## ORIGINAL PAPER

# Synthesis and Characterization of the Adducts of Bis(*O*-amyldithiocarbonato)nickel(II) with Nitrogen Donors and X-ray Structure of Bis(*O*-amyldithiocarbonato)bis (3,5-dimethylpyridine)nickel(II)

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Abstract A series of complexes with general formula  $M(Xan)_2L_2$  (M = Ni(II), Xan = O-amyldithiocarbonato, L = 3-methylpyridine, 2,4-; 3,4-; 3,5-dimethylpyridines and 2,4,6-trimethylpyridine) have been synthesized and characterized by elemental analysis and various physico-chemical techniques such as magnetic susceptibility measurements, conductivity measurements, UV-Visible, Infrared spectral data. On the basis of electronic spectra and magnetic susceptibility measurements, an octahedral geometry has been proposed for all the complexes. IR spectral data shows that the substituted pyridines in all these complexes coordinate to the metal ion through nitrogen atoms occupying fifth and sixth axial positions where as O-alkyldithiocarbonate act as monoanion bidentate ligand and occupy the planar positions of octahedral structures. The X-ray diffraction analysis of one of the adducts bis(O-amyldithiocarbonato)bis(3,5-dimethylpyridine)nickel(II) is also investigated. The complex crystallizes in the monoclinic space group P21/c with unit cell parameters a = 9.167(2) Å, b = 18.255(4) Å, c =9.299(2) Å and  $\beta = 103.47(2)^{\circ}$ . The dihedral angle between dithio-groups and the pyridine ring is 88.9(1)°. The crystal structure of the molecule is stabilized by  $\pi - \pi$  interactions.

**Keywords** X-ray structure  $\cdot$  Metal–organic  $\cdot \pi - \pi$ interaction  $\cdot$  Packing interactions  $\cdot$  Single crystal

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## Introduction

Dithioacid ligands,  $X-CS_2^-$  (X = OR), have a rich coordination and organometallic chemistry [1, 2]. These ligands are obtained easily by the addition of the nucleophiles RO<sup>-</sup> to carbon disulfide [3-5]. Dithioacid ligands and their metal complexes have received considerable attention due to their interesting structural and chemical properties as well as their wide range of application in biological systems [6, 7]. They have been generally prepared by metatheses reactions of transition metal halides with the free ligands. In most cases the ligand is bonded to the metal in a chelate fashion through the two S-atoms. However, several complexes in which the mode of coordination of the dithioacid ligands is monodentate have been obtained and characterized [8, 9]. These O-alkyldithiocarbonates (dithioacid ligands) are used on a large scale as collectors in flotation processes in metal recovery, have been investigated as adsorbents on coinage metals [10, 11] and are known to form very strong bonds with metals. Recently some cyclic dithiocarbonates as a new class of in situ gelling biomaterials is reported. Cyclic dithiocarbonates with degradable ester linkages have been synthesized and characterized [12]. In this paper we report the synthesis and characterization of the adducts of bis(O-amyldithiocarbonato)nickel(II) with substituted pyridines. The X-ray structure of bis(O-amyldithiocarbonato)bis(3,5-dimethylpyridine)nickel(II) is also being reported.

## Experimental

Preparation of Potassium Amyldithiocarbonate

Into a 500 ml round bottomed flask, fitted with a reflux condenser, 4.2 g (0.075 mol) of potassium hydroxide

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pellets were placed and 19.271 g (23.472 ml, 0.26 mol) of n-amyl alcohol was added. The reaction mixture was heated under reflux for 1 h. The contents were then cooled and liquid from reaction mixture was decanted off into another dry 500 ml flask. To this flask, was added 5.7 g (4.5 ml, 0.075 mol) of carbon disulphide slowly with constant stirring. The contents of the flask were filtered (after cooling in ice) on a sintered glass funnel at the pump and washed with three 2.5 ml portions of ether. The resulting product potassium *O*-amyldithiocarbonate was dried in a vacuum desiccator over anhydrous calcium chloride.

Preparation of Bis(O-amyldithiocarbonato)nickel(II)

The saturated aqueous solutions of NiCl<sub>2</sub>·6H<sub>2</sub>O (2.37 g, 0.01 mol) and potassium *O*-amyldithiocarbonate (4.04 g, 0.02 mol) were prepared separately and then mixed with constant stirring. Dark green precipitates were formed which were filtered immediately and dried in a vacuum desiccator over anhydrous calcium chloride. The composition of the complex was established to be [Ni(S<sub>2</sub>. COC<sub>5</sub>H<sub>11</sub>)<sub>2</sub>] by the elemental analysis. Found (Calc.) C = 36.11 (37.43), H = 5.01 (5.71), S = 32.98 (33.27), Ni = 14.50 (15.25).

