

# Investigations on Preparation, Crystal Structure and Thermal Stability of Bis( *O*-ethylcarbonodithiolato-*S*, *S'* ) ( 1,10-phenanthroline-*N*<sup>1</sup>, *N*<sup>10</sup> )cobalt( II ) Complex : [ Co( Et-XA )<sub>2</sub> · phen ] · H<sub>2</sub>O ( XA = xanthate )

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[ Co( Et-XA )<sub>2</sub> · phen ] · H<sub>2</sub>O was prepared by adding 1,10-phenanthroline to the EtOH solution of bis( *O*-ethylcarbonodithiolato )cobalt( II ) [ Co( Et-XA )<sub>2</sub> ]. The single crystal structure has been determined by X-ray diffraction analysis. The compound is orthorhombic with space group *Pna*2<sub>1</sub> and unit-cell parameters *a* = 1.0290( 2 ) nm, *b* = 1.4550( 3 ) nm and *c* = 1.4860( 3 ) nm. The geometry of each Co atom which coordinates with four S atoms from two xanthate anions and two N atoms from phenanthroline ligand, is a distorted octahedron. The brown crystals were examined by elemental analysis, FT-IR, UV spectra and thermogravimetric-differential thermal analysis ( TG-DTA ). Thermal decomposition of the compound takes place in several steps. In the first step, the compound releases 1,10-phenanthroline ligand, then loses the H<sub>2</sub>O molecules. In the second step, the complex decomposes to CoS<sub>3</sub>. The final product of thermal decomposition is CoS. Elemental analysis, IR and UV spectra are in agreement with the proposed structure.

**Keywords** 1,10-phenanthroline, ( *O*-ethylcarbonodithiolato )cobalt( II ), FT-IR spectra, TG-DTA, single crystal structure

## Introduction

The increasing commercial value of transition metal complexes of xanthates has aroused considerable interest in their chemistry. While their analytical applications are well known,<sup>1</sup> they are now finding extensive use in vulcanization of rubber, froth floatation process for concentration of sulphide ores, as antioxidants, lubricants,<sup>2,3</sup> and have been found to possess fungicidal and insecticidal activities.<sup>4</sup> Recently, molecular recognition between host and guest molecules, inclusion phenomena and noncovalent molecular interaction are fundamental problems at the frontiers of both organic and inorganic chemistry.<sup>5</sup> Inclusion compounds with the special cavities, windows and channels have received increasing attention in recent years partly because they are useful as molecular sieves and in catalysis.<sup>6</sup> Furthermore, inclusion formation affects both the

physicochemical properties of the guest and chemical reaction.<sup>7</sup> Also, the inclusion compounds derived from the adduct of Ni( XA )<sub>2</sub> with neutral nitrogen bases have been extensively studied in the past decade.<sup>8-10</sup> Gable and coworkers reported inclusion compounds [ Ni( Et-XA )<sub>2</sub> · ( 2,2'-diphenylamine ) · C<sub>6</sub>H<sub>6</sub> ] and [ Ni( Et-XA )<sub>2</sub> · ( 4,4'-bipy ) · 2CCl<sub>4</sub> ] in which the guest molecules are respectively engaged in the host lattice and channels.<sup>8</sup> Pang and coworkers also investigated the clathrate ability of Ni( Et-XA )<sub>2</sub> · phen for CCl<sub>4</sub> by <sup>35</sup>Cl NQR techniques.<sup>9</sup> Xiong and coworkers reported the crystallographic structure of the inclusion of water molecules of [ Ni( Et-XA )<sub>2</sub> · phen ] · 3H<sub>2</sub>O.<sup>10</sup> However, to the best of our knowledge, there are no reports on the inclusion compound of the adduct of Co( R-XA )<sub>2</sub> with neutral phenanthroline ligand. In this paper, we report the thermal analyses and structure of bis( *O*-ethylcarbonodithiolato-*S*, *S'* ) ( 1,10-phenanthroline-*N*<sup>1</sup>, *N*<sup>10</sup> )cobalt( II ) inclusion compounds with water molecules.

