Synthesis and Crystal Structure of (Carbonato)bis(1,10-phenanthroline)-cobalt(III) Nitrate Trihydrate, $[\text{Co}(\text{phen})_2\text{CO}_3]\text{NO}_3 \cdot 3\text{H}_2\text{O}$

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The chemical preparation and crystal structure are given for a (carbonato)bis(1,10-phenanthroline)cobalt(III) nitrate trihydrate, $[\text{Co}(\text{phen})_2\text{CO}_3]\text{NO}_3 \cdot 3\text{H}_2\text{O}$, in the solid state. This complex crystallized in the triclinic space group $P\bar{1}$ with the following unit-cell parameters: $a = 8.022(2)\text{Å}$, $b = 10.329(2)\text{Å}$, $c = 15.998(3)\text{Å}$, $\alpha = 106.09(1)^\circ$, $\beta = 102.74(1)^\circ$, $\gamma = 90.88(2)^\circ$, $Z = 2$ and $V = 1238.2(4)\text{Å}^3$. The final R value is 0.0581 for 4885 measured reflections.

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1,10-Phenanthroline (phen) complexes have been studied extensively. Phen is a well-known *N*-heterocyclic chelating agent with a rigid planar structure. The metal chelating properties of 1,10-phenanthroline have been widely utilized in all aspects of coordination chemistry such as ligand substitution, redox reactions, photochemical reactions and photophysical properties, as well as in its recent applications to develop biomimetic models of metalloenzymes and to prepare supramolecules, self-assembling systems, or metal complexes with interesting anticancer properties.^{1,2} In this work, we synthesized the title compound and determined its crystal structure.

Preparation. The title compound, Fig. 1, was prepared by adding 1,10-phenanthroline (396 mg, 2 mmol) to a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (291 mg, 1 mmol) in 50 ml water under N_2 . To the orange solution was then added $(\text{NH}_4)_2\text{CO}_3$ (96 mg, 1 mmol) and stirred at 60°C for 30 min. The dark-brown solution was then aerated for 3 h. The resulting red precipitate was filtered and recrystallized from water to yield the title complex as red crystals.

The X-ray data were collected on a diffractometer (Mo K_α radiation, graphite monochromator) at 293(2)K. The crystal data and the experimental parameters are given in Table 1. The non-hydrogen atoms were refined anisotropically, and all

hydrogen atoms were located from sequential difference Fourier maps and refined with the riding model to final R indices of $R_1(0.0581)$ and $wR_2(0.1412)$.

A view of this compound, including the atomic numbering scheme, is illustrated in Fig. 2. Selected bond distances and bond angles are given in Table 2.

Table 1 Crystal and experimental data

Formula: $\text{C}_{25}\text{H}_{22}\text{CoN}_5\text{O}_9$	
Formula weight = 595.41	
Crystal system: triclinic	
Space group: $P\bar{1}$	$Z = 2$
$a = 8.0222(16)\text{Å}$	$\alpha = 106.087(14)^\circ$
$b = 10.3285(19)\text{Å}$	$\beta = 102.737(14)^\circ$
$c = 15.998(3)\text{Å}$	$\gamma = 90.880(15)^\circ$
$V = 1238.2(4)\text{Å}^3$	
$D_x = 1.597\text{ g/cm}^3$	
Absorption coefficient = 0.759 mm^{-1}	
$F(0\ 0\ 0) = 612$	
Crystal size = $0.40 \times 0.10 \times 0.08\text{ mm}^3$	
θ range for data collection 2.06 to 26.80°	
No. of reflections used = 4885	
No. of parameters = 385	
$2\theta_{\text{max}} = 53.6$ with Mo K_α	
$R_1 = 0.0581 [I > 2\sigma(I)]$	
$wR_2 = 0.1412$	
Goodness-of-fit on $F^2 = 0.972$	
$(\Delta\rho)_{\text{max}} = 0.517\text{ eÅ}^{-3}$	
$(\Delta\rho)_{\text{min}} = -0.842\text{ eÅ}^{-3}$	
Measurement: STOE IPDSII	
Program system: X-Area 1.31	
Structure determination: direct methods	
Refinement: full matrix least-squares on F^2	

CCDC 600520 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.com.ac.uk/data_request/cif.

Fig. 1 Chemical structure of $[\text{Co}(\text{phen})_2\text{CO}_3]\text{NO}_3 \cdot 3\text{H}_2\text{O}$.

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Fig. 2 ORTEP diagram of the $[\text{Co}(\text{phen})_2\text{CO}_3]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ showing 30% probability ellipsoids.

