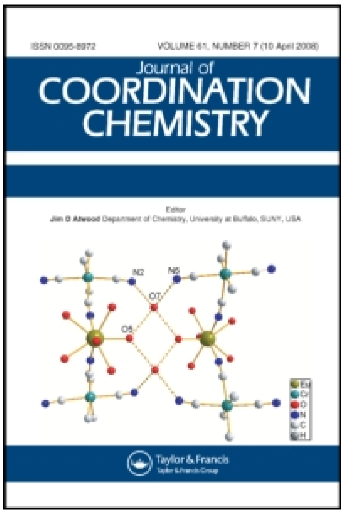

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Structure, spectroscopic, and magnetic properties of a new cobalt(II) complex with 5-sulfoisophthalic anion

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Structure, spectroscopic, and magnetic properties of a new cobalt(II) complex with 5-sulfoisophthalic anion

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A complex of $[Co(H_2SIP)(Phen)(H_2O)_3] \cdot H_2O$ ($H_2SIP = $ 5-sulfoisophthalic anion, Phen = 1,10-phenanthroline) has been synthesized by hydrothermal reaction. Crystal structure determination revealed that the complex crystallizes in the monoclinic space group $P2(1)/c$, in which Co(II) is distorted octahedral coordinating with one carboxylate sulfonate ligand, one phen, and three coordinated waters. Molecules of $[Co(H_2SIP)(Phen)(H_2O)_3] \cdot H_2O$ are connected to form a 3-D structure by intermolecular hydrogen bonds and π–π stacking interactions. IR spectra, UV-Vis spectra, and magnetic susceptibilities have been analyzed to obtain values of the ligand field and magnetic parameters: $A = 1.33$, $\lambda = -102.3\,cm^{-1}$, $\kappa = 0.96$, and $\Delta = 252.2\,cm^{-1}$.

Keywords: Cobalt(II) ions; 5-Sulfoisophthalic acid monosodium salt (NaH_2SIP); Magnetic properties

1. Introduction

A variety of mononuclear and/or polynuclear complexes of transition metals with interesting spectroscopic and X-ray crystallographic studies have been reported [1–6]. Cobalt(II) in octahedral or pseudo octahedral surroundings has attracted increasing attention due to the unquenched orbital moment ($^4T_{1g}$). Orbital degeneracy leads to high anisotropy, associated closely with single-molecule magnetism, single-chain magnetism as well as the effects of solvents on magnetic ground states in some porous magnets [7–10].

Carboxylate groups have a strong ability to bond various metal ions and afford abundant coordination modes; rigid multi-carboxylate ligands have been widely used for the design and synthesis of a variety of structures [11–21]. However, relatively little attention has been paid to sulfonate-based assemblies, despite the fact that the sulfonate group bears diversified coordinating modes and ligating sensitivity to the nature (hardness) of the metal ions [22–24]. We chose 5-sulfoisophthalic acid (H_3SIP) as our target. Here, we have reported a new cobalt(II) complex with carboxylate sulfonate ligand by hydrothermal reaction. The crystal structure of the complex has been

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determined and UV-Vis spectra and magnetic susceptibilities have been measured and analyzed to obtain the values of the ligand field and magnetic parameters.

2. Experimental

2.1. *Materials and methods*

All chemicals and solvents were of reagent grade and used as received, including 5-sulfoisophthalic acid monosodium salt (Alfa). The complex was synthesized by a hydrothermal method under autogenous pressure. Elemental analysis was carried out on a Perkin Elmer elemental analyzer (Model 240) and FT-IR spectra was measured on a Bruker Tensor 27 Fourier transform infrared spectrometer from 4000 to 400 cm^{-1} as KBr disks. The UV-Vis spectra was measured on a JASCO V-570 spectrophotometer. Variable-temperature magnetic susceptibilities were measured on a SQUID magnetometer between 2.0 and 300 K in a magnetic field of 2000 G. The molar magnetic susceptibility was corrected from the sample holder and diamagnetic contributions of all constituent atoms by using Pascal's constants.

