Crystal structure of tetraaqua(*o*-phenanthroline)cobalt(II) sulfate dihydrate, $[\text{C}_{12}\text{H}_8\text{N}_2]\text{Co}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot 2\text{H}_2\text{O}$

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Abstract

$\text{C}_{12}\text{H}_{20}\text{CoN}_2\text{O}_{10}\text{S}$, orthorhombic, *Pbca* (No. 61), $a = 8.856(1) \text{ \AA}$, $b = 18.318(3) \text{ \AA}$, $c = 21.918(5) \text{ \AA}$, $V = 3555.6 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.031$, $wR_{\text{ref}}(F^2) = 0.070$, $T = 292 \text{ K}$.

Source of material

$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ (1 g) was dissolved in water (5 ml) and was added to *tert*- $\text{C}_4\text{H}_9\text{OOH}$ (5 ml). With stirring to the solution was added a solution of phenanthroline (5 mmol in 5 ml of acetonitrile). Dichloromethane (5 ml) was carefully injected to the bottom of the above solution. The resulting solution with a clear layer was stood still in air. Five hours later a great amount of light pink crystals suitable for X-ray were deposited at the bottom of the flask. The product was washed with water and methanol, and dried in vacuum under CaCl_2 . Analysis: found: C 32.5%, H 4.5%, N 6.18%, $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_{10}\text{SCo}$ requires C 32.5%, H 4.6%, N 6.32%.

Discussion

The discovery that certain cobalt complexes are potent antiviral agents [1] prompted us to initiate an investigation of cobalt interactions with proteins and nucleic acids. Since complexes with relatively labile axial ligands exhibit higher activities, Gray and co-workers [2] assumed that axial binding of cobalt to biological targets was somehow involved in the mechanism (or mechanisms) of action. Herein we report the preparation and single and crystal structure of a cobalt(II) complex with two very labile axial H_2O ligands.

The title complex comprises a discrete phenanthrolinecobalt(II) tetrahydrated di-cation, a sulfate anion and two uncoordinated water molecules. In the cation, each cobalt(II) atom is six-coordinated, with two nitrogen atoms from a phenanthroline ligand and four oxygen atoms from four molecules in a slightly distorted octahedral geometry. The two nitrogen atoms of a phenanthroline ligand and two O atoms from two H_2O molecules constitute the basal plane (plane I) with a small mean deviation of $0.026 \text{ \AA}$. Cobalt(II) atom is located by $0.118 \text{ \AA}$ from the basal plane towards the O4 atom. The two apical positions are occupied by O1 and O4 atoms. The average Co—O bond length ($2.103(2) \text{ \AA}$) is in the normal range for cobalt(II) hydrate complexes. The mean Co—N contact ($2.136(2) \text{ \AA}$) and N1—Co—N2 angle ($77.20(8)^\circ$) are nearly the same as those ($2.137(2) \text{ \AA}$ for the contact and $77.3(5)^\circ$ for the angle) of $[\text{Co}(\text{phen})(3,5\text{-DTBSQ})] \cdot \text{C}_6\text{H}_5\text{CH}_3$ [3]. The dihedral angle (8.1°) between plane I and the phenanthroline inside the molecule is mostly parallel. Two kinds of one-dimensional chains coming from appreciable phen...phen interactions between the molecules are found. Inside each chain, the phen rings are parallel to each other, and the interplanar distance is $3.45 \text{ \AA}$, slightly shorter than that ($3.48 \text{ \AA}$) in the complex of literature [3]. Between the neighboring chains the phen rings are nearly perpendicular one another with the dihedral angle $77.4(8)^\circ$. All oxygen atoms, including those from the sulfate anion, coordinated and uncoordinated water molecules in the title complex, contribute to the formation of hydrogen bonds, and a large number of interlinked inter- and intramolecular hydrogen bonds join the molecules to form a network structure.

Table 1. Data collection and handling.

Crystal:	pink prism, size $0.44 \times 0.46 \times 0.52 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71073 \text{ \AA}$)
μ :	11.38 cm^{-1}
Diffraction, scan mode:	Siemens P4, ω
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3840, 3130
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2339
$N(\text{param})_{\text{refined}}$:	284
Program:	SHELXTL-plus [4]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(1)	8c	0.1304	0.5403	0.6164	0.054
H(2)	8c	0.0456	0.6020	0.7017	0.072
H(3)	8c	0.1200	0.5639	0.7971	0.075
H(5)	8c	0.2675	0.4715	0.8619	0.076
H(6)	8c	0.4220	0.3747	0.8662	0.077
H(8)	8c	0.5754	0.2775	0.8101	0.072
H(9)	8c	0.6564	0.2301	0.7196	0.068
H(10)	8c	0.5791	0.2828	0.6289	0.054
H(1A)	8c	0.486(4)	0.542(1)	0.595(1)	0.06(1)
H(1B)	8c	0.568(3)	0.515(2)	0.5510(9)	0.06

