



CRYSTAL STRUCTURE OF BIS(O-AMYLDITHIOCARBONATO)BIS(3-BROMOPYRIDINE)NICKEL(II)

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The complex crystallizes in orthorhombic crystal system with space group *Pbca*. The unit cell parameters are: $a=12.346(15)$ Å, $b=9.0931(9)$ Å, $c=25.136(5)$ Å, $Z=4$. The asymmetric unit comprises of half molecule with nickel(II) cation lies on an inversion centre. The Ni(II) atom is coordinated in a distorted octahedral arrangement. The variation in C–S bond lengths involving the xanthate ligands indicates the presence of double bond character due to delocalization over the two C–S bonds. The crystal structure was refined to a final reliability index (R-value) of 0.0594 for 1714 observed reflections. The amyl chain attached to the dithiocarbonato group contains disorder over two sets of sites with occupancy ratios of 0.683: 0.317. The crystal structure is stabilized by weak C–H... π interactions.

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3-bromopyridine (0.82 g, 0.0052 mol) was added. The mixture was stirred for two to three hours and kept undisturbed for one to two days when dark green colored micro-crystals of the adduct were obtained. The product so obtained was filtered and dried in vacuum desiccator over anhydrous calcium chloride. Chemical structure of the complex is shown in Figure 1.

Introduction

Dithiocarbonates are sulfur and oxygen containing ligands which can form complexes with various transition metals through the mechanism of coordinated complex formation. Transition metal dithiolate complexes exhibited versatile and interesting chemistry that have been studied extensively during the last decades.¹ Xanthates can form bidentate, monodentate, or network solids, showing a wide range of coordination behaviour.²⁻⁵ Metal xanthates are extensively used as corrosion inhibitors⁶ and agricultural reagents.^{7,8} Dithiocarbonates have also found important use in medicine as antitumor agents^{9,10} and for treating Alzheimer's disease.¹¹ Nickel thiolate complexes have received special attention in recent years because sulfur-ligated nickel complexes mimic the [Fe–Ni] hydrogenase active site and dimeric metal complexes based on nickel thiolate hydrides have been shown to be catalytically active for proton reduction.¹²

Experimental

Synthesis

Bis(O-amyldithiocarbonato)nickel(II) required for preparation of the adduct was obtained by mixing aqueous solutions of potassium salt of O-amyldithiocarbonate (4.04 g, 0.02 mol) and NiCl₂·6H₂O (2.37 g, 0.01 mol). The precipitates of bis(O-amyldithiocarbonato)nickel(II) were formed which were filtered immediately and dried in vacuum desiccators. Bis(O-amyldithiocarbonato)nickel(II) (1 g, 0.0026 mol) was then dissolved in acetone (60 ml) and stirred for about 10-20 minutes. To the resulting solution,

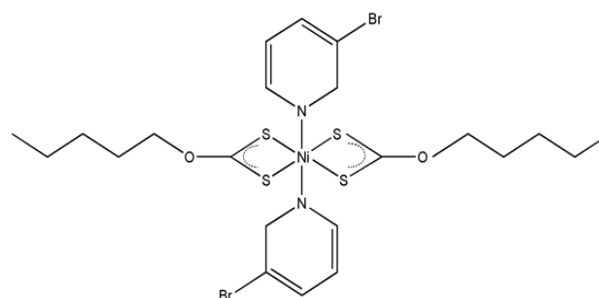


Figure 1. Chemical structure of bis(O-amyldithiocarbonato)bis(3-bromopyridine)nickel(II)

Crystal structure determination and refinement

A green block shaped single crystal having good morphology (0.3 x 0.2 x 0.1 mm) was chosen for three-dimensional X-ray intensity data collection using X'calibur CCD area-detector diffractometer equipped with graphite monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å). The crystal selection was made by Leica polarizing microscope. The diffractometer provides reflections of a large number of individual planes and their corresponding intensities were recorded electronically with the help of a CCD camera. The unit cell dimensions were determined by least squares fit of angular settings of 1597 reflections in the θ range 3.99 to 27.85°. A total of 7072 reflections were recorded for θ ranging from 3.64 to 25.98° and out of these reflections, 2754 were found unique. 1714 reflections were treated as observed ($-15 \leq h \leq 14$, $-11 \leq k \leq 10$, $-15 \leq l \leq 31$) using ($I > 2\sigma(I)$) as criterion. Data were corrected for Lorentz-polarization, extinction and multi-scan absorption corrections.

The structure was solved by direct methods using SHELXS97.¹³ All non-hydrogen atoms of the molecule were located from the E-map. Full-matrix least-squares refinement was carried out by using SHELXL97 software.¹³ The geometry of the molecule is determined by PLATON.¹⁴ All H atoms were positioned geometrically and were treated as riding on their parent C atoms, with C-H distances of 0.93–0.97 Å; with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, except for the methyl group where $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. The final refinement cycles yielded an *R*-factor of 0.0594 ($wR(F^2) = 0.1195$) for the observed data. The residual electron density ranges from -0.62 to 0.59 eÅ⁻³.

Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). The crystallographic data are summarized in Table 1. CCDC – 1061096 contains the supplementary crystallographic data for this paper.

