

Research Article

Synthesis, Characterization, and X-Ray Structure of Bis(O-butylthiocarbonato)bis(3-ethyl pyridine)nickel(II)

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A new series of additional complexes of bis(O-butylthiocarbonato)nickel(II) with ethylpyridines have been prepared and characterized by physicochemical techniques like elemental analysis, molar conductance measurements, TGA-DTA and UV-visible electronic spectroscopy, and IR-spectral data. The structure of $[\text{Ni}(\text{S}_2\text{COC}_4\text{H}_9)_2(\text{C}_7\text{H}_9\text{N})_2]$ has been established by X-ray crystallography. The complex crystallizes in the monoclinic space group $P1/n$ with unit cell parameters $a = 14.0721(6)$, $b = 7.0078(2)$, and $c = 15.3604(7)$ Å and $\alpha = 90.00$, $\beta = 108.065(5)$, and $\gamma = 90.00^\circ$. The Ni atom in the title complex is octahedrally coordinated within a trans- N_2S_4 donor set, with the Ni atom located on a centre of inversion. Crystal structure was solved by direct methods and refined by full matrix least squares procedures to a final R -value of 0.0545 for 1984 observed reflections. The butyl chain is disordered over two sets of sites, with occupancy ratio of 0.572 : 0.427.

1. Introduction

O-alkylthiocarbonate (ROCS_2^-), named xanthate, represents an important class of 1, 1 dithiolato ligands which have been studied extensively [1, 2]. These compounds form water insoluble complexes with most of the transition metals and are thus extensively employed for the separation and quantitative determination of cations of transition metals [3]. Beside this these ligands are also investigated for nonlinear optical application and as a synthetic precursor for the generation of metal sulfide nanoparticles [4, 5]. Xanthates as ligand are also extensively studied for a wide variety of structural features. They are known to coordinate as a monodentate, bidentate, or as a bridging ligand. Xanthate complexes of composition $[\text{Ni}(\text{Rxa})_2]$ ($\text{R} = \text{alkyl}$; $\text{xa} = \text{xanthate}$) are partially unsaturated and thus they can react easily with monodentate or bidentate nitrogen donor ligands and afford octahedral nickel(II) complexes with either cis or trans geometry. As a part of our ongoing research on nickel(II) xanthate complexes with substituted pyridines,

we report here the synthesis and characterization of 1:2 adducts of bis(O-butylthiocarbonato)nickel(II) with ethyl pyridines and also the crystal structure of the adduct bis(O-butylthiocarbonato)bis(3-ethylpyridine)nickel(II).

2. Experimental

2.1. Material and Measurement. Carbon, hydrogen, sulphur, and nitrogen contents of the addition complexes are determined on elemental analyzer CHNS 932, LECO Corporation, USA. Molar conductance of adducts was determined on their millimolar solutions in DMF by using digital conductivity meter “Century CC 601.” Infrared spectra of the complexes over the region $4000\text{--}200\text{ cm}^{-1}$ were recorded using KBr pellets on the infrared spectrometer (PerkinElmer FT-IR spectrometer). The electronic spectra of adducts were recorded in DMF on systronics 119 UV-visible spectrophotometer. Magnetic moments were recorded at room temperature by VSM method (Princeton applied research model number 155). The analytical data, molar conductance, and magnetic

TABLE 1: Physical and analytical data of the adducts of bis(O-butylthiocarbonato)nickel(II) with substituted pyridines.

Complex	Formula Wt.	M.P (°C)	μ_{eff} (B.M)	Found (calculated) %			
				C	H	N	S
Bis(O-butylthiocarbonato)bis(2-ethylpyridine)nickel(II)	572.69	79.8	3.10	50.28 (48.95)	6.28 (5.88)	4.88 (4.35)	22.35 (22.05)
Bis(O-butylthiocarbonato)bis(3-ethylpyridine)nickel(II)	572.69	80	3.27	50.28 (49.01)	6.28 (5.93)	4.88 (4.05)	22.35 (22.0)
Bis(O-butylthiocarbonato)bis(4-ethylpyridine)nickel(II)	572.69	80.2	3.28	50.28 (48.82)	6.28 (6.01)	4.88 (4.43)	22.35 (21.95)

TABLE 2: Infrared and electronic spectral data of the adducts of bis(O-butylthiocarbonato)nickel(II) with substituted pyridines.

