

Short communication

Synthesis, Characterization and X-ray Structure of the Adducts of Bis(*O*-butyldithiocarbonato)nickel(II) with Substituted Pyridines

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Abstract

Some mixed ligand complexes of Ni(II) with *O*-butyldithiocarbonate as a primary ligand and substituted pyridines as secondary ligands have been isolated and characterized on the basis of analytical data, molar conductance, magnetic susceptibility, electronic and infrared spectral studies. The molar conductance studies show their non-electrolytic behavior. Magnetic and electronic spectral studies suggest octahedral stereochemistry around Ni(II) ions. Infrared spectral studies suggest bidentate chelating behavior of *O*-butyldithiocarbonate monoanion while other ligands show unidentate behavior in their complexes. One of the adduct bis(*O*-butyldithiocarbonato)bis(3,5-dimethylpyridine)nickel(II) crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters. The crystal structure has been solved by direct methods and refined by full matrix least-squares procedures to a final R-value of 0.0379 for 2460 observed reflections. The Ni²⁺ ion is in an octahedral coordination environment formed by an N₂S₄ donor set, defined by two chelating dithiocarbonate anions as well as two 3,5-dimethylpyridine ligands with the Ni²⁺ ion located at the inversion centre. The packing of layers of molecules is stabilized by weak π - π and C-H... π interactions.

Keywords: Adducts, Xanthates (dithiocarbonates), Octahedrally coordinated, direct methods, crystal structure, π - π and C-H... π interactions.

1. Introduction

O-alkyldithiocarbonates (xanthates) belong to 1,1-dithiolate family and are the reaction product of carbon disulfide, an alcohol, and an alkali. They are extensively used as pharmaceuticals, fungicides, pesticides, rubber accelerators, corrosion inhibitors, agricultural reagents and quite recently in therapy for HIV infections.¹⁻³ Metal xanthate complexes and their adducts with a variety of Lewis bases have been extensively studied.⁴⁻⁶ The soluble alkali metal xanthates are widely used in extraction and purification of Hg, Ag, Cd etc.⁷ Xanthates react with *t*-amine to give quaternary ammonium salts at room temperature, and dithiolcarbonates at elevated temperatures.⁸ *N*-methylethylxanthocarbamate has been used as an analytical reagent for the determination of trace amount of

calcium in standard alloys, biological samples.⁹ Xanthates of platinum, palladium, gold, nickel, rhodium and bismuth are known to possess antitumoral activities.¹⁰ In this article we report the synthesis and characterization of 1:2 adducts of bis(*O*-butyldithiocarbonato) nickel(II) with substituted pyridines such as 3-methylpyridine (**1**), 2,4- ; 3,4- ; 3,5-dimethyl-pyridines (**2**, **3**, **4**) and 2,4,6-trimethylpyridine (**5**) and the crystal structure of Bis(*O*-butyldithio-carbonato)bis(3,5-dimethylpyridine)nickel(II).

2. Experimental

2.1. Materials and Instrumentations

Carbon, hydrogen, nitrogen and sulphur contents of the addition complexes were determined on Elemental

Table 1. Physical and analytical Data of the adducts of Bis(*O*-butyldithiocarbonato)nickel(II) with substituted pyridines