Table 1: Crystal data and other experimental details

CCDC Number	1061096
Crystal description	Block
Crystal size	0.30 x 0.20 x 0.10 mm
Empirical formula	C ₂₂ H ₃₀ Br ₂ N ₂ NiO ₂ S ₄
Formula weight	701.25
Radiation, Wavelength	Mo K α , 0.71073 Å
Unit cell dimensions	$a = 12.346(15)$ Å, $b = 9.0931(9)$ Å, $c = 25.136(5)$ Å, $\alpha = \beta = \gamma = 90^\circ$
Crystal system, Space group	Orthorhombic, Pbca
Unit cell volume	2821.9(7)Å ³
No. of molecules per unit cell, Z	4
Absorption coefficient	3.838 mm ⁻¹
<i>F</i> (000)	1416
θ range for entire data collection	3.99 < θ < 27.85 °
Reflections collected / unique	7072 / 2754
Reflections observed $I > 2\sigma(I)$	1714
Range of indices	$h = -15$ to 14, $k = -11$ to 10, $l = -15$ to 31
No. of parameters refined	158
Final R-factor	0.0594
$wR(F^2)$	0.1195
<i>R</i> _{int}	0.0496
<i>R</i> _{sigma}	0.0753
Goodness-of-fit	1.096
(Δ/σ) _{max}	0.001
Final residual electron density	-0.62 < $\Delta\rho$ < 0.59 e Å ⁻³

Results and discussion

The X-ray crystal structure analysis reveals that the Ni atom lies on a crystallographic center of symmetry and has octahedral coordination geometry. An ORTEP¹⁵ view of the molecule with atomic labeling is shown in Figure 2. Its geometry was calculated using the PLATON¹⁴ and PARST¹⁶ software. The Ni atom is six-coordinated by the tertiary N donor atom of two bromopyridine molecules (situated axially intranspositions, N-Ni-N=180°) and four S atoms of two coordinated dithiocarbonato ligands which are situated

in the equatorial plane. The Ni atom is located on a centre of inversion. The Ni-S bond lengths involving the xanthates ligands are 2.4484(16) Å for Ni-S1 and 2.4418(18) Å for Ni-S2 and these values of bond distances are in good agreement with those reported for other analogous Ni-dithiocarbonato complexes.^{17–19} Selected bond lengths and bond angles are given in Table 2.

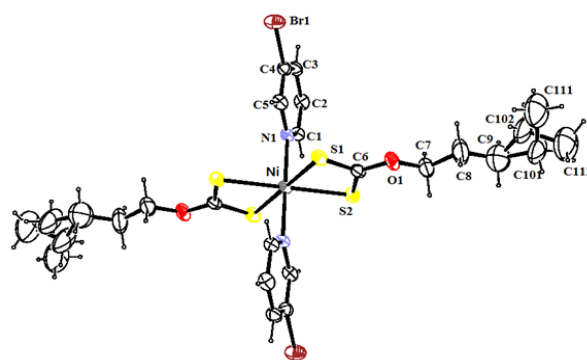


Figure 2. ORTEP plot of the molecule with 40% probability thermal ellipsoids

The dihedral angle between the pyridine ring and the four planar atoms Ni/S1/C6/S2 is 84.57(14)°. The mean value of C_{ar}=N (pyridine) distance is 1.356(7) Å. The sum of the bond angles [C5-N1-Ni, C1-N1-Ni, C5-N1-C1] around N1 is 360.00(13)° indicating sp² hybridization. The C–S bond lengths involving the xanthate ligands are: C6-S1 = 1.681(7)Å and C6-S2 = 1.684(7)Å. These values are approximately same and shows a double bond character due to delocalization over the two C–S bonds.²⁰ As a consequence of the hybridization of the carbon atom, the O1–C6 bond has a distance [1.317(7) Å] shorter than that of O1–C7 [1.438(9) Å].

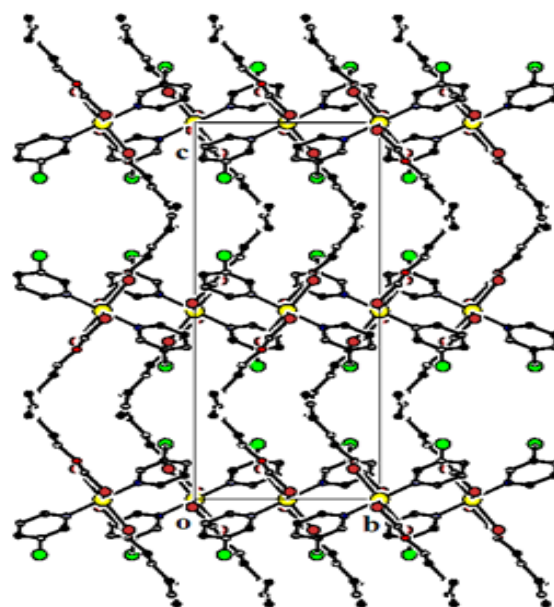


Figure 3. The crystal packing of the complex viewed down a-axis

Table 2. Selected bond lengths (Å) and bond angles