2.2. *Preparation of [Co(H_2SIP)(Phen)(H_2O)$_3$]$\cdot H_2O$ (1)*

A mixture of $CoSO_4 \cdot 7H_2O$ (0.4 mmol), Dy_2O_3 (0.2 mmol), 1,10-phenanthroline (0.1 mmol) and 15 mL aqueous solution of 5-sulfoisophthalic acid monosodium salt (0.4 mmol) were sealed into a bomb equipped with a Teflon liner and then allowed to react at 120°C for 4 days and cooled to room temperature at 6°Ch^{-1}. After several days, the resulting pink block-shaped crystalline product was filtered, washed with distilled water, and dried at ambient temperature. Yield: 43% (based on Co). Anal. Calcd for $C_{20}H_{20}CoN_2O_{11}S$ (555.37) (%): C 43.21, H 3.60, N 5.04, O 31.69, S 5.76; Found (%): C 43.32, H 3.55, N 4.96, O 31.51, S 5.66. IR data (KBr, cm^{-1}): 3410(vs), 3232(w), 1672(s), 1604(m), 1554(w), 1519(w), 1428(s), 1382(s), 1290(s), 1211(s), 1183(vs), 1106(s), 1042(s), 767(s), 729(m), 695(m), and 625(s).

Although Dy_2O_3 was added into the reaction system, we obtained only a cobalt(II) complex with the carboxylate sulfonate ligand, not a heteronuclear complex containing Dy(III), suggesting that the former is thermodynamically favored over to the latter at 120°C.

2.3. *X-ray structure determination*

The crystal of **1** was mounted on a glass fiber. Determination of the unit cell and data collection were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å) on an APEX II CCD area detector equipped with a CCD camera. The ω–φ scan technique was employed. The structure was solved by direct methods followed by Fourier difference techniques and was refined by full-matrix least squares. The computations were performed with the SHELXL-97 program [25, 26]. Non-hydrogen atoms were refined anisotropically. Hydrogens were set in calculated positions and refined as riding with a common fixed isotropic thermal parameter.

3. Results and discussion

3.1. *Description of crystal structure*

The ORTEP of **1** is shown in figure 1, with data collection and refinement parameters in table 1 and important bond lengths and angles in table 2. Single-crystal X-ray diffraction analysis revealed that **1** crystallizes in monoclinic space group *P2*(1)/*c*. The structure consists of $[Co(H_2SIP)(Phen)(H_2O)_3]$ and one water molecule. Co1 is distorted octahedral, in which the equatorial plane coordinates two nitrogens (N1, N2) from phen, one oxygen (O4) from carboxylate of H_2SIP, and another oxygen (O3) from water (with bond lengths of 2.108(3), 2.156(3), 2.080(3), and 2.115(3) Å, respectively). The axial positions are occupied by two (O1, O2) water molecules (with bond lengths of 2.162(3) and 2.108(3) Å). The Co1–N bond distances are close to Co–N bond distances found in other cobalt(II) complexes with nitrogen donors [27, 28] and longer than those found in cobalt(III) complexes [29–31]. The N1–Co1–N2 angle (77.14°) in **1** differs from that in a pure octahedron, giving a distorted octahedral environment, which can be attributed to the restriction imposed by the chelating phen.

In the crystal lattice, there are hydrogen bonding and π–π stacking interactions. The hydrogen bonding interactions are given in table 3. The crystallographic packing diagram of **1** is shown in figure 2; there exist intermolecular hydrogen bonding interactions between the oxygens of sulfonate and coordinated water (with bond lengths of O1 ··· O10, 2.784 Å; O2 ··· O8, 2.678 Å; O3 ··· O9, 2.840 Å), and also the interactions between the oxygens from carboxylate and coordinated water as well as uncoordinated water (lengths: O1 ··· O6, 2.771 Å; O2 ··· O6, 2.813 Å; O7 ··· O11, 2.590 Å). Meanwhile, the plane-to-plane distance (3.44 Å) between two parallel rings from adjacent phen and H_2SIP indicate π–π stacking interactions. The combination of coordination,