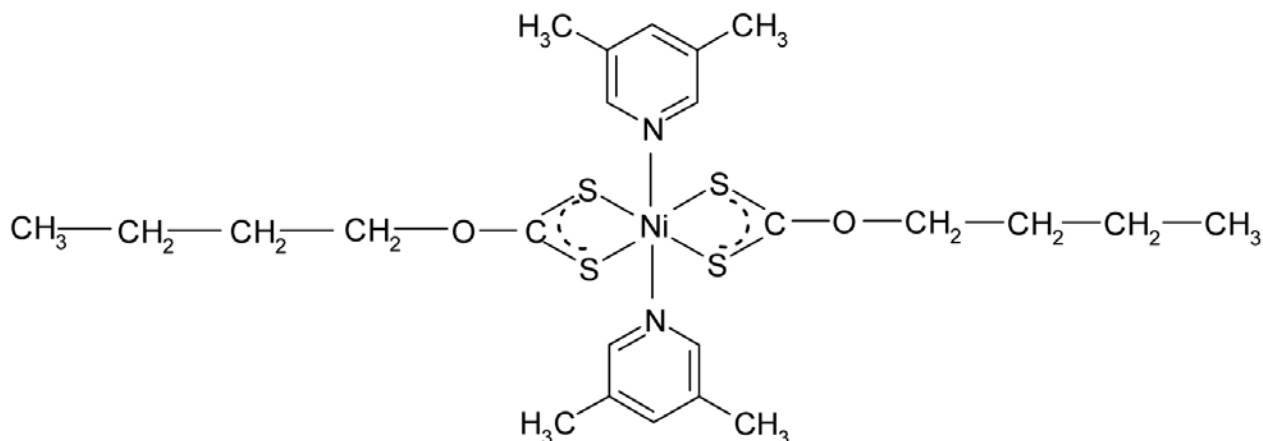
Complex No.	Formula Wt.	M.P (°C)	μ_{eff} (B.M)	Found (calculated) %			
				C	H	N	S
6	542.01 g	81	3.11	46.63 (45.90)	5.14 (5.01)	5.44 (5.12)	24.86 (23.84)
7	571.01 g	82.5	3.08	48.62 (47.50)	5.89 (5.01)	5.16 (4.99)	23.57 (22.85)
8	571.01 g	75	3.19	50.09 (49.51)	6.26 (5.11)	4.90 (4.12)	22.41 (21.55)
9	571.01 g	78	3.18	50.09 (49.25)	6.26 (5.88)	4.90 (4.01)	22.41 (21.85)
10	599.01	80	3.05	52.08 (51.45)	6.67 (5.98)	4.67 (4.12)	21.36 (20.85)

Table 2. Infrared and electronic spectral data of the adducts of Bis(*O*-butyldithiocarbonato) nickel(II) with substituted pyridines

Complex No.	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
6	1279	1125	1035	15313	20080	27548
7	1268	1152	1044	15196	20876	26954
8	1280	1195	1055	15288	20790	27397
9	1275	1176	1063	14970	20878	26143
10	1255	1184	1059	14727	20618	26702

analyzer, CHNS-932, LECO corporation, USA. Molar conductance of the adducts was determined on the millimolar solution in Dimethylformamide by using Digital conductivity meter “Century CC 601”. Infrared spectra of the complexes over the region 4000–200 cm⁻¹ were recorded using KBr pellets on the Infrared spectrophotometer (Perkin Elmer FT-IR spectrometer). The electronic spectra of the adducts were recorded in DMF on Systronics 119 UV-Visible spectrophotometer. Magnetic moments were determined at the room temperature by VSM method (Princeton Applied Research-Model No. 155). The analytical data, molar conductance and magnetic moments of the adducts isolated are presented 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*-butyldithiocarbonato)bis(3,5-dimethylpyridine)nickel(II) (Fig. 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 CrysAlis^{RED}.¹¹ The final refinement cycles converged to an $R = 0.0379$ and $wR(F^2) = 0.0890$ for observed data. The residual electron densities ranged from $-0.324 < \Delta\rho < 0.641 \text{ e\AA}^{-3}$. The structure was solved by SHELXS97¹² and refined with SHELXL97.¹² 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 $1.5U_{\text{eq}}(\text{methyl C})$.

