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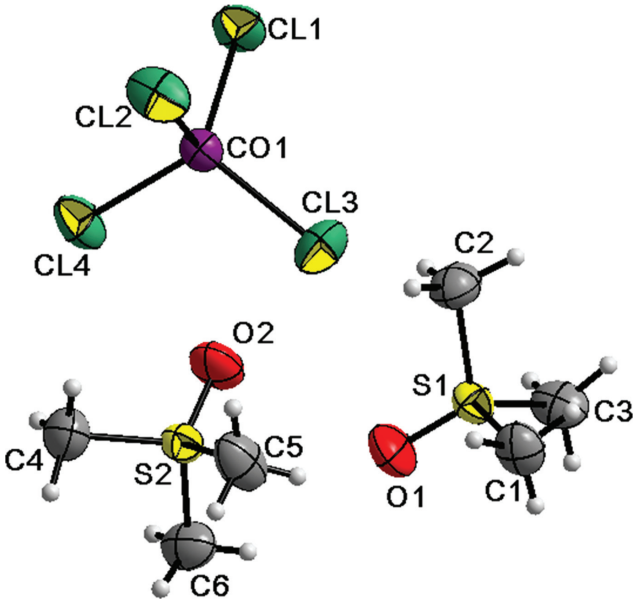
Crystal structure of trimethylsulfoxonium tetrachloridocobaltate(II) $[(CH_3)_3SO]_2CoCl_4$



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Abstract

$C_6H_{18}S_2O_2CoCl_4$, monoclinic, $P2_1/c$ (no. 14), $a = 8.4397(3)$ Å, $b = 15.6692(5)$ Å, $c = 12.5989(4)$ Å, $\beta = 93.8580(10)°$, $V = 1662.35(10)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0408$, $wR_{ref}(F^2) = 0.0965$, $T = 293(2)$ K.

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The asymmetric unit of the title structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Blue plate
Size:	0.17 × 0.10 × 0.03 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.91 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture, φ and ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	24807, 4145, 0.051
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2695
$N(param)_{refined}$:	208
Programs:	Bruker [1], SHELX [2, 3], WinGX/ORTEP [4], Diamond [5]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Co1	0.72195(5)	0.09385(3)	0.73655(3)	0.04694(13)
Cl1	0.77928(12)	0.09471(7)	0.91518(7)	0.0701(3)
Cl2	0.92334(13)	0.15793(7)	0.65821(8)	0.0829(3)
Cl3	0.48827(13)	0.15965(7)	0.69899(10)	0.0852(3)
Cl4	0.71007(15)	−0.04238(6)	0.68017(8)	0.0799(3)
S1	0.73731(10)	0.83701(5)	0.00564(7)	0.0513(2)
S2	0.76471(10)	0.39074(5)	0.84130(6)	0.0524(2)
O1	0.7364(3)	0.75429(16)	0.0527(2)	0.0820(8)
O2	0.7328(4)	0.40322(18)	0.72946(19)	0.0815(8)
C1	0.7771(7)	0.9174(3)	0.0997(4)	0.0715(12)
C2	0.5589(5)	0.8644(4)	−0.0625(5)	0.0747(12)
C3	0.8786(6)	0.8481(4)	−0.0882(4)	0.0722(12)
C4	0.6212(6)	0.3301(4)	0.9002(5)	0.0788(13)
C5	0.7792(10)	0.4861(3)	0.9106(4)	0.0860(16)
C6	0.9412(6)	0.3345(4)	0.8709(4)	0.0766(13)
H1	0.695(5)	0.911(2)	0.140(3)	0.077(13)*
H2	0.770(5)	0.969(3)	0.063(4)	0.106(17)*
H3	0.873(6)	0.906(3)	0.128(4)	0.096(18)*
H4	0.488(5)	0.863(3)	−0.009(3)	0.081(13)*
H5	0.572(5)	0.920(3)	−0.096(3)	0.088(14)*
H6	0.538(5)	0.821(3)	−0.101(4)	0.099(18)*
H7	0.972(5)	0.837(3)	−0.056(3)	0.084(14)*
H8	0.865(5)	0.903(3)	−0.122(4)	0.102(16)*
H9	0.851(5)	0.805(3)	−0.132(4)	0.100(17)*
H10	1.006(5)	0.374(3)	0.854(3)	0.076(14)*
H11	0.926(6)	0.281(3)	0.835(4)	0.12(2)*
H12	0.943(5)	0.329(3)	0.946(4)	0.085(13)*
H13	0.657(6)	0.325(3)	0.978(4)	0.119(18)*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H14	0.608(6)	0.284(4)	0.862(4)	0.12(2)*
H15	0.539(6)	0.370(3)	0.894(4)	0.102(17)*
H16	0.796(5)	0.476(3)	0.984(4)	0.105(16)*
H17	0.865(5)	0.512(3)	0.887(4)	0.088(17)*
H18	0.687(6)	0.511(3)	0.893(4)	0.097(19)*

Source of material

The starting materials of $CoCl_2 \cdot 6\ H_2O$ (0.238 g, 1 mmol) and trimethylsulfoxonium chloride (0.129 g, 1 mmol) were dissolved in deionized water with two drops of concentrated hydrochloric acid (37 wt%), resulting in a clear red solution. With slow evaporation at room temperature, blue plate crystals of the title compound were obtained within 2 days.

Experimental details

The structure was solved by direct methods and refined by full-matrix least-squares calculations. All the calculations were performed using the SHELX package [2, 3] and WinGX [4]. Hydrogen atoms were picked from difference Fourier maps and refined without any constraints or restraints.

Comment

Organic-inorganic hybrid compounds often exhibit a great variety of interesting structures as well as physical properties. The inorganic components, if containing transition metals, are likely to be a source to activate electrical transport, magnetism, ferroelectric properties, while the organic counterparts usually serve as a guest and sometimes account for additional variations in polarizability, luminescence, and chromophoric group [6]. As composed of both organic and inorganic components, hybrid compounds are expected to adopt combined properties that arise from both components or emerge new properties. In organometallic complexes, transition metals with one or more empty d-orbitals enable ligand-field-assisted d–d transitions, usually resulting in absorption in visible light range.

In the crystal structure, two types of discrete motifs with opposite charges exist. Co(II) is tetrahedrally coordinated with Cl, forming a distorted negatively-charged tetrahedron $[CoCl_4]^{2-}$, which is surrounded by the organic cation trimethylsulfoxonium $[(CH_3)_3SO]^+$, to stabilize the structure by electrostatic force. The Co—Cl bond lengths vary from 2.2474(11) Å to 2.2700(10) Å. Compared with the reported values for $[CoCl_4]^{2-}$ in other hybrids [7–9], these bond lengths are slightly shorter, presumably due to the absence of hydrogen bonding. The Cl—Co—Cl angles are in an expected range of 107.63(5)° to 112.31(5)°. The $[(CH_3)_3SO]^+$ motif is of pyramidal geometry with an approximate *3m* symmetry, similar to that in trimethylsulfoxonium metal-halides [10, 11]. Within this motif, the S—C bond lengths (1.731(5)–1.749(5) Å) and the O—S—C angles (112.3(2)°–113.8(2)°) lie in known ranges. There are no hydrogen bonds detected in the crystal structure, unlike the positively-charged or neutral organic motifs in some other hybrids [7–9, 12].

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