Preparation of Adducts of Bis (*O*-amyldithiocarbonato)nickel(II) with Substituted Pyridines

The 1:2 adducts of bis(*O*-amyldithiocarbonato)nickel(II) with substituted pyridines were prepared by stirring  $[Ni(S_2COC_5H_{11})_2]$  (1 g, 0.0026 mol) in about 70 ml of acetone for about 20 min followed by the addition of substituted pyridine [3-methylpyridine = 0.480 g, 2,4-dimethylpyridine = 0.567 g, 3,4-dimethylpyridine = 0.567 g, 3, 5-dimethylpyridine = 0.567 g and 2,4,6-trimethylpyridine = 0.63 g (0.0052 mol)] and mixture was again stirred for 20 min. The contents of the reaction mixture were then filtered and allowed to stand for 20–24 h, depositing shining green crystalline solids which were then washed with the solvent used in their preparation and dried over calcium chloride at room temperature.

## X-ray Structure Determination

Detailed structural information on the conformation of the molecule in the crystalline state was obtained by employing X-ray crystallographic techniques. A dark green blocked-shaped single crystal of the title compound measuring  $0.30 \times 0.20 \times 0.20$  mm was picked up for X-ray intensity data collection on a CCD area-detector diffractometer (X'calibur system—Oxford diffraction make, UK)

which is equipped with graphite monochromated MoK<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å). A total number 32,738 of reflections were collected of which 2,278 reflections were treated as observed [I >  $2\sigma$ (I)]. Data were corrected for Lorentz and polarization and absorption factors. The structure was solved by direct methods using SHELXS97 and refined by SHELXL97 [13]. All the hydrogen atoms were located from a difference electron density map and their positional and isotropic thermal parameters were included in the refinement. The final refinement cycle yielded an R-factor of 0.0420 and wR (F<sup>2</sup>) = 0.1049 for the observed data. The residual electron density ranges from  $-0.466 < \Delta \rho < 0.676$  eÅ<sup>-3</sup>. The CIF for this structure has been deposited at Cambridge Crystal Data Centre (CCDC 875502).

## Methods

Carbon, hydrogen, nitrogen and sulphur contents of the addition complexes were determined on Elemental 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  $4,000-200 \text{ cm}^{-1}$  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.

### **Results and Discussion**

The adducts of bis(*O*-amyldithiocarbonato)nickel(II) with substituted pyridines are all microcrystalline green solids and are soluble in common organic solvents like acetone, chloroform, dimethylformamide and dimethylsulphoxide but insoluble in benzene, carbontetrachloride, nitrobenzene and water. The analytical results of the adducts isolated suggest that they have the stoichiometry 1:2 and may be assigned the formula Ni(S<sub>2</sub>COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>L<sub>2</sub> (where L = 3-methylpyridine, 2,4-; 3,4-; 3,5-dimethylpyridines and 2,4,6-trimethylpyridine). 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  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup> suggesting that these

Table 1 Physical and analytical data of the adducts of bis(O-amyldithiocarbonato)nickel(II) with substituted pyridines

Adduct	Formula	% Found			% Calculated				Molar	$\mu_{\rm eff}$			
		С	Н	Ν	S	Ni	С	Н	Ν	S	Ni	conductance $(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	(BM)
Bis(O-amyldithiocarbonato)bis (3-methylpyridine)nickel(II)	$C_{23}H_{36}O_2S_4Ni$	50.44	6.30	4.90	22.42	10.28	49.65	5.98	4.50	21.98	9.71	44.98	3.09
Bis(O-amyldithiocarbonato)bis (2,4-imethylpyridine)nickel(II)	$C_{25}H_{40}O_2S_4Ni$	52.08	6.67	4.69	21.37	9.79	51.67	6.11	4.02	20.18	9.10	24.22	3.11
Bis(O-amyldithiocarbonato)bis (3,4-imethylpyridine)nickel(II)	$C_{25}H_{40}O_2S_4Ni$	52.08	6.67	4.69	21.37	9.79	51.25	6.21	4.01	20.85	8.99	22.51	3.22
Bis(O-amyldithiocarbonato)bis (3,5-imethylpyridine)nickel(II)	$C_{25}H_{40}O_2S_4Ni$	52.08	6.67	4.69	21.37	9.79	51.25	6.01	4.33	20.85	9.01	39.79	3.12
Bis( <i>O</i> -amyldithiocarbonato)bis (2,4,6-trimethylpyridine)nickel(II)	$C_{25}H_{44}O_2S_4Ni$	51.67	7.01	4.46	20.41	9.36	51.45	5.98	4.12	20.85	8.81	68.33	3.06