Complex	IR-spectral data (cm ⁻¹)			Electronic spectral data (cm ⁻¹)		
	ν_{as} (C–O–C)	ν_{s} (C–O–C)	ν (C–S)	ν_1	ν_2	ν_3
Bis(O-butylthiocarbonato)bis(2-ethylpyridine)nickel(II)	1202	1123	1033	14440	19800	26400
Bis(O-butylthiocarbonato)bis(3-ethylpyridine)nickel(II)	1199	1134	1035	13980	20220	25670
Bis(O-butylthiocarbonato)bis(4-ethylpyridine)nickel(II)	1199	1140	1037	14250	19225	24565

moments of adducts are represented in Table 1. Important IR bands and electronic spectral data are cited in Table 2.

The X-ray intensity data for the compound, bis(O-butylthiocarbonato)bis(3-ethylpyridine)nickel(II) (Figure 1), were collected by using X'calibur Oxford diffraction system with graphite monochromatic MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Data were collected by using CrysAlis^{Pro} software and reduced with CrysAlisRED [6]. The final refinement cycles converged to an $R = 0.0545$ and $wR(F^2) = 0.1293$ for observed data. The residual electron densities had the range of $-0.419 < \Delta\rho < 0.790 \text{ e\AA}^{-3}$. The structure was solved by SHELXS97 [7] and refined with SHELXL97 [7]. The H atoms were positioned geometrically and were treated as riding on their parent C atoms, with C–H distance of 0.93–0.97 \AA and with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

2.2. Synthesis of the Title Complex

2.2.1. Preparation of Potassium Butylthiocarbonate.

The potassium salt of O-butylthiocarbonate was prepared by the standard published method [8]. Into a 500 mL round bottomed flask, fitted with a reflux condenser, 42 g (0.075 mol) of potassium hydroxide pellets was placed and 192 g (234 mL, 2.6 mol) of n-butanol was added. The reaction mixture was heated under reflux for 1 hour. The contents were then cooled and the liquid from the reaction mixture was decanted off into another dry 500 mL flask. To this flask, 57 g (45 mL, 0.075 mol) of carbon disulphide was added slowly with constant heating. The contents of the flask were filtered (after cooling in ice) on a sintered glass funnel at the pump and washed with three 25 mL portions of ether. The resulting product potassium O-butylthiocarbonate was dried in a vacuum desiccator over anhydrous calcium chloride.

2.2.2. Synthesis of Bis(O-butylthiocarbonato)nickel(II).

The complex bis(O-butylthiocarbonato)nickel(II) was prepared by stirring aqueous solutions of nickel(II) chloride and potassium salt of O-butylthiocarbonate in the molar ratio of 1:2 when green colored precipitates of bis(O-butylthiocarbonato)nickel(II) were obtained.

2.2.3. Synthesis of Bis(O-butylthiocarbonato)bis(ethylpyridine)nickel(II).

To a solution of $[\text{Ni}(\text{S}_2\text{COC}_4\text{H}_9)_2]$ (0.79 g, 0.0026 mole) in acetone (50 mL) corresponding ethylpyridine (2-ethylpyridine, 3-ethylpyridine, and 4-ethylpyridine) (each 0.56 g, 0.0052 mol) was added with constant stirring for 30 minutes. The color of the solution changes to bright green. The resulting solution was allowed to stand for few days at room temperature when bright green crystals of $[\text{Ni}(\text{S}_2\text{COC}_4\text{H}_9)_2(\text{C}_7\text{H}_9\text{N})_2]$ were obtained.

3. Results and Discussion

3.1. Preliminary Investigations.

The adducts of bis(O-butylthiocarbonato)nickel(II) with 2-, 3-, and 4-ethylpyridine are bright green colored microcrystalline solids which are soluble in acetone, chloroform, DMF, and DMSO. On the basis of elemental analysis the adducts isolated having 1:2 stoichiometry are assigned formula $[\text{Ni}(\text{S}_2\text{COC}_4\text{H}_9)_2] \text{L}_2$ where L = 2-, 3-, and 4-ethylpyridine.