**Fig. 1.** Chemical structure of Bis(*O*-butyldithiocarbonato)bis(3,5-dimethylpyridine)nickel(II) (9)

2. 2. Synthesis of the Title Complex

2. 2. 1. Preparation of Potassium Butyldithiocarbonate

The potassium salt of *O*-butyldithiocarbonate was prepared by the standard published method.¹³ Into a 500 ml round bottomed flask, fitted with a reflux condenser, 4.2 g (0.075 mol) of potassium hydroxide pellets were placed and 19.271g (23.472 ml, 0.26 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, 5.7 g (4.5 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*-butyldithiocarbonate was dried in a vacuum desiccator over anhydrous calcium chloride.

2. 2. 2. Preparation of Bis(*O*-butyldithiocarbonato)nickel(II)

The saturated aqueous solutions of NiCl₂ · 6H₂O (2.37g, 0.01 mol) and potassium *O*-butyldithiocarbonate (3.7 g, 0.02 mol) were prepared separately and then mixed with constant stirring. Dark green precipitates were formed which were filtered immediately and were dried in a vacuum desiccator over anhydrous calcium chloride. The composition of the complex was established to be [Ni(S₂COC₄H₉)₂] by the elemental analysis. Found (Calc.) C = 33.25(33.56), H = 4.89(4.99), S = 35.52 (35.95), Ni = 15.63(16.45).

2. 2. 3. Preparation of Adducts of Bis(*O*-butyldithiocarbonato)nickel(II) with Substituted Pyridines

The 1:2 adducts of bis(dithiocarbonato)nickel(II) with substituted pyridines were prepared by stirring bis(*O*-butyldithiocarbonato)nickel(II) (0.92 g, 0.0026

mol) in about 70 ml of acetone for about 20 minutes followed by the addition of substituted pyridine [3-methylpyridine (1) = 0.484 g, 2,4-dimethylpyridine (2) = 0.557g, 3,4-dimethylpyridine (3) = 0.557g, 3,5-dimethylpyridine (4) = 0.557 g and 2,4,6-trimethylpyridine (5) = 0.630 g (0.0052 mol)] and mixture was again stirred for 20 minutes. The contents of the reaction mixture were then filtered and allowed to stand for 20–24 hours, depositing shining green crystalline solids which were then washed with the solvent used in their preparation and dried over calcium chloride at room temperature. The adducts thus obtained were recrystallised from acetone.

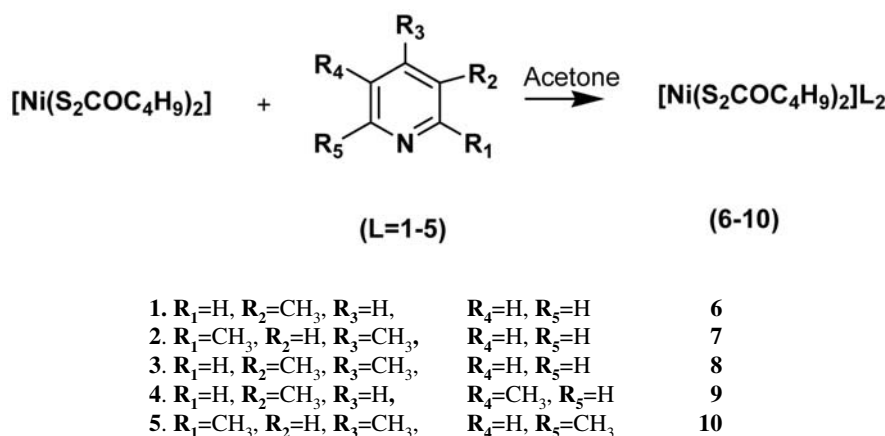
3. Results and Discussion

3. 1. Preliminary Investigations

The adducts of Bis(*O*-butyldithiocarbonato)nickel(II) with substituted pyridines are all microcrystalline shining green solids and are soluble in common organic solvents like acetone, chloroform, dimethylformamide and dimethylsulphoxide but insoluble in benzene, carbon tetrachloride, nitrobenzene and water. The analytical result of the adducts isolated suggests that they have the stoichiometry 1:2 and may be assigned the formula Ni(S₂COC₄H₉)₂(C₆H₇N)₂ (6), Ni(S₂COC₄H₉)₂(C₇H₉N)₂ (7), Ni(S₂COC₄H₉)₂(C₇H₉N)₂ (8), Ni(S₂COC₄H₉)₂(C₇H₉N)₂ (9), Ni(S₂COC₄H₉)₂(C₈H₁₁N)₂ (10).