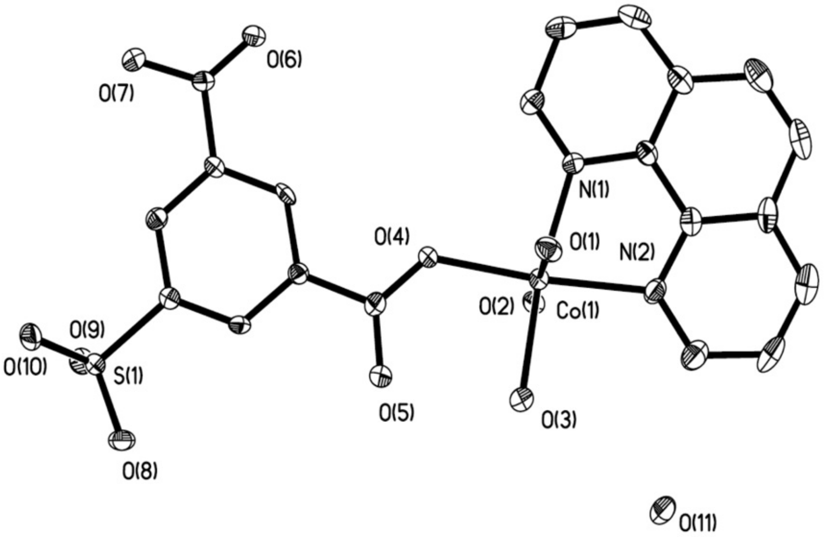

Figure 1. ORTEP drawing of the coordination environments of **1** with 30% thermal ellipsoids.

hydrogen bonding, and π–π stacking interactions stabilize a 3-D supramolecular solid-state architecture.

3.2. *IR spectra*

The FT-IR spectrum of **1** shows a broad band at 3410 cm^{-1}, attributable to the O–H stretching of water. This value is close to 3359 cm^{-1} in the extended water tapes [32]. Strong absorptions at 1604, 1554 cm^{-1} [$\nu_{asym}(CO_2)$] and 1428, 1382 cm^{-1} [$\nu_{sym}(CO_2)$] are assigned to a carboxylate [33, 34]. There is also a strong absorption at 1672 cm^{-1},

Table 1. Summary of crystal parameters for **1**.

Empirical formula	$C_{20}H_{20}CoN_2O_{11}S$
Formula weight	555.37
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*P2(1)/c*
Unit cell dimensions (Å, °)	
a	10.968(2)
b	13.881(3)
c	15.872(3)
α	90
β	109.59(3)
γ	90
Volume (Å^3), Z	2276.6(8), 4
Calculated density (mg m^{-3})	1.620
Absorption coefficient (mm^{-1})	0.910
$F(000)$	1140
θ range for data collection (°)	3.09–25.01
Limiting indices	$-10 \le h \le 13$; $-16 \le k \le 16$; $-18 \le l \le 18$
Reflections collected	13,705
Independent reflection	3995 [R(int) = 0.0760]
Completeness to $\theta = 25.01$ (%)	99.8
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8986 and 0.8831
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3995/12/349
Goodness-of-fit on F^2	1.137
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0609$, $wR_2 = 0.0983$
R indices (all data)	$R_1 = 0.0938$, $wR_2 = 0.1076$
Largest difference peak and hole (e Å^{-3})	0.300 and −0.345

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Co(1)–O(4)	2.080(3)	Co(1)–O(3)	2.115(3)
Co(1)–O(2)	2.108(3)	Co(1)–N(2)	2.156(3)
Co(1)–N(1)	2.108(3)	Co(1)–O(1)	2.162(3)
O(4)–Co(1)–O(2)	92.66(11)	O(3)–Co(1)–N(2)	94.47(12)
O(4)–Co(1)–N(1)	97.83(11)	O(4)–Co(1)–O(1)	88.73(11)
O(2)–Co(1)–N(1)	92.53(12)	O(2)–Co(1)–O(1)	178.14(13)
O(4)–Co(1)–O(3)	90.59(11)	N(1)–Co(1)–O(1)	86.04(12)
O(2)–Co(1)–O(3)	93.68(12)	O(3)–Co(1)–O(1)	87.55(12)
N(1)–Co(1)–O(3)	169.30(12)	N(2)–Co(1)–O(1)	91.36(12)
O(4)–Co(1)–N(2)	174.94(11)	O(2)–Co(1)–N(2)	87.14(12)
N(1)–Co(1)–N(2)	77.14(12)		

which clearly indicates a protonated carboxylate in the structure. Absorptions at 1000–1230 cm^{-1} are typical for sulfonate [35]. Strong absorptions at 695 and 625 cm^{-1} are due to $\nu_{\mathrm{S–O}}$.