## Experimental

[ Co( Et-XA )<sub>2</sub> · phen ] · H<sub>2</sub>O was prepared as follows: a calculated amount of Co( Et-XA )<sub>2</sub> was added gradually to the EtOH solution of phenanthroline with stirring. After stirring in air for about 2 h, the green solution was filtered. The parent solution was evaporated for a few weeks at room temperature to yield the brown crystals [ yield 92%, based on Co( Et-XA )<sub>2</sub> ]. Single crystals suitable for X-ray measurements were obtained by recrystallization with distilled water at room temperature. Dimensions of the single crystal were 0.2 mm × 0.2 mm × 0.3 mm. The C, H and N content were determined by elemental analysis ( Anal. calcd for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>CoO<sub>3</sub>S<sub>4</sub>: C 43.42, H 3.62, N 5.63;

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found C 43.32, H 3.75, N 5.18).

Elemental analyses were performed on a Perkin-Elmer 1400C analyzer. IR spectra (4000—400  $\text{cm}^{-1}$ ), as KBr pellets, were recorded on a Nicolet FT-IR 170X spectrophotometer. Electronic spectra were taken on a UV-Vis-NIR spectrophotometer. TG and DTA curves were recorded on a NETZSCH-Geratebau GmbH thermoanalyser in flow of  $\text{N}_2$ , in the temperature range from 20  $^\circ\text{C}$  to 1000  $^\circ\text{C}$ , with a heating rate of 10  $^\circ\text{C}/\text{min}$ .

A summary of the key crystallographic information is given in Table 1. In the determination of the structure of the single crystal, X-ray intensities were recorded by four-circle CAD4 automatic diffractometer using graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.071073 \text{ nm}$ ). In the range of  $1.96 < \theta < 24.94^\circ$ , 2036 independent reflections were obtained. The final conventional  $R_1$  is 0.0855 and  $wR_2$  is 0.2564 for 1068 observable independent reflections with reflection intensity  $I > 2\sigma(I)$ . All the non-hydrogen atoms were refined on  $F^2$  anisotropically by full-matrix least squares method. Hydrogen atoms were located from the difference Fourier map and added to the structure calculations, but their positions were not refined. The contributions of these hydrogen atoms were included in structure-factor calculations.

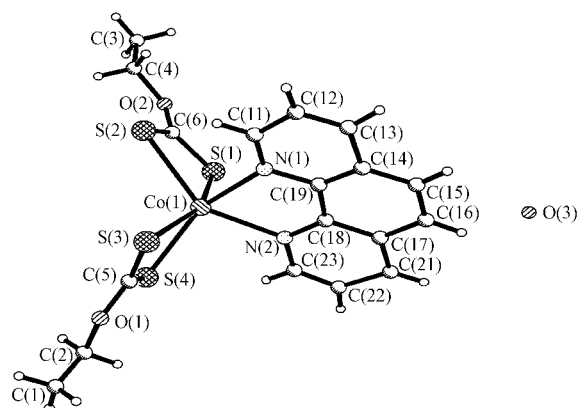
## Results and discussion

The solid reflectance electronic spectrum exhibits two bands at 220 and 262 nm. These bands belong to  $\pi-\pi^*$  or  $n-\pi^*$  orbital transitions of the phen ligand.<sup>11</sup> The band at 349 nm is due to a charge-transfer transition. The IR spectrum exhibits the characteristic strong bands at 1591 (C=C), 1514, 1425 (C=N), 845 ( $\nu_{\text{C-H}}$  benzene ring) and 726  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$  pyridine ring) for the coordinate phen ligands.<sup>12</sup> The bands at 1514 and 1425  $\text{cm}^{-1}$  are shifted from their positions for the free ligand (1503 and 1420  $\text{cm}^{-1}$ ), indicating nitrogen coordination.<sup>13</sup> The strong band at 1039  $\text{cm}^{-1}$  is attributed to the  $\nu_{\text{C-O}}$  stretching vibration. The band at 845  $\text{cm}^{-1}$ , belonging to the  $\nu_{\text{C-S}}$  stretching vibration,<sup>14,15</sup> is considered indicative of xanthate acting as a bidentate ligand.<sup>16,17</sup> A broad band at 3444  $\text{cm}^{-1}$ , which is the characteristic of the OH group of  $\text{H}_2\text{O}$ , shows that  $\text{H}_2\text{O}$  molecules exist in the crystal, in agreement with the elemental analysis. Also, a medium absorption band at 1622  $\text{cm}^{-1}$  may be assigned to non-coordinated water, consistent with the results of crystal structure determinations mentioned below.