3. 2. Conductance and Magnetic Measurements

The molar conductance measurements of the millimolar solutions of the adducts under study were carried out in dimethylformamide. The molar conductivity values are in the range of 22.51–68.33 ohm⁻¹ mol⁻¹ cm² suggesting that these complexes are neutral and non-ionic in nature.^{14–15} The magnetic moment values of the adducts come in the range of 2.86–3.19 B.M which is in agreement with the magnetic moment values observed for the octahedral complexes of nickel.^{16–17}



Scheme 1

3. 3. IR Spectra

A comparison of the infrared spectra of prepared adducts with that of the free ligands reveals that most of the bands of free ligands are shifted from their respective positions. The C–H out of plane deformation bands in the free methylpyridine and dimethylpyridine molecule shows red shifts while all other modes specially the bands arising due to C...C and C...N ring stretching modes, in plane and out of plane ring deformation in the free methylpyridine and dimethylpyridine show blue shift in the adducts indicating that these secondary ligands are coordinated to metal ion through nitrogen atom.

3. 4. Electronic Spectra

The electronic spectra of 1:2 adducts of Bis(*O*-butyldithiocarbonato)nickel(II) have been recorded in DMF and shows three bands in the range 11000–15408 cm^{-1} , 19000–22858 cm^{-1} and 26143–27548 cm^{-1} , which are assigned to: ${}^3A_{2g} \rightarrow {}^3T_{2g}(\text{F})(\nu_1)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})(\nu_2)$ and ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})(\nu_3)$ transitions respectively. These three broad bands along with shoulders show that adducts have trans octahedral geometry around nickel (II) ion.¹⁸

3. 5. X-ray Crystallographic Studies of bis(*O*-butyldithiocarbonato)bis(3,5-dimethylpyridine) Nickel(II) [Complex 9]

The crystallography data for bis(*O*-butyldithiocarbonato)bis(3,5-dimethylpyridine) nickel(II) are presented in Table 3. Selected bond distances and bond angles for non-hydrogen atoms are listed in Table 4. A general view of the molecule indicating atom numbering scheme is shown in Fig. 2. *Ortep-3* software¹⁹ was used for making the thermal ellipsoids. The geometry of the molecule was calculated using *PLATON*²⁰ and *PARST*²¹ software.

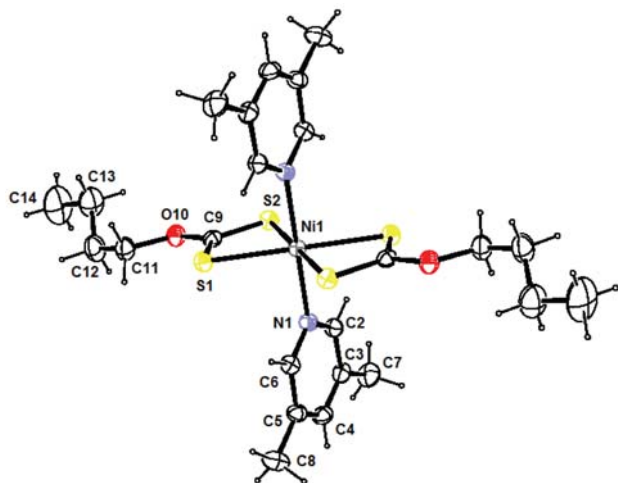


Fig. 2. ORTEP view of the molecule with displacement ellipsoids drawn at 50% probability level. H atoms are shown as small spheres of arbitrary radii

