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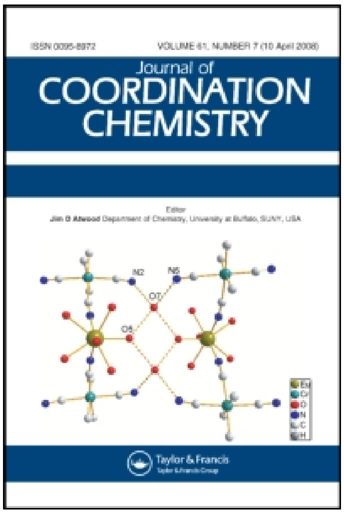

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Synthesis, crystal structure and thermal stability of bis(1,10-phenanthroline) cobalt(II) cyanide ethanol solvate dihydrate

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SYNTHESIS, CRYSTAL STRUCTURE AND THERMAL STABILITY OF BIS(1,10-PHENANTHROLINE) COBALT(II) CYANIDE ETHANOL SOLVATE DIHYDRATE

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The compound $[Co(phen)_2(CN)_2] \cdot EtOH \cdot 2H_2O$ was obtained by reaction of $Co(CN)_2$ and 1,10-phenanthroline (phen) in 95% EtOH solution and characterized using IR and UV spectroscopy, thermogravimetric-differential thermal analysis (TG-DTA) and X-ray crystallography. The deep-brown crystal is triclinic, space group $P\bar{1}$, with lattice parameters $a = 10.356(2)$, $b = 10.505(2)$, $c = 12.148(2)$ Å, $\alpha = 79.19(3)$, $\beta = 79.68(3)$, $\gamma = 86.71(3)^\circ$ and $Z = 2$. The compound contains a six-coordinate cobalt atom chelated by two phen ligands and two cyanide anions in a *cis* arrangement. One ethanol solvate molecule and two water molecules complete the crystal structure. In the solid state, the title compound forms a network structure through hydrogen bonds. Intermolecular hydrogen bonds connect the $[Co(phen)_2(CN)_2]$, ethanol and H_2O moieties. TG data indicate that thermal decomposition of the compound takes place in four steps, and the final product of thermal decomposition is CoC_2. Elemental analysis, IR and UV spectra are in agreement with the structural data.

Keywords: 1,10-Phenanthroline; Cobalt(II) cyanides; Inclusion compounds; TG-DTA

INTRODUCTION

Metal complexes of the type $[ML_m]^{n+}$, where L is either 1,10-phenanthroline (phen) or a modified phen ligand, are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA [1,2]. The ligands or the metal in these complexes can be varied in an easily controlled manner to facilitate an individual application, thus providing easy access for understanding details involved in DNA bonding and cleavage [3]. Some $[Co(phen)_2X_2]$ complexes have DNA-binding and photochemical DNA-cleavage characteristics [4]. Cobalt complexes with phen have also been studied in connection with the mechanism of irreversible autoxidation reactions [5], subsequent *cis–trans* isomerization [6] and equilibrium in solution at different

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pH values [7]. Transition metal cyanides [8,9] are of interest as inclusion compounds [10], composite inorganic–organic zeolitic materials [11] (some metal cyanide complexes, such as $[Fe^{III}(\mu\text{-CN-SnMe}_3\text{-NC})_3]^{3+}_{\infty}$ and $[Co^{III}(\mu\text{-CN-SnMe}_3\text{-NC})_3]^{3+}_{\infty}$, exhibit zeolite-type behavior of metal–organic host lattices), catalysts [12] (e.g. $[Co(CN)_5]^{3-}$ and $[Fe(phen)_2(CN)_2](PF_6)_2$ as hydrogenation catalysts), and molecular-based magnets [13] (e.g. combining $[M(CN)_6]^{q-}$ with a Lewis acid L^{p+} as a room-temperature organometallic magnet). To our knowledge, few crystal structures of Co(II) cyanides with phen ligands have been reported. In this paper, we report the thermal analysis and structure of bis(1,10-phenthroline-N^1,N^{10}) cobalt(II) cyanide inclusion compounds with ethanol and water molecules.