3.2. Conductance and Magnetic Measurements.

The molar conductivity value calculated from the conductivity measurements of millimolar solution of the title complex in DMF supports the neutral and nonionic nature of the complex [9, 10]. The effective room temperature magnetic moment of the complex prepared was found to be 3.28 B.M. which

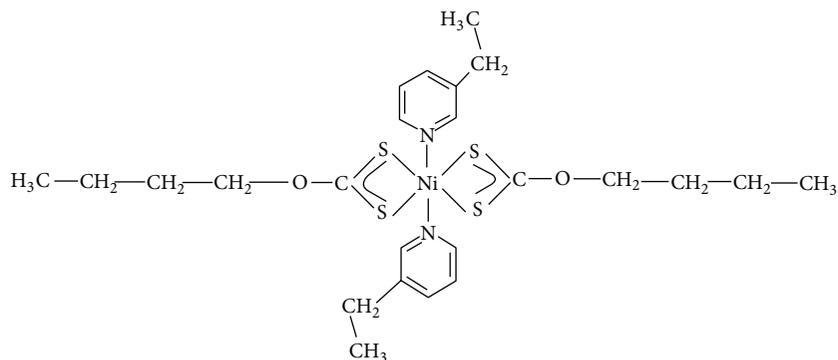


FIGURE 1: Chemical structure of bis(O-butylthiocarbonato)bis(3-ethylpyridine)nickel(II).

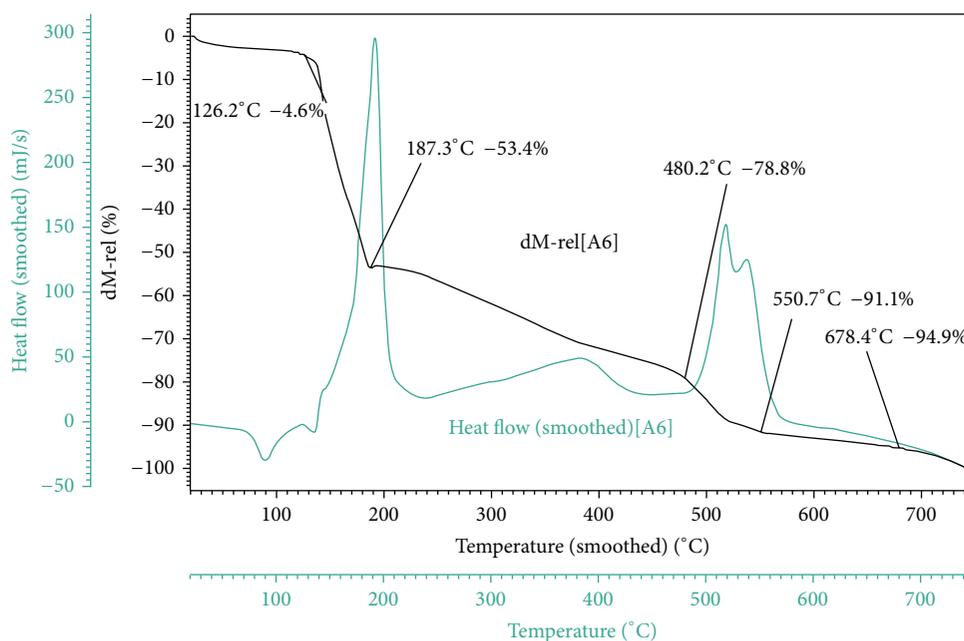


FIGURE 2: TGA curve of the bis(O-butylthiocarbonato)bis(3-ethylpyridine)nickel(II).

is in agreement with magnetic moment values observed for paramagnetic octahedral complexes of nickel(II) [11].

3.3. IR and Electronic Spectra. The infrared spectrum of the complex $[\text{Ni}(\text{S}_2\text{CoC}_4\text{H}_9)_2(\text{C}_7\text{H}_9\text{N})_2]$ exhibits characteristic bands for xanthato ligand [12] at 1201 and 1144 cm^{-1} which are attributed to the stretching vibration of the C–O–C group, while the bands at 1037 cm^{-1} and 614 cm^{-1} belong to $\nu(\text{C–S})$ vibration [13]. The bands at 1580 and 1540 for $\nu(\text{C=N})$, and at 1450 cm^{-1} for $\nu(\text{C=C})$, belong to coordinated 3-ethylpyridine ligand. The electronic absorption spectra show absorption bands ν_1 (14800 cm^{-1}), ν_2 (19200 cm^{-1}), and ν_3 (23500 cm^{-1}), which probably corresponds to the d-d transitions ${}^3\text{A}_2\text{g} \rightarrow {}^3\text{T}_2\text{g}(\text{F})$, ${}^3\text{A}_2\text{g} \rightarrow {}^3\text{T}_1\text{g}(\text{F})$, and ${}^3\text{A}_2\text{g} \rightarrow {}^3\text{T}_1\text{g}(\text{P})$, respectively. Appearance of these three broad bands along with shoulders shows that adduct is having trans octahedral geometry around nickel(II) metal ion [14].