Table 2 Infrared and electronic spectral data of the adducts of bis(O-amyldithiocarbonato)nickel(II) with substituted pyridines

Name of adducts	Formula	IR spectral data (cm <sup>-1</sup> )			Electronic spectral data (cm <sup>-1</sup> )		
		$v_{as}(C-O-C)$	v <sub>s</sub> (C– O–C)	v(C–S)	<i>v</i> <sub>1</sub>	<i>v</i> <sub>2</sub>	v <sub>3</sub>
Bis(O-amyldithiocarbonato)bis (3-methylpyridine)nickel(II)	Ni(S <sub>2</sub> COC <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>7</sub> N) <sub>2</sub>	1,258	1,143	1,035	15,408	22,321	27,472
Bis(O-amyldithiocarbonato)is (2,4-dimethylpyridine)nickel(II)	$Ni(S_2COC_5H_{11})_2(C_7H_9N)_2$	1,260	1,155	1,026	15,313	20,920	29,411
Bis(O-amyldithiocarbonato)bis (3,4-dimethylpyridine)nickel(II)	$Ni(S_2COC_5H_{11})_2(C_7H_9N)_2$	1,245	1,135	1,085	15,037	21,052	27,932
Bis( <i>O</i> -amyldithiocarbonato)bis (3,5-dimethylpyridine)nickel(II)	$Ni(S_2COC_5H_{11})_2(C_7H_9N)_2$	1,254	1,186	1,025	14,925	21,085	27,624
Bis( <i>O</i> -amyldithiocarbonato)bis (2,4,6-trimethylpyridine)nickel(II)	$Ni(S_2COC_5H_{11})_2(C_8H_{11}N)_2$	1,233	1,143	1,094	14,892	21,231	26,954

complexes are neutral and non-ionic in character [14, 15]. The magnetic moment values of 1:2 adducts of bis(Oamyldithiocarbonato)nickel(II) with nitrogen donors come in the range of 3.06-3.22 BM which is in agreement with the magnetic moment values observed for the octahedral complexes of nickel [16, 17]. 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 substituted pyridines are coordinated to metal ion through nitrogen atom. The electronic spectra of 1:2 adducts of bis(O-amyldithiocarbonato)nickel(II) have been recorded in DMF and shows three bands in the range 11,000-15,408, 19,000-22,321 and 26,954-29,411 cm<sup>-1</sup>, which are assigned to  ${}^{:3}A_{2g} \rightarrow {}^{3}T_{2g}(F) (v_1), {}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F) (v_2) \text{ and } {}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P) (v_3) \text{ transitions respectively. These bands are characteristic of nickel(II) complexes in octahedral environment [18].$ 

### X-ray Crystallographic Studies

The crystallography data for bis(*O*-amyldithiocarbonato)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. 1. *Ortep-3* software [19] was used for making the thermal ellipsoids. The geometry of the molecule was calculated using *PLATON* [20] and PARST [21] software.

The asymmetric unit comprises of half molecule and nickel(II) cation lies on an inversion centre. The Ni1–N4 bond length is 2.121(2) Å. The bond angles in the pyridine ring vary from  $115.1(5)^{\circ}$  to  $124.3(6)^{\circ}$ , the average value