Table 2 Selected bond lengths (Å) and bond angles (°)

Bond lengths			
Co(1)-O(1)	1.893(2)	N(5)-O(4)	1.242(9)
Co(1)-O(2)	1.885(2)	N(5)-O(5)	1.146(7)
Co(1)-N(1)	1.929(3)	N(5)-O(6)	1.081(11)
Co(1)-N(2)	1.966(3)	O(1)-C(25)	1.315(4)
Co(1)-N(3)	1.926(3)	O(2)-C(25)	1.318(4)
Co(1)-N(4)	1.958(3)	O(3)-C(25)	1.225(4)
Co(1)-C(25)	2.315(3)		
Bond angles			
O(1)-Co(1)-O(2)	69.30(10)	N(3)-Co(1)-C(25)	92.79(11)
O(1)-Co(1)-N(1)	90.79(11)	N(4)-Co(1)-C(25)	131.47(12)
O(1)-Co(1)-N(2)	98.07(11)	Co(1)-O(1)-C(25)	90.52(17)
O(1)-Co(1)-N(3)	92.20(11)	Co(1)-O(2)-C(25)	90.77(19)
O(1)-Co(1)-N(4)	165.56(11)	C(1)-N(1)-Co(1)	128.50(2)
O(2)-Co(1)-N(1)	91.52(10)	C(12)-N(1)-Co(1)	113.10(2)
O(2)-Co(1)-N(2)	166.52(10)	C(10)-N(2)-Co(1)	130.10(3)
O(2)-Co(1)-N(3)	90.28(11)	C(11)-N(2)-Co(1)	111.30(2)
O(2)-Co(1)-N(4)	96.76(10)	C(13)-N(3)-Co(1)	129.1(2)
N(1)-Co(1)-N(2)	83.76(12)	C(24)-N(3)-Co(1)	112.6(2)
N(1)-Co(1)-N(3)	176.90(10)	C(22)-N(4)-Co(1)	129.90(3)
N(1)-Co(1)-N(4)	93.42(11)	C(23)-N(4)-Co(1)	111.5(2)
N(2)-Co(1)-N(3)	95.03(12)	C(1)-N(1)-C(12)	118.40(3)
N(2)-Co(1)-N(4)	96.11(11)	C(10)-N(2)-C(11)	118.50(3)
N(3)-Co(1)-N(4)	83.86(11)	C(13)-N(3)-C(24)	118.3(3)
N(1)-Co(1)-C(25)	90.13(11)	C(22)-N(4)-C(23)	118.40(3)
N(2)-Co(1)-C(25)	132.35(11)		

The ligands are bidentate, and each of the phen ligands is linked to the Co(III) *via* two N atoms. Thus, the metal ion is six-coordinated, the bonding being provided by two N atoms per phen ligand and two O atoms from the bidentate chelating carbonate anion. The Co(III) possesses a distorted octahedral environment where, *e.g.*, O(2), N(4), N(2) and N(1) form the base of the octahedron and the apical positions are occupied by the O(1) and N(3) atoms. The carbonate ligand is greatly strained in its coordination about the Co(III) ($\text{O}(1)-\text{Co}-\text{O}(2) =$

Table 3 Hydrogen bond geometry (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A	Equivalent position
O7-H7B...O3	0.72(7)	2.07(8)	2.79(7)	173.4(7)	X-1,Y,Z
O7-H7C...O8	0.84(5)	1.99(6)	2.81(7)	162.0(6)	-X,-1,-Y,-Z
O8-H8C...O7	0.98(9)	1.85(9)	2.80(7)	163.3(9)	X,Y-1,Z

Fig. 3 A view of $[\text{Co}(\text{phen})_2\text{CO}_3]\text{NO}_3 \cdot 3\text{H}_2\text{O}$, showing hydrogen bondings in the network (dashed lines).

$69.30(10)^\circ$). In the five-membered chelate ring, the N-Co-N angle is smaller than the N-Co-N angle, defined by two ligands, ($\text{N}(1)-\text{Co}-\text{N}(2) = 83.8(1)^\circ$ and $\text{N}(3)-\text{Co}-\text{N}(4) = 83.9(1)^\circ$). The pyridyl rings of the each phen ligand are nearly coplanar. The Co-O bond lengths are slightly shorter than the Co-O bond length in $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$. These geometries can be ascribed to the electrostatic interaction between Co(III) and the π -system of the CO_3^{2-} ligand. A number of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds are observed in the structure, Table 3, linking the cobalt complex and water molecules into two-dimensional network, Fig. 3.

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