**Table 1** Crystal data and structure refinement for the title compound

Empirical formula	$\text{C}_{18}\text{H}_{18}\text{CoN}_2\text{O}_3\text{S}_4$
Formula weight	497.51
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system, space group	Orthorhombic, $Pna2_1$
Unit cell dimensions	$a = 1.029(2) \text{ nm}$ $b = 1.455(3) \text{ nm}$ $c = 1.486(3) \text{ nm}$
Volume	2.224(8) $\text{nm}^3$
$Z$ , Calculated density	4, 1.485 $\text{Mg}/\text{m}^3$
Absorption coefficient	1.167 $\text{mm}^{-1}$
$F(000)$	1020
Crystal size	0.2 mm $\times$ 0.2 mm $\times$ 0.3 mm
$\theta$ range for data collection	1.96 $^\circ$ to 24.94 $^\circ$
Limiting indices	$0 \leq h \leq 12, 0 \leq k \leq 17, 0 \leq l \leq 17$
Reflections collected/unique	2036/2036 [ $R_{\text{int}} = 0.0000$ ]
Completeness to $\theta = 24.94$	100.0%
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	2036/1/254
Goodness-of-fit on $F^2$	1.368
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0855, wR_2 = 0.2564$
$R$ indices (all data)	$R_1 = 0.1652, wR_2 = 0.3538$
Extinction coefficient	0.0004(18)
Largest diff. peak and hole	7386 and $-1657 \text{ e} \cdot \text{nm}^{-3}$

Fig. 1 shows a perspective view of the title compound [ Co( Et-XA )<sub>2</sub> · phen ] · H<sub>2</sub>O with atomic numbering scheme. Table 2 lists atomic coordinates and equivalent temperature factors for non-hydrogen atoms. Selected bond lengths and angles are listed in Table 3.



**Fig. 1** Molecular structure for [ Co( Et-XA )<sub>2</sub> · phen ] · H<sub>2</sub>O with the atomic numbering scheme.

The title compound contains a six-coordinated cobalt atom chelated by two xanthate anions and one phen ligand. The cobalt atom is in a distorted octahedral environment. The guest water molecules are included in the crystal. The Co—S bond lengths [ 0.2593( 9 )—0.2767( 2 ) nm ] in [ Co( Et-XA )<sub>2</sub> · phen ] · H<sub>2</sub>O are longer than those found in other Co<sup>2+</sup> with S atom coordinated complexes, for example, 0.25550( 9 ) nm [ CoCl<sub>2</sub>( C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> ) ( CH<sub>4</sub>-N<sub>2</sub>S ) ( H<sub>2</sub>O ) ] · CH<sub>4</sub>N<sub>2</sub>S ).<sup>18</sup> The bond distances of Co—N are in the range of 0.230( 3 )—0.238( 3 ) nm. Also, these lengths are longer than those found in the similar structures