<b>Table 3</b> Crystal and experimental dat	Table 3	Crystal	and	experimental	data
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CCDC no crystal size	875502	atoms (e.s.d's in parenthesis)			
Crystal description	Block shaped, green	Bond lengths (Å)			
Empirical formula	$C_{26}H_{40}N_2NiO_2S_4$	Ni–N4			
Formula weight	599.55	Ni1-S3			
Melting point	95 °C	S3-C12			
Measurement	X'Calibur System (now varian)	O13–C14			
Radiation, wavelength	MoK., 0.71073 Å	Ni1–S2			
Unit cell dimensions	a = 9.167(2) Å, $b = 18.255(4)$ Å,	S2-C12			
	c = 9.299(2)  Å	C12–O13			
	$\beta = 103.47(2)^{\circ}$	Bond angles (°)			
Crystal system	Monoclinic	N4-Ni1-S2			
Space group	P2 <sub>1</sub> /c	S2-Ni1-S3			
Unit cell volume	1513.55(6) Å <sup>3</sup>	C12-S3-Ni1			
Density (calculated)	1.316 g/m <sup>3</sup>	C5–N4–Ni1			
Temperature	293(2) K	O13-C12-S2			
Absorption coefficient	$0.942 \text{ mm}^{-1}$	C12-O13-C14			
F (000)	636	S2-C12-S3			
Scan mode	$\omega$ scan	C12-S2-Ni1			
$\theta$ range for entire data	$3.56^\circ < \theta < 28.99^\circ$	C5-N4-C9			
collection		C9–N4–Ni1			
Range of indices	-10 < h < 10, -21 < k < 21,	O13-C12-S3			
Deflections collected/	-11 < 1 < 11	O13-C14-C15			
unique	52,738/2,027				
R <sub>int</sub>	0.0414	avaated it is avident from			
R <sub>sigma</sub>	0.0172	lation of the puriding ring th			
Structure determination	Direct methods	and C11 stoms from the pl			
Refinement	Full Matrix Least Squares on F <sup>2</sup>	nificant As a consequence			
Weighing scheme	$[I/\sigma^2 (Fo^2) + (0.0497P)^2 + 1.5725P]$ where P = $(Fo^2 + 2Fc^2)/3$	carbon atom, the O13–( [1.326(2) Å] shorter than th			
No. of parameters refined	163	The short value of bond dista			
Final R	0.0420	with a significant contribution			
wR $(F^2)$	0.1049	xanthate anion that features			
Goodness-of-fit	1.096	charge on each of S atom [2			
$(\Delta/\sigma)_{\rm max}$	$-0.001$ for $\times$ S1	The packing of the mo			
Final residual electron density	$-0.466 < \Delta \rho < 0.676 \text{ Å}^{-3}$	shown in Fig. 2. Molecules the form of layers and with			

being  $120(2)^{\circ}$ . The Ni–S bond lengths involving the xanthate ligands are 2.455(8) Å for Ni1–S1 and 2.459(8) Å for Ni1–S2 and these values of bond angles and bond distances are in good agreement with those reported for other analogous Ni-dithiocarbonato complexes [22–24]. The C–S bond lengths involving the xanthate ligands are: S2– C12 = 1.679(3) and S3–C12 = 1.686(3) Å. These values show double bond character due to the delocalization over the two C–S bonds [25]. The dihedral angle between dithio-groups and the pyridine ring is 88.9(1)°. As

**Table 4** Bond lengths (Å) and bond angles (°) for nonhydrogen atoms (e.s.d's in parenthesis)

Bond lengths (Å)	
Ni–N4	2.121(2)
Ni1–S3	2.459(8)
S3-C12	1.686(3)
O13–C14	1.459(4)
Ni1–S2	2.455(8)
S2-C12	1.679(3)
C12–O13	1.335(4)
Bond angles (°)	
N4-Ni1-S2	90.34(7)
S2-Ni1-S3	73.23(3)
C12–S3–Ni1	82.62(11)
C5–N4–Ni1	120.6(2)
O13-C12-S2	116.4(2)
C12-O13-C14	119.6(3)
S2-C12-S3	121.21(18)
C12–S2–Ni1	82.90(1)
C5-N4-C9	117.5(3)
C9–N4–Ni1	121.9(2)
O13-C12-S3	122.4(2)
O13-C14-C15	108.7(3)

expected, it is evident from the least-squares plane calculation of the pyridine ring that the atomic deviation of C10 and C11 atoms from the plane of pyridine ring is not significant. As a consequence of the hybridization of the carbon atom, the O13–C12 bond has a distance [1.326(2) Å] shorter than that of O13–C14 [1.460(2) Å]. The short value of bond distance for O13–C12 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 [26].

The packing of the molecule within the unit cell is shown in Fig. 2. Molecules in the unit cell are arranged in the form of layers and within the layers the molecules are parallel to each other. The crystal structure of the molecule is stabilized by  $\pi$ - $\pi$  interaction existing between pyridine rings of one molecule with the pyridine ring of symmetry related molecule (values are given in the table below).

Geometry of  $\pi$ - $\pi$  Interaction

CgI–Cg(J)	CgI…CgJ (Å)	CgI…P (Å)	α (°)	β (°)	$\Delta$ (Å)
$Cg(3)$ – $Cg(3)^i$	3.869(2)	3.509	0.00	24.92	1.62

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

Fig. 1 ORTEP view of the molecule with displacement ellipsoids drawn at 50 % probability level. H atoms are shown as *small spheres* of arbitrary radii







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