EXPERIMENTAL

Physical Measurements

Elemental analyses were measured with a Perkin-Elmer 1400C instrument. IR spectra (KBr pellets) in the range 4000–400 cm^{-1} were recorded on a Nicolet FT-IR 170X spectrophotometer. Electronic spectra were measured on a UV–Vis–NIR spectrophotometer. TG and DSC curves were recorded on a NETZSCH-Geratebau GmbH thermoanalyzer in flow of N_2, in the temperature range 20–680°C, at a heating rate of 10°C/min.

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Preparation of $[Co(phen)_2(CN)_2] \cdot EtOH \cdot 2H_2O$

All solvents and chemicals were analytical grade and were used without further purification. Fresh $Co(CN)_2$ (*ca* 0.5 g, 0.0045 mol) was obtained by reacting NaCN (0.5 g, 25% aqueous solvent, 0.01 mol) with $CoSO_4 \cdot 6H_2O$ (1.3 g, 30% aqueous solvent, 0.0051 mol). Solid $Co(CN)_2$ 0.3 g (0.0027 mol) was added gradually to an EtOH (50 mL, 95%) solution of phenanthroline ($C_{12}H_8N_2 \cdot H_2O$, 1.5 g, 0.0076 mol) with stirring. After stirring in air for about 2 h, the brown solution was filtered. The parent solution was evaporated for a few weeks at room temperature to yield the deep-brown crystals of the title compound (1.4 g, yield 95%, based on $Co(CN)_2$]. Single crystals suitable for X-ray measurements were obtained by recrystallization from distilled water and ethanol mixed solution ($H_2O : EtOH = 1 : 9$) at room temperature. C, H and N contents were determined by elemental analysis. Anal. Calcd. $[Co(phen)_2(CN)_2] \cdot EtOH \cdot 2H_2O$(%): C, 60.76; H, 4.70; N, 15.19. Found: C, 60.12; H, 4.43; N, 14.88.

Crystallographic Data Collection and Solution of Structure

A summary of the key crystallographic information is given in Table I. The diffraction data were collected on a Rigaku Raxis-IV diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å, $T = 293$ K). The technique used was ω-scan with limits $1.73 < \theta < 27.51°$. Empirical absorption correction was carried out using the *SADABS* [14] program.

The structure of the title compound was solved by direct methods and refined by least squares on F^2 using the *SHELXTL* [15] software package. All nonatoms were refined

TABLE I Summary of crystallographic data for the title compound

Empirical formula	$C_{28}H_{26}CoN_6O_3$
Formula weight	554.49
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 10.356(2)$ Å, $\alpha = 79.19(3)^\circ$ $b = 10.505(2)$ Å, $\beta = 79.68(3)^\circ$ $c = 12.148(2)$ Å, $\gamma = 86.71(3)^\circ$
Volume	1276.7(4) $Å^3$
Z, Calculated density	2, 1.442 Mg/m^3
Absorption coefficient	0.715 mm^{-1}
$F(000)$	576
Theta range for data collection	1.73 to 27.51°
Limiting indices	$-13 \leq h \leq 13$, $-13 \leq k \leq 0$, $-15 \leq l \leq 15$
Reflections collected/unique	4451/4451 [$R_{\text{int}} = 0.0000$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4451/0/359
Goodness-of-fit on F^2	1.016
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0621$, $wR_2 = 0.1325$
R indices (all data)	$R_1 = 0.1037$, $wR_2 = 0.1452$
Largest diff. peak and hole	0.422 and –0.565 e $Å^{-3}$

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anisotropically. Hydrogen atoms were located by difference synthesis and refined isotropically. The final conventional $R = 0.0621$ and $R_w = 0.1325$ for 3113 reflections with $I > 2\sigma(I)$ using the weighting scheme $w = 1/[\sigma^2(F_0^2) + (0.0743P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. The molecular graphics were plotted using *SHELXTL*. Atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* [16].