3.4. TGA/DTA Studies. The TGA/DTA studies of the complex prepared were carried out from 20 to 750°C at the rate of 10°C/min. The TGA curve of the title complex is shown in Figure 2. The complex first decomposes at 126.2°C showing the loss of an alkyl moiety (weight loss found = 4.7%, calculated = 4.5%). The DTA curve shows a sharp endothermic peak below 100°C indicating that the water molecules are present outside the coordination sphere. A major loss occurs at 187.3°C which corresponds to the loss of xanthato group (weight loss = 53.3% calculated = 49.5%). This loss has also been supported by sharp exothermic curve at the same temperature. With the rise in temperature, the weight loss was found to be 88.9% at 678.4°C indicating the loss of both the molecules of 3-ethylpyridine (weight loss found = 88.9%, calculated = 88.3%). It has also been supported by the DTA curve. The weight loss continues at a slower rate up to 750°C leaving behind stable NiO.

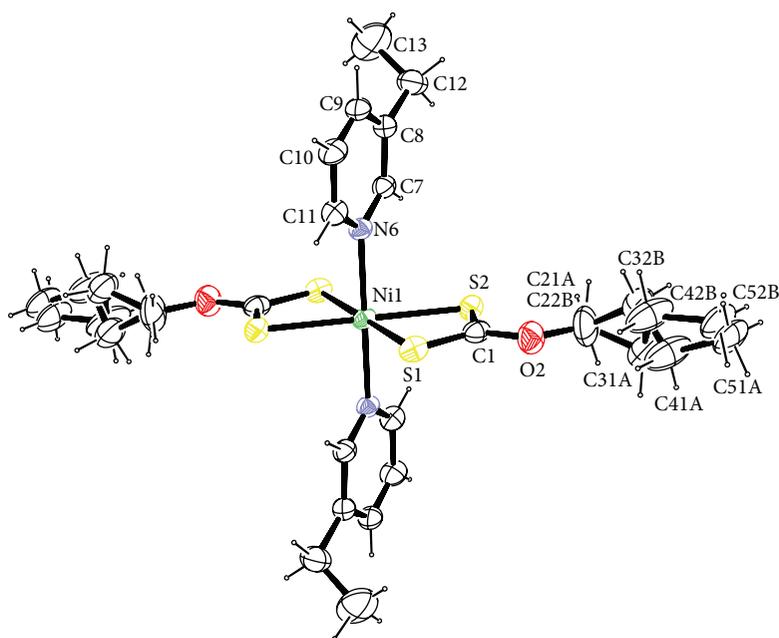


FIGURE 3: ORTEP view of the molecule with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

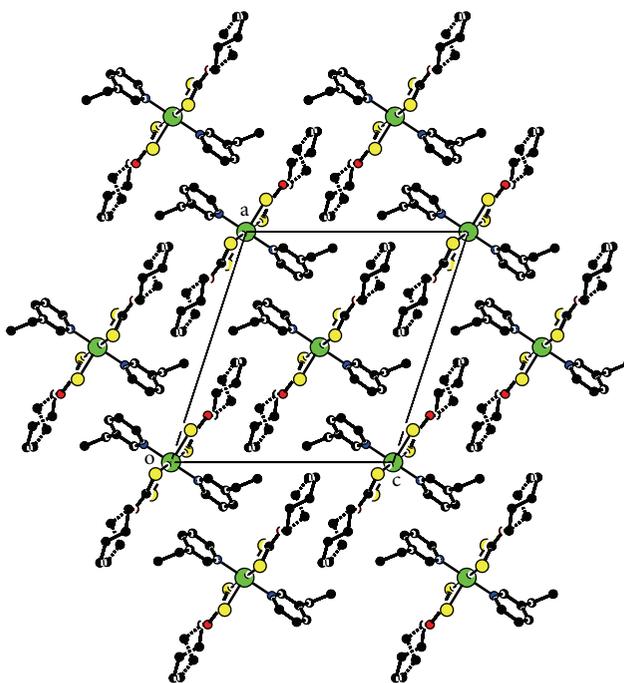


FIGURE 4: The packing arrangement of molecules viewed down the *b*-axis.

3.5. *X-Ray Crystallographic Studies.* The crystallography data for bis(O-butylthiocarbonato)bis(3-ethyl pyridine) nickel(II) are presented in Table 3. Selected bond distances and bond angles for nonhydrogen atoms are listed in Table 4. A general view of the molecule indicating atom numbering scheme is shown in Figure 3. *Ortep-3* software [15] was used for making the thermal ellipsoids. The geometry of

the molecule was calculated using *PLATON* [16] and *PARST* [17] software.