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(2A)	8c	0.175(3)	0.441(2)	0.495(1)	0.06
H(2B)	8c	0.225(4)	0.5060(7)	0.511(1)	0.06
H(3A)	8c	0.501(3)	0.3159(7)	0.515(1)	0.043(9)
H(3B)	8c	0.599(2)	0.369(2)	0.519(2)	0.07(1)
H(4A)	8c	0.253(3)	0.2835(9)	0.580(1)	0.07
H(4B)	8c	0.145(3)	0.316(2)	0.556(1)	0.07
H(9A)	8c	0.226(3)	0.326(2)	0.415(1)	0.07
H(9B)	8c	0.318(5)	0.273(2)	0.429(1)	0.12(2)
H(10A)	8c	0.368(2)	0.649(2)	0.617(1)	0.06(1)
H(10B)	8c	0.511(2)	0.656(1)	0.623(1)	0.037(9)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co	8c	0.36393(4)	0.41309(2)	0.58466(2)	0.0293(2)	0.0229(2)	0.0297(2)	0.0016(2)	0.0007(2)	-0.0008(2)
S	8c	-0.09317(7)	0.34328(3)	0.47092(3)	0.0280(3)	0.0217(3)	0.0489(4)	0.0005(3)	-0.0072(3)	-0.0012(3)
O(1)	8c	0.5127(2)	0.5033(1)	0.5791(1)	0.038(1)	0.029(1)	0.043(1)	-0.0065(9)	0.007(1)	-0.003(1)
O(2)	8c	0.2435(2)	0.4623(1)	0.5129(1)	0.042(1)	0.024(1)	0.050(1)	-0.001(1)	-0.016(1)	0.001(1)
O(3)	8c	0.5098(2)	0.3588(1)	0.5255(1)	0.036(1)	0.030(1)	0.055(1)	-0.002(1)	0.014(1)	-0.013(1)
O(4)	8c	0.2150(2)	0.3238(1)	0.5785(1)	0.033(1)	0.026(1)	0.050(1)	0.0024(9)	-0.008(1)	-0.004(1)
O(5)	8c	0.0425(2)	0.3829(1)	0.45010(9)	0.030(1)	0.044(1)	0.067(1)	-0.0114(9)	-0.002(1)	-0.004(1)
O(6)	8c	-0.1718(2)	0.3117(1)	0.41826(9)	0.043(1)	0.030(1)	0.055(1)	-0.0053(9)	-0.019(1)	-0.002(1)
O(7)	8c	-0.1941(2)	0.39398(9)	0.50299(9)	0.041(1)	0.025(1)	0.070(1)	0.0048(9)	0.004(1)	-0.005(1)
O(8)	8c	-0.0461(2)	0.28457(9)	0.51297(9)	0.051(1)	0.030(1)	0.055(1)	0.0062(9)	-0.017(1)	0.004(1)
O(9)	8c	0.2939(3)	0.3003(2)	0.4009(1)	0.046(2)	0.063(2)	0.070(2)	-0.005(1)	0.000(1)	-0.005(2)
O(10)	8c	0.4414(3)	0.6302(1)	0.6331(1)	0.042(1)	0.037(1)	0.060(1)	-0.003(1)	-0.010(1)	0.005(1)
N(1)	8c	0.2577(2)	0.4700(1)	0.6578(1)	0.031(1)	0.025(1)	0.042(1)	-0.003(1)	0.005(1)	-0.003(1)
N(2)	8c	0.4527(2)	0.3594(1)	0.6637(1)	0.029(1)	0.031(1)	0.038(1)	-0.001(1)	-0.003(1)	0.002(1)
C(1)	8c	0.1634(3)	0.5252(2)	0.6546(1)	0.044(2)	0.035(2)	0.056(2)	0.002(1)	0.013(2)	0.000(2)
C(2)	8c	0.1103(4)	0.5623(2)	0.7060(2)	0.048(2)	0.043(2)	0.090(3)	0.007(2)	0.025(2)	-0.013(2)
C(3)	8c	0.1545(4)	0.5396(2)	0.7625(2)	0.060(2)	0.069(2)	0.060(2)	-0.012(2)	0.030(2)	-0.030(2)
C(4)	8c	0.2511(3)	0.4803(2)	0.7683(1)	0.036(2)	0.060(2)	0.050(2)	-0.015(2)	0.017(2)	-0.019(2)
C(5)	8c	0.3007(4)	0.4503(2)	0.8257(1)	0.060(2)	0.099(3)	0.030(2)	-0.021(2)	0.013(2)	-0.013(2)
C(6)	8c	0.3928(4)	0.3928(2)	0.8284(2)	0.061(2)	0.096(3)	0.035(2)	-0.023(2)	-0.003(2)	0.005(2)
C(7)	8c	0.4473(3)	0.3587(2)	0.7744(1)	0.040(2)	0.062(2)	0.036(2)	-0.020(2)	-0.006(1)	0.010(2)
C(8)	8c	0.5441(4)	0.2984(2)	0.7735(2)	0.052(2)	0.067(2)	0.061(2)	-0.014(2)	-0.018(2)	0.030(2)
C(9)	8c	0.5923(4)	0.2703(2)	0.7201(2)	0.050(2)	0.049(2)	0.072(2)	0.003(2)	-0.017(2)	0.018(2)
C(10)	8c	0.5447(3)	0.3023(2)	0.6655(1)	0.039(2)	0.040(2)	0.055(2)	0.003(1)	-0.006(2)	0.001(2)
C(11)	8c	0.4043(3)	0.3873(2)	0.7172(1)	0.027(1)	0.041(2)	0.033(2)	-0.012(1)	-0.001(1)	0.003(1)
C(12)	8c	0.3023(3)	0.4475(2)	0.7142(1)	0.031(2)	0.040(2)	0.033(2)	-0.013(1)	0.006(1)	-0.005(1)

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