Crystallographic data for the title compound have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 220321. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Spectroscopic Properties

The solution ultraviolet spectrum of the title compound in EtOH exhibits three intense bands at 195, 224 and 267 nm. These bands belong to π–π^* or n–π^* orbital transitions of the phen ligand [17]. The IR spectrum exhibits characteristic strong bands at 1636 (C=C), 1508, 1429 (C=N), 845 ($\nu_{\text{C–H}}$ benzene ring) and 669 cm^{-1} ($\nu_{\text{C–H}}$ pyridine ring) for the coordinated phen ligands [18]. The bands at 1508 and 1429 cm^{-1} are shifted from their positions for the free phen ligands (1503 and 1420 cm^{-1}), indicating nitrogen coordination. The bands at 2066 and 2079 cm^{-1} attributed to $\nu(\text{C}\equiv\text{N})$ and a feature at *ca* 3000 cm^{-1} are consistent with the presence of water of crystallization [19]. A broad strong absorption band at *ca* 3396 cm^{-1} is attributed to O–H stretching modes from the ethanol solvate molecule.

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Structure of $[Co(phen)_2(CN)_2] \cdot EtOH \cdot 2H_2O$

The X-ray structure of the complex $[Co(phen)_2(CN)_2] \cdot EtOH \cdot 2H_2O$ consists of the $[Co(phen)_2(CN)_2]$ molecules, one ethanol molecule and two uncoordinated water molecules. Figure 1 shows a perspective view of the title compound with the atom numbering scheme, and Fig. 2 shows a perspective view of the crystal packing in the unit cell. Selected bond lengths and angles are presented in Table II.

The title compound contains a six-coordinate cobalt atom chelated by two phen ligands and two cyanides in a *cis* arrangement with the angles NC–Co(1)–CN = 90.7(2)°. Each cobalt ion is octahedral. The angles of the coordination sphere in the title compound differ from the ideal 90°. This distortion can be rationalized by considering the restriction imposed by the ligands. The bite angles between the phen chelate rings and cobalt atom are nearly the same [82.14(14)° and 82.44(14)°], and smaller than that of $[Co(phen)_2(H_2O)_2](NO_3)_3 \cdot 2H_2O$ [84.5(1)°] [20]. This can be

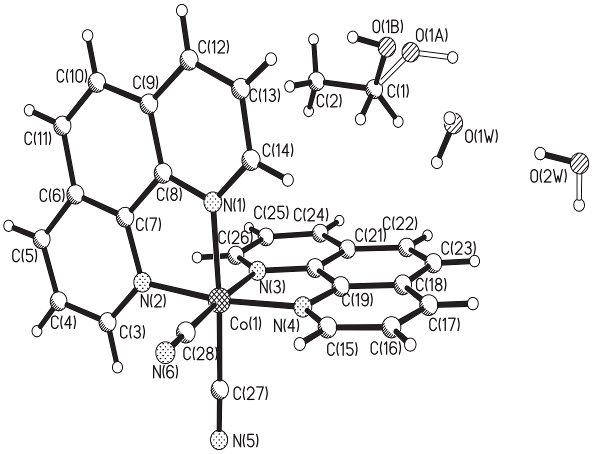

FIGURE 1 Molecular structure of $[Co(phen)_2(CN)_2] \cdot EtOH \cdot 2H_2O$ with the atom numbering scheme.

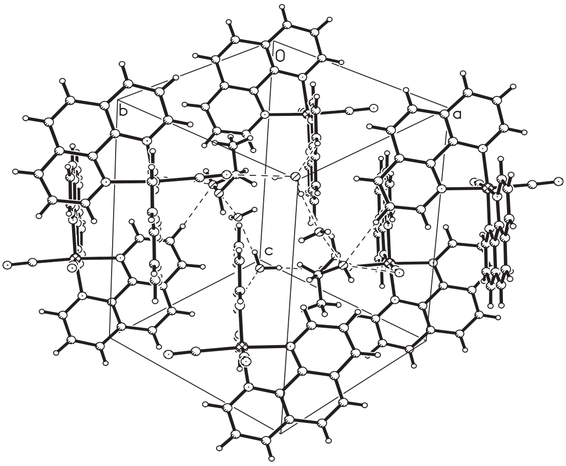

FIGURE 2 A view of the crystal packing down the *a* axis for the title compound.