3.3. *Electronic spectra*

The UV-Vis spectrum of **1** was measured in the solid state. Two d–d bands at *ca.* 884 nm ($\nu_1 \sim 11{,}312\,\mathrm{cm}^{-1}$) and 499 nm ($\nu_3 \sim 20{,}040\,\mathrm{cm}^{-1}$) are observed, which are near those observed in similar Co(II) compounds assigned to ${}^4T_{1g} \xrightarrow{\nu_1} {}^4T_{2g}$ and ${}^4T_{1g} \xrightarrow{\nu_3} {}^4T_{1g}$ (P) [36], assuming Co^{2+} in a pseudo octahedral geometry. Because ${}^4T_{1g} \xrightarrow{\nu_2} {}^4A_{2g}$ involving the

Table 3. Hydrogen bonds parameters in **1**.

D–H···A	D–H (Å)	H···A (Å)	∠DHA (°)	D···A (Å)
O3–H3C···O5	0.857	1.747	170.32	2.596
O3–H3C···O4	0.857	2.550	112.18	2.982
O3–H3D···O9	0.855	2.008	164.07	2.840
O7–H7···O11	0.820	1.772	174.77	2.590
O11–H11A···O9	0.847	2.001	172.36	2.842
O11–H11B···O1	0.850	2.166	144.61	2.901
O2–H2C···O8	0.846	1.852	164.71	2.678
O2–H2C···S1	0.846	2.960	150.72	3.721
O1–H1C···O10	0.850	1.938	173.41	2.784
O1–H1C···S1	0.850	2.907	148.59	3.660
O2–H2D···O6	0.848	1.994	162.26	2.813
O1–H1D···O6	0.847	1.926	174.93	2.771

Symmetry transformations used to generate equivalent atoms: A: $x, y, z-1$; B: $-x+1, -y, -z$; C: $x, -y+1/2, z+1/2$; D: $x+1, -y+1/2, z+1/2$.

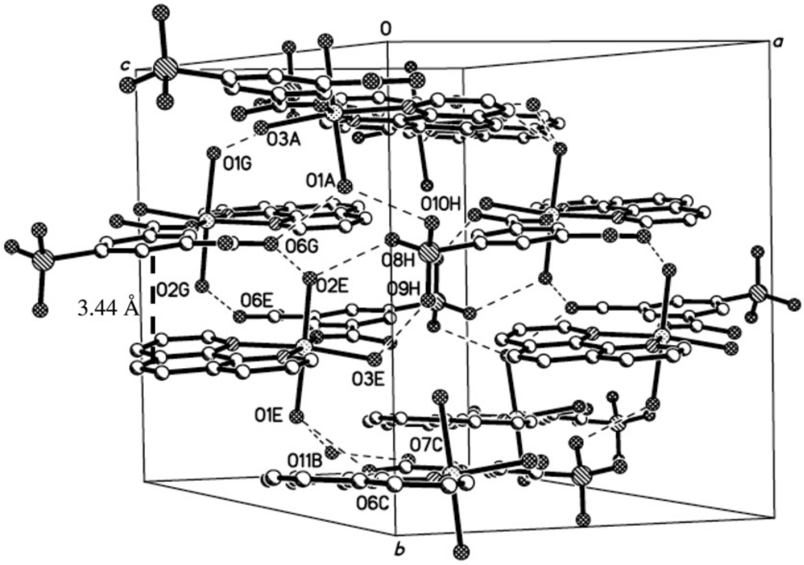

Figure 2. The packing diagram of **1** with hydrogen bonds. All H atoms have been omitted for clarity.

excitation of two electrons is forbidden, it is not easily observed [37]. According to equations (1)–(3), the ligand field parameter Dq ($1247\,\mathrm{cm}^{-1}$), the Rach parameter B ($659\,\mathrm{cm}^{-1}$), and ν_2 ($18{,}902\,\mathrm{cm}^{-1}$) can be obtained [38].

