0003 (6)	0.0060 (5)	-0.0021 (6)

Geometric parameters (Å, °)

Co1—O1W	2.1660 (13)	O2W—H4W	0.79 (2)
Co1—O1W ⁱ	2.1660 (13)	C3—C4	1.515 (3)
Co1—O2W	2.2455 (12)	C3—C2	1.529 (4)
Co1—O2W ⁱ	2.2455 (12)	C3—H3A	0.97
Co1—Cl1	2.5102 (5)	C3—H3B	0.97
Co1—Cl1 ⁱ	2.5102 (5)	C4—H4A	0.97
S1—O12	1.4456 (14)	C4—H4B	0.97
S1—O11	1.4478 (16)	C1—C2	1.518 (3)
S1—C4	1.7730 (18)	C1—H1A	0.97
S1—C1	1.7820 (19)	C1—H1B	0.97
O1W—H1W	0.758 (16)	C2—H2A	0.97
O1W—H2W	0.812 (17)	C2—H2B	0.97
O2W—H3W	0.830 (16)		
O1W—Co1—O1W ⁱ	168.24 (8)	H3W—O2W—H4W	115 (2)
O1W—Co1—O2W	88.05 (5)	C4—C3—C2	106.16 (18)
O1W ⁱ —Co1—O2W	83.27 (5)	C4—C3—H3A	110.5
O1W—Co1—O2W ⁱ	83.27 (5)	C2—C3—H3A	110.5
O1W ⁱ —Co1—O2W ⁱ	88.05 (5)	C4—C3—H3B	110.5
O2W—Co1—O2W ⁱ	84.92 (7)	C2—C3—H3B	110.5
O1W—Co1—Cl1	95.34 (4)	H3A—C3—H3B	108.7
O1W ⁱ —Co1—Cl1	92.24 (4)	C3—C4—S1	103.73 (13)

O2W—Co1—C11	171.61 (4)	C3—C4—H4A	111
O2W ⁱ —Co1—C11	87.85 (3)	S1—C4—H4A	111
O1W—Co1—C11 ⁱ	92.24 (4)	C3—C4—H4B	111
O1W ⁱ —Co1—C11 ⁱ	95.34 (4)	S1—C4—H4B	111
O2W—Co1—C11 ⁱ	87.85 (3)	H4A—C4—H4B	109
O2W ⁱ —Co1—C11 ⁱ	171.61 (4)	C2—C1—S1	105.63 (15)
C11—Co1—C11 ⁱ	99.66 (2)	C2—C1—H1A	110.6
O12—S1—O11	116.50 (9)	S1—C1—H1A	110.6
O12—S1—C4	110.32 (9)	C2—C1—H1B	110.6
O11—S1—C4	109.92 (10)	S1—C1—H1B	110.6
O12—S1—C1	112.01 (10)	H1A—C1—H1B	108.7
O11—S1—C1	109.14 (10)	C1—C2—C3	107.97 (17)
C4—S1—C1	97.26 (10)	C1—C2—H2A	110.1
Co1—O1W—H1W	114 (2)	C3—C2—H2A	110.1
Co1—O1W—H2W	120 (2)	C1—C2—H2B	110.1
H1W—O1W—H2W	118 (3)	C3—C2—H2B	110.1
Co1—O2W—H3W	114.7 (17)	H2A—C2—H2B	108.4
Co1—O2W—H4W	106.8 (18)		
C2—C3—C4—S1	-42.0 (2)	O11—S1—C1—C2	115.94 (17)
O12—S1—C4—C3	140.20 (15)	C4—S1—C1—C2	1.88 (19)
O11—S1—C4—C3	-89.99 (17)	S1—C1—C2—C3	-27.0 (2)
C1—S1—C4—C3	23.45 (17)	C4—C3—C2—C1	45.6 (3)
O12—S1—C1—C2	-113.53 (17)		

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1W—H1W \cdots C11 ⁱⁱ	0.77 (3)	2.44 (3)	3.1885 (15)	165 (3)
O1W—H2W \cdots O11	0.81 (2)	1.99 (2)	2.782 (2)	165 (2)
O2W—H3W \cdots C11 ⁱⁱⁱ	0.83 (2)	2.41 (2)	3.2289 (16)	171 (2)
O2W—H4W \cdots O12	0.79 (3)	2.05 (3)	2.835 (2)	174 (3)

Symmetry codes: (ii) $-x+1, -y+1, -z$; (iii) $x, -y+1, z+1/2$.