The asymmetric unit comprises half molecule and nickel(II) cation lies on an inversion centre. The Ni(II) atom is coordinated by a distorted octahedral arrangement of four sulphur atoms from two chelating xanthate ligands and two nitrogen atoms from two cyanopyridines ligands.

TABLE 3: Crystal and experimental data.

Empirical formula	$C_{24}H_{36}N_2NiO_2S_4$
Formula weight	571.50
Temperature	293(2) K
Wavelength	0.71073 Å
Unit cell dimensions	
a , Å	14.0721(6)
b , Å	7.0078(2)
c , Å	15.3604(7)
α , °	90.00
β , °	108.065(5)
γ , °	90.00
Z	2
Space group	$P2_1/n$
Crystal system	monoclinic
Calculated density, g/cm^{-3}	1.318
Absorption coeff., mm^{-1}	0.986
$F(000)$	604
Crystal size mm	0.30 × 0.20 × 0.10
Color	Green
Theta range for entire data collection	3.43–29.07 deg.
Limiting indices	$-17 \leq h \leq 17, -8 \leq k \leq 8, -18 \leq l \leq 18$
Refinement method	Full matrix least squares on F^2
Reflections collected	14671
Used in refinement	1984
Parameters	167
Goodness-of-fit on F^2	1.045
R indices	$R_1 = 0.0545, wR_1 = 0.1293$
Largest diff. peak and hole	0.79 and $-0.42 e\text{Å}^{-3}$

CCDC 956444 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallography Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(0) 1223-336033.

TABLE 4: Bond lengths (Å), bond angles, and torsion angles (°).

Bond distances (Å)			
Ni1 N6	2.112(3)	Ni1 S2	2.4436(11)
Ni1 S1	2.4551(10)	S2 C1	1.677(5)
S1 C1	1.684(4)	C12 C13	1.466(8)
C8 C12	1.507(6)	O2 C1	1.340(5)
O2 C2B	1.426(9)	O2 C2A	1.432(8)
Bond angles (°)			
N6–Ni1–S2	90.31(9)	N6–Ni1–S1	89.26(9)
S2–Ni1–S1	106.63(4)	C1–S2–Ni1	83.03(14)
C1–S1–Ni1	82.53(16)	C13–C12–C8	115.2(5)
O2–C1–S2	117.5(3)	O2–C1–S1	121.5(3)
Torsion angles (°)			
C9–C8–C12–C13	–66.2(8)	N6–Ni1–S2–C1	–88.76(16)
C7–C8–C12–C13	113.5(6)	S2–Ni1–N6–C7	–55.4(3)
C10–C9–C8–C12	–179.2(5)	C9–C8–C12–C13	–66.2(8)

The Ni1–N6 bond length is 2.112(3) Å. The Ni–S bond lengths involving the xanthate ligands are 2.455(1) Å for Ni1–S1 and 2.444(1) Å for Ni1–S2. The O2–C1 bond distance [1.340(5) Å] is shorter than O2–C2A [1.432(8) Å] as a consequence of the hybridization of the carbon atom. The short value of bond distance for O4–C3 is consistent with a significant contribution of the resonance form of the xanthate anion that features a formal C=O and a negative charge on each of S atom [18]. The C–S bond lengths involving the xanthate ligands are S1–C1 = 1.684(4) and S2–C1 = 1.677(5) Å. These values show double bond character due to the delocalization over the two C–S bonds [19].

The bond angles in the pyridine ring vary from 117.8(4) to 124.1(4)°, the average value being 119.9(8)°, and these values of bond angles and bond distances are in good agreement with those reported for some analogous Ni-dithiocarbonato complexes [20–23]. The plane formed by the atoms Ni1, S1, C1, and S2 makes a dihedral angle of 88.20(9)° with the plane of ethyl-pyridine ring, meaning thereby that both planes are held almost perpendicular to each other. The atom C13 of the ethyl group is deviated significantly from the plane of pyridine ring [deviation being 1.200(8) Å]. The butyl chain attached to the dithiocarbonato group contains disorder over two sets of sites with occupancy ratio of 0.572 : 0.427.

The packing of the molecule within the unit cell viewed down the *b*-axis is shown in Figure 4. Molecules in the unit cell are arranged in the form of layers and within the layers the molecules are parallel to each other. Nickel atom is located at each corner of the unit cell and also within the unit cell. The molecules are packed with Van der Waals contacts.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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