$$\nu_1 = 5Dq - 7.5B + 1/2\,(225B^2 + 100Dq^2 + 180DqB)^{1/2} \tag{1}$$

$$\nu_2 = 15Dq - 7.5B + 1/2\,(225B^2 + 100Dq^2 + 180DqB)^{1/2} \tag{2}$$

$$\nu_3 = (225B^2 + 100Dq^2 + 180DqB)^{1/2} \tag{3}$$

3.4. *Magnetic properties*

The temperature dependence of magnetic susceptibilities for **1** is shown in figure 3 as plots of χ_M and $\chi_M T$ *versus* T (χ_M is the magnetic susceptibility per mol of **1**). The $\chi_M T$ at 300 K is $3.04\,\mathrm{cm^3\,mol^{-1}\,K}$, significantly larger than the spin-only value of $1.875\,\mathrm{cm^3\,mol^{-1}\,K}$ for an isolated cobalt(II) center, indicating an orbital contribution from the ${}^4T_{1g}$ ground state. When lowering the temperature, $\chi_M T$ first decreases very slowly until 55 K, then drops sharply and reaches $1.83\,\mathrm{cm^3\,mol^{-1}\,K}$ at 2 K. This may be due to the depopulation of the excited crystal field state of cobalt(II) [39]. For **1**, the cobalt(II) has pseudo octahedral and under axial distortion, the ${}^4T_{1g}$ ground state splits into ${}^4A_2$ and ${}^4E$ with an energy gap of Δ. Using the *T–P* analogy, the full Hamiltonian describing the magnetic properties of **1** is given as equation (4) [40], where λ is the spin–orbit coupling constant that has a lower value than expected for free cobalt(II) ($\lambda = -170\,\mathrm{cm}^{-1}$), κ is the orbital reduction factor associated with the covalent character of the cobalt(II)–ligand bonds. The typical value of κ lies within the range of 0.75–1.0 for cobalt(II) in a pseudo octahedral geometry [41]. The A factor providing measures of ligand field strength taking values between 3/2 (weak field limit) and 1 (strong field limit) can be calculated from Dq and B through equations 5 and 6 [42]. For **1**, the electronic spectrum gives $A = 1.33$. Because from the above Hamiltonian (S), no analytical expression for the magnetic susceptibility as a function of κ, λ, and Δ can be derived, the values of these parameters must be determined through a numerical matrix diagonalization method. This has been done using MagSaki program [43, 44],

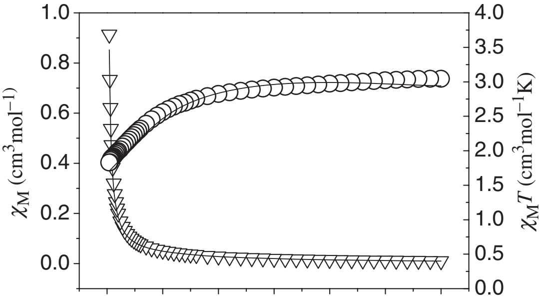

Figure 3. Temperature dependence of χ_M (∇) and $\chi_M T$ (O) for **1** at 2000 G. The solid lines represent the theoretical values based on the corresponding equations.

giving $\lambda = -102.3\,\text{cm}^{-1}$, $\kappa = 0.96$, $\Delta = 252.2\,\text{cm}^{-1}$ with agreement factor $R = 5.16 \times 10^{-3}$ ($R = \Sigma(\chi_{\text{obsd}} - \chi_{\text{cacld}})^2/\Sigma(\chi_{\text{obsd}})^2$). The κ value smaller than 1 and the λ absolute value smaller than $|-170|\text{cm}^{-1}$ show the covalent character of cobalt(II)-ligands. The positive Δ value indicates that $^4A_2$ is lowest.

$$\hat{\mathrm{H}} = -A\kappa\lambda\hat{\mathrm{L}}\hat{\mathrm{S}} + \Delta\left[\hat{\mathrm{L}}_z^2 - 1/3L(L+1)\right] + \beta(-A\kappa\hat{\mathrm{L}} + g_e\hat{\mathrm{S}})H \tag{4}$$

$$A = (3/2 - c^2)/(1 + c^2) \tag{5}$$

$$c = 0.75 + 1.875B/Dq - 1.25\left[1 + 1.8B/Dq + 2.25(B/Dq)^2\right]^{1/2} \tag{6}$$

4. Conclusions

We have obtained a new cobalt(II) compound with a 5-sulfoisophthalic acid monosodium salt under the hydrothermal condition. Co(II) exists in a distorted octahedral environment, coordinated with one carboxylate sulfonate ligand, one phen, and three waters. Molecules of $[\text{Co(H}_2\text{SIP)(Phen)(H}_2\text{O)}_3] \cdot \text{H}_2\text{O}$ are connected to form a 3-D structure by intermolecular hydrogen bonds and π–π stacking interactions. The complex has also been characterized by IR spectra, UV-Vis spectra, and magnetic measurement. The temperature dependence of magnetic susceptibilities give values of magnetic parameters: $A = 1.33$, $\lambda = -102.3\,\text{cm}^{-1}$, $\kappa = 0.96$, $\Delta = 252.2\,\text{cm}^{-1}$.

Supplementary material

CCDC 735670 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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