Table 3. Crystal and experimental data

Empirical formula	$\text{C}_{24}\text{H}_{36}\text{N}_2\text{NiO}_2\text{S}_4$
Formula weight	571.50
Temperature	293(2)K
Wavelength	0.71073 Å
Unit cell dimensions	
a, Å	8.9819(2)
b, Å	18.0977(5)
c, Å	9.2871(2)
α , °	90.00
β , °	104.032(3)
γ , °	90.00
Z	2
Space Group	$P2_1/c$
Calculated density, g/cm^{-3}	1.296
Absorption coeff., mm^{-1}	0.970
F(000)	604
Crystal size mm	0.30 × 0.20 × 0.20
Color	Green
Theta range for entire data collection	3.62 – 24.99 deg
Limiting indices	–11 ≤ h ≤ 11, –22 ≤ k ≤ 22, –11 ≤ l ≤ 11
Refinement method	Full matrix least squares on F^2
Reflections collected	25017
Used in refinement	2460
Parameters	154
Goodness-of-fit on F^2	1.075
R indices	$R_1 = 0.0379$, $wR_1 = 0.0890$
Largest diff. peak and hole	0.57 and –0.27 $\text{e} \text{ \AA}^{-3}$

CCDC 866871 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via 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. Selected bond lengths (Å) and bond angles (°) for non-hydrogen atoms (e.s.d's in parenthesis)

Bond lengths (in Å)			
Ni1-N1	2.117(2)	Ni1-S1	2.4537(6)
Ni1-S2	2.4578(7)	S1-C9	1.682(3)
S2-C9	1.688(3)	C3-C7	1.504(4)
C5-C8	1.506(4)	C9-O10	1.332(3)
O10-C11	1.458(4)		
Bond angles (°)			
N1-Ni1-S1	89.85(6)	S1-Ni1-S2	73.30(2)
N1-Ni1-S2	90.07(6)	C2-N1-Ni1	120.64(17)
C6-N1-Ni1	121.74(17)	C9-S1-Ni1	83.00(9)
C9-S2-Ni1	82.75(9)	C4-C3-C7	122.2(3)
C2-C3-C7	121.0(3)	C4-C5-C8	122.1(3)
C6-C5-C8	120.8(3)	O10-C9-S1	116.53(19)
O10-C9-S2	122.6(2)	S1-C9-S2	120.89(15)

The asymmetric unit cell comprises of half molecule. The nickel (II) cation lies on an inversion centre. The Ni1-N1 bond length is 2.117(2) Å while the Ni1-S1 and

Ni1-S2 bond lengths are 2.4537(6) and 2.4578(7) Å, respectively. The bond angles in the pyridine ring vary from 116.8(3)° to 123.8(2)°, the average value being 119.98(3)°. The six bond lengths in the pyridine ring lie in the range 1.333(3)–1.389(4) Å; the average value being 1.367(3) Å. All these values are in agreement with some reported structures.^{22–24} The two sulphur-carbon distances C9-S1 [1.688(3)Å] and C9-S2 [1.682(3)Å] have almost identical values, since the nature of the double bond inside the four atom moiety is resonating. The dihedral angle between the plane consisting of four atoms (Ni1, S1, C9, S2) and the pyridine ring is 88.91(7)° meaning thereby that both these units are held almost perpendicular to each other.

The packing arrangement of molecules viewed down c-axis is shown in Fig.3. Molecules are arranged in a manner to form layers which adopt a zig-zag configuration. This observation is in agreement with the findings obtained in case of similar molecules, viz. bis(O-ethylthiocarbonato-k²S,S¹)bis(pyridine-3-carbonitrile-kN¹)nickel(II) and bis(O-ethyl dithiocarbonato)bis(4-ethylpyridine)nickel(II).^{24–25} The overlap of six-membered pyridine rings results into the formation of π - π interactions in the crystal structure. The molecular packing is stabilized by C-H... π and π - π interactions. The geometry of π - π C-H... π interactions is represented in Table 5 and Table 6 respectively.