TABLE II Selected bond lengths (Å) and angles (°) of the title compound

Co(1)–C(28)	1.917(5)	Co(1)–C(27)	1.929(5)
Co(1)–N(2)	1.960(3)	Co(1)–N(4)	1.968(3)
Co(1)–N(3)	2.012(4)	Co(1)–N(1)	2.014(4)
O(1A)–C(1)	1.21(3)	O(1B)–C(1)	1.394(17)
N(5)–C(27)	1.142(6)	N(6)–C(28)	1.145(5)
C(28)–Co(1)–C(27)	90.7(2)	C(28)–Co(1)–N(2)	92.83(15)
C(27)–Co(1)–N(2)	92.80(16)	C(28)–Co(1)–N(4)	92.76(16)
C(27)–Co(1)–N(4)	92.64(16)	N(2)–Co(1)–N(4)	172.14(15)
C(28)–Co(1)–N(3)	175.20(14)	C(27)–Co(1)–N(3)	89.51(17)
N(2)–Co(1)–N(3)	91.95(13)	N(4)–Co(1)–N(3)	82.44(14)
C(28)–Co(1)–N(1)	91.37(17)	C(27)–Co(1)–N(1)	174.60(15)
N(2)–Co(1)–N(1)	82.14(14)	N(4)–Co(1)–N(1)	92.22(14)
N(3)–Co(1)–N(1)	88.80(14)		

interpreted in terms of the rigidity of the phen ligands and the different valence state of cobalt. The two phen ligands are bidentate to cobalt, forming five-membered chelate rings. The Co–N bond distances [1.960(3)–2.014(4) Å] are shorter than the Co–N bond distances found in other Co^{2+} complexes with N atoms [2.1–2.2 Å] [21,22] and a little longer than those found in Co^{3+} coordinated complexes [1.922(5)–1.951(5) Å] [23,24]. The bond distances of Co–N(1) and Co–N(3), which are *trans* to the two cyanide anions, are slightly longer than those of Co–N(2) and Co–N(4), which are *cis* to the two cyanide anions. The Co–C bond lengths of 1.917(5) and 1.929(5) Å are comparable to similar reported complexes [1.916(5)–1.941(6) Å] [25,26]. The C≡N bond lengths of 1.142(6) and 1.145(5) Å are in good agreement with nonbridging C≡N bond distances [1.139(8)–1.149(7) Å] [27]. The bond distances of C–N and C–C in the phen ring fall within the range of literature values [28]. The two aromatic ring systems in each phen are coplanar within experimental error. The dihedral angle between the two phen ligands is 83.89°. There is some disorder in atoms O(1A) and O(1B) with a site occupancy of 0.5 for each.

In the crystal lattice, there are some intermolecular hydrogen bonds, potentially weak C–H···O hydrogen-bond intermolecular interactions [29], π–π stacking interactions and C–H···π supramolecular interactions [30,31]. The two lattice water molecules are hydrogen bonded to each other, and two CN^- form hydrogen-bond networks with two water molecules. The donor and acceptor distances are 2.9050 Å for O(1w)–H(11w)···N(6) (symmetry code: $-x, -y, 1-z$), 2.8492 Å for O(2w)–H(12w)···O(1w) (symmetry code: $1-x, 1-y, 1-z$) and 2.9143 Å for O(2w)–H(22w)···N(5) (symmetry code: $x, 1+y, z$), respectively. The O(1) of ethanol and O(2w) with the C atom in the phen ligands form potentially weak C–H···O intermolecular hydrogen-bond interactions. The donor and acceptor distances are 3.5284 Å for C(13)···O(1) (symmetry code: $-x, 1-y, 1-z$), bond angle 174.47° and 3.2869 Å for C(24)···O(2w) (symmetry code: x, y, z), bond angle 144.32°. There are eight types of π–π stacking interactions between the chelate ring, pyridine ring and phenyl ring. The center-to-center distances are in the range 3.825–3.899 Å. The shortest interplanar distances above are in the range 3.396–3.522 Å. There are six types of C–H···π supramolecular interactions between C–H with the chelate rings and aromatic rings in the crystal lattice. The distances between C–H and the chelate rings are 2.914 and 2.989 Å, and between C–H to the aromatic ring are in the range 2.993–3.104 Å, respectively. In the solid state, all the intermolecular interactions connect $[Co(phen)_2(CN)_2]$, H_2O and ethanol solvent molecules together stabilizing the crystal structure.