with usual octahedral coordination environment of Co( II ) complexes, such as [ CoCl<sub>2</sub>( C<sub>4</sub>H<sub>4</sub>N<sub>2</sub> )<sub>2</sub> ] and [ CoBr<sub>2</sub>( C<sub>4</sub>H<sub>4</sub>N<sub>2</sub> )<sub>2</sub> ] [ Co—N distances are 0.2200 and 0.2212 nm, respectively ],<sup>19</sup> Co( bipy )<sub>2</sub>( sac )<sub>2</sub>( H<sub>2</sub>O ) [ average Co—N 0.2149 nm, bipy = 4 *A'*-bipyridine, sac = saccharinate ],<sup>20</sup> Co( BBP )Cl<sub>2</sub>( MeOH )<sub>2</sub> [ average Co—N 0.216 nm, BBP = 2,6-bis( benzimidazol-2'-yl )pyridine ],<sup>21</sup> and Co( DIAFO )<sub>2</sub>( NCS )<sub>2</sub> [ average Co—N 0.2171 nm, DIAFO = 4,5-diazafluoren-9-one ].<sup>22</sup> The bite angles between the phen chelate rings and cobalt atom are 71.1( 6 )° which is smaller than that of [ Co( phen )<sub>2</sub>( H<sub>2</sub>O )<sub>2</sub> ] [ NO<sub>3</sub> ]<sub>3</sub> · 2H<sub>2</sub>O,<sup>23</sup> [ Co( phen )<sub>2</sub>( Cl )<sub>2</sub>( H<sub>2</sub>O ) ]<sup>+</sup>,<sup>24</sup> and [ Co( phen )<sub>2</sub>Cl<sub>2</sub> ]Cl · 3H<sub>2</sub>O.<sup>25</sup> This can be interpreted in terms of the rigidity of phen ligands and in the difference of valence state of cobalt. The two xanthate ligands are bidentately bonded to cobalt, forming four-member chelate rings. The bite angles between the two xanthate chelate rings and cobalt atom are 66.3( 4 )° and 67.1( 4 )°, respectively. The bond distances of C—N and C—C in the title compound fall within the range of the literature values.<sup>26</sup> The three aromatic ring systems in each phenanthroline with Co atom are coplanar, with the maximum deviation of 0.0065 nm. The dihedral angles between the phen ligand and two CoS<sub>2</sub>C chelate ring are 76.50° and 67.31°, respectively.

The TG/DTC curves of the title compound are presented in Fig. 2. Thermogravimetric analysis ( TGA ) of [ Co( Et-XA )<sub>2</sub> · phen ] · H<sub>2</sub>O reveals that the decomposition events mainly take place at 145.8, 203.1 and 283.9 °C, respectively. There are two heat-releasing peaks ( 162.2 °C and 249.2 °C ). It shows no decomposition before 145 °C; but, at 145.8 °C, decomposition occurs with a strong heat releasing phenomenon. On the base of weight

**Table 2** Atomic coordinates ( × 10<sup>4</sup> ) and equivalent isotropic displacement parameters ( nm<sup>2</sup> × 10 ) for the title compound

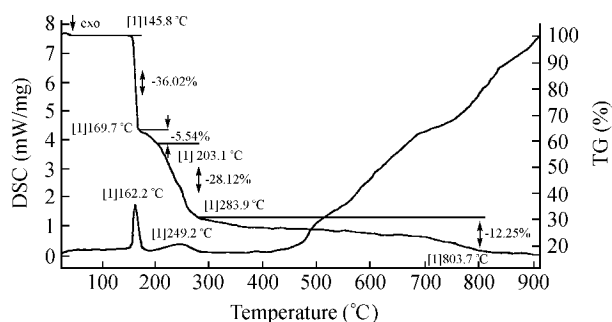
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>a</sup>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>a</sup>
Co( 1 )	259( 3 )	499( 4 )	234( 7 )	28( 1 )	C( 21 )	453( 4 )	200( 3 )	365( 3 )	9( 1 )
S( 2 )	32( 8 )	598( 6 )	226( 8 )	81( 3 )	C( 23 )	451( 3 )	369( 2 )	355( 3 )	7( 1 )
S( 3 )	354( 8 )	532( 7 )	68( 8 )	83( 3 )	C( 5 )	471( 3 )	586( 2 )	128( 3 )	8( 1 )
S( 4 )	468( 7 )	598( 7 )	237( 9 )	89( 3 )	C( 13 )	40( 4 )	211( 3 )	111( 5 )	13( 2 )
S( 1 )	148( 8 )	533( 8 )	401( 9 )	94( 3 )	C( 6 )	29( 3 )	589( 2 )	339( 3 )	8( 1 )
O( 1 )	572( 2 )	616( 2 )	80( 2 )	92( 8 )	C( 15 )	196( 4 )	119( 3 )	198( 4 )	11( 2 )
N( 2 )	350( 2 )	369( 2 )	295( 2 )	7( 8 )	C( 11 )	57( 3 )	366( 3 )	114( 3 )	8( 1 )
C( 19 )	194( 2 )	283( 2 )	203( 3 )	7( 1 )	C( 2 )	678( 3 )	663( 3 )	123( 2 )	9( 1 )
N( 1 )	149( 2 )	368( 2 )	176( 2 )	6( 7 )	C( 3 )	278( 1 )	8( 2 )	722( 2 )	9( 5 )
C( 18 )	297( 2 )	289( 2 )	266( 2 )	5( 8 )	C( 4 )	-174( 4 )	667( 3 )	353( 6 )	24( 5 )
C( 14 )	149( 3 )	202( 2 )	170( 3 )	8( 1 )	C( 16 )	295( 4 )	116( 2 )	257( 4 )	11( 2 )
C( 22 )	504( 4 )	297( 4 )	388( 3 )	14( 2 )	C( 2 )	-65( 2 )	624( 2 )	394( 2 )	9( 8 )
C( 17 )	349( 3 )	202( 3 )	297( 3 )	7( 1 )	C( 3 )	-272( 3 )	687( 3 )	419( 3 )	8( 1 )
C( 12 )	α( 4 )	286( 2 )	76( 3 )	7( 1 )	C( 1 )	766( 5 )	690( 5 )	69( 4 )	19( 4 )