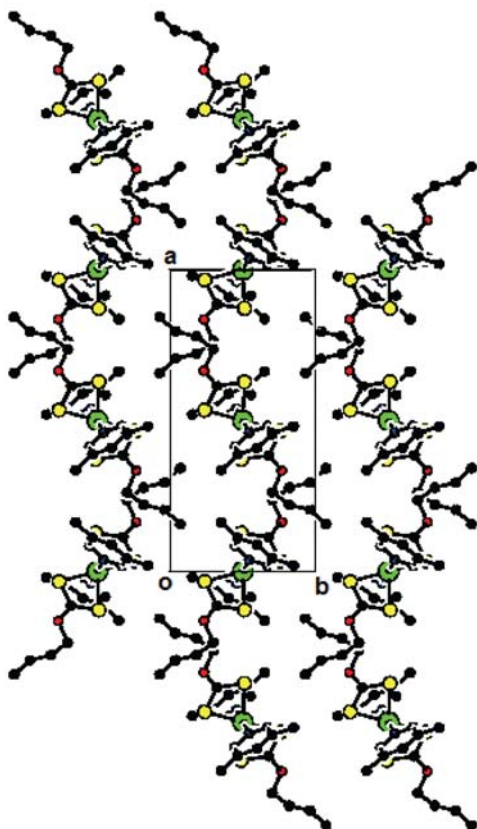


Fig. 3. Packing diagram viewed down c-axis

Table 5. The Geometry of π - π interactions. Cg1 represents the centre of gravity of pyridine ring.

CgI...CgJ	CgI...CgJ (Å)	CgI...P (Å)	α (°)	Δ (Å)
Cg1 - Cg1 ⁽ⁱ⁾	3.855(2)	3.487	0.00	1.64

Symmetry code: (i) 1-x, -y, 1-z

Table 6. The Geometry of C-H... π interactions. Cg1 represents the centre of gravity of the pyridine ring.

D-H...A	D-H(Å)	D...A(Å)	H...A(Å)	D-H...A(Å)
C11-H11A...Cg1 ⁱ	0.9700	3.825(3)	3.2579	119.13
C12-H12B...Cg1 ⁱ	0.9700	3.831(4)	3.1489	128.70

Symmetry code (i) 1-x, 1/2+y, 1/2-z (ii) x, 1/2-y, 1/2+z

4. Acknowledgements

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5. Supplementary Material

CCDC no. 866871 contain the supplementary crystallographic data for the compound Bis(O-butylthiocarbonato)bis(3,5-dimethylpyridine)nickel(II). The data can be obtained free of charge via 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) 1223-33603

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Povzetek

Avtorji v prispevku poročajo o sintezi kompleksov Ni(II) z mešanimi ligandi, z *O*-butilditiokarbonatom kot primarnim ligandom in substituiranimi piridini kot sekundarnimi ligandi. Komplekse so karakterizirali s kemijsko analizo, ter meritvami molske prevodnosti, magnetne susceptibilnosti, elektronske in infrardeče spektroskopije. Na osnovi spektroskopskih študij so ugotovili, da je nikeljev ion oktaedrično koordiniran in da so *O*-butilditiokarbonatni ligandi dvovezni, ostali ligandi pa enovezni. Z rentgensko strukturno analizo smo okarakterizirali enega od aduktov, bis(*O*-butilditiokarbonato) bis(3,5-dimetilpiridin)Ni(II). Adukt je monoklinski, prostorska skupina je P21/c. Nikeljev ion je oktaedrično koordiniran z dvema kelatnima ditiokarbonatnima anionoma in dvema 3,5-dimetilpiridinskima ligandoma z nikeljevim ionom kot inverznim centrom. Plasti molekul so povezane s šibkimi interakcijami π - π in C-H... π .