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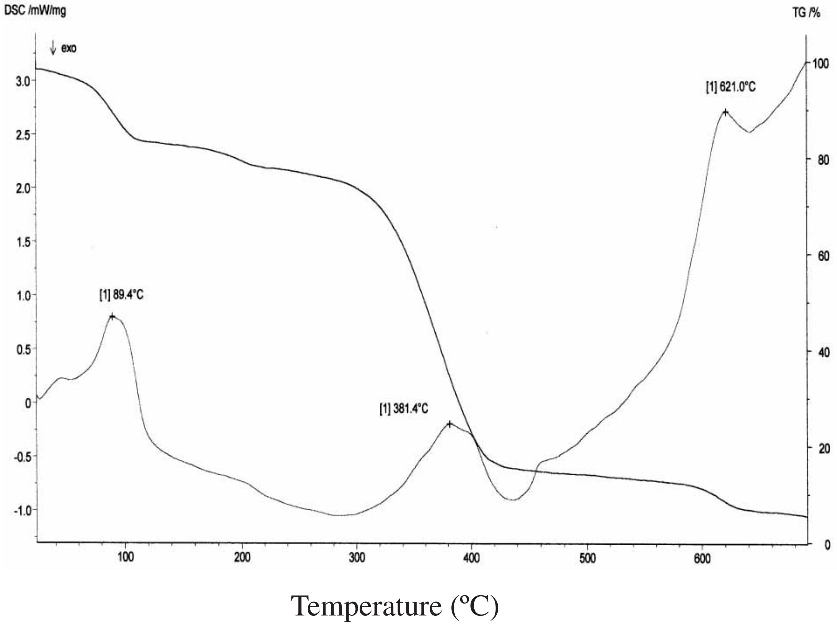

FIGURE 3 TG/DSC curves for $[Co(phen)_2(CN)_2]\cdot EtOH\cdot 2H_2O$.

Thermal Studies

The TG-DSC curves for $[Co(phen)_2(CN)_2]\cdot EtOH\cdot 2H_2O$ (2.595 mg sample), presented in Fig. 3, show four weight-loss steps, and the decomposition events mainly take place at 89.4, 381.4 and 621.0°C with three heat-absorption peaks. On the basis of the weight changes, the first weight-loss step (15.13%, residual = 2.202 mg) corresponds to the loss of ethanol and two water (solvate) molecules (found 15.13%, calcd. 14.79%) as an endothermic phenomenon; the second weight-loss step (residual = 2.067 mg) may be related to loss of N_2 with the breaking of C≡N bonds (found 5.22%, calcd. 5.05%). There is a broad endothermic peak in the DSC curve at 381.4°C, with 63.06% weight loss (residual = 0.4305 mg) in the TG curve between 220 and 450°C, which is attributed to the loss of two phen groups (found 64.86%, calcd. 64.92%). The residual weight of 14.79% (0.3838 mg) suggests that the residue may be CoC_2 (found 14.79%, calcd. 14.95%). In the temperature range 435–685°C, there is a weak endothermic peak at 621.0°C, and about 8.83% weight loss (residual = 0.1547 mg). From the weight loss we suggest that the transition process may be attributed to sublimation of part of CoC_2.

Acknowledgments

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