<sup>a</sup> *U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

**Table 3** Selected bond lengths (nm) and angles ( $^{\circ}$ ) for the title compound

Cd(1)—N(2)	0.230(3)	Cd(1)—N(1)	0.238(3)
Cd(1)—S(4)	0.259(9)	Cd(1)—S(3)	0.270(2)
Cd(1)—S(2)	0.275(9)	Cd(1)—S(1)	0.277(2)
S(2)—C(6)	0.167(5)	S(3)—C(5)	0.168(4)
S(4)—C(5)	0.163(5)	S(1)—C(6)	0.175(4)
C(1)—C(5)	0.134(4)	C(1)—C(2)	0.143(4)
N(2)—C(18)	0.136(4)	N(2)—C(23)	0.137(4)
C(19)—N(1)	0.138(3)	N(1)—C(11)	0.133(4)
C(18)—C(17)	0.144(5)	C(17)—C(21)	0.147(5)
N(2)—Cd(1)—N(1)	71.1(6)	N(2)—Cd(1)—S(4)	96.8(7)
N(1)—Cd(1)—S(4)	147.6(7)	N(2)—Cd(1)—S(3)	110.8(8)
N(1)—Cd(1)—S(3)	88.8(8)	S(4)—Cd(1)—S(3)	67.1(4)
N(2)—Cd(1)—S(2)	143.0(7)	N(1)—Cd(1)—S(2)	90.1(5)
S(4)—Cd(1)—S(2)	114.3(3)	S(3)—Cd(1)—S(2)	100.0(4)
C(14)—C(19)—N(1)	124(3)	C(14)—C(19)—C(18)	123(4)
N(1)—C(19)—C(18)	113(3)	C(11)—N(1)—C(19)	115(3)

changes, the first process of the weight loss (36.02%) corresponds to the loss of phen (found 36.02%, calcd 36.04%), with an exothermal phenomenon; then, the second event of the weight loss may be related to the loss of water (found 5.54%, calcd 3.62%). Then, over 203.1  $^{\circ}\text{C}$ ,  $\text{Co}(\text{Et-XA})_2$  begins to decompose with an exothermal peak; the two *O*-ethylcarbonodithiolato moieties start to dissociate. The weight loss of 69.87% suggests that the residue may be  $\text{CoS}_3$  (calcd 68.65%), which indicates a complete loss of ethylcarbonate and one sulfur atom of coordination chromophore  $\text{CoS}_4$ . Finally, a 12.25% weight loss at 803.7  $^{\circ}\text{C}$  indicates loss of two sulfur atoms, the residue may be  $\text{CoS}$  (found 17.92% calcd 18.29%). It is interesting to note that at 145.8  $^{\circ}\text{C}$  the release of phen molecule takes place first, suggesting that the water molecules are firmly clathrated in the channel which is confirmed by the X-ray crystal structural determination described above.

**Fig. 2** TG/DSC curves of  $[\text{Co}(\text{Et-XA})_2 \cdot \text{phen}] \cdot \text{H}_2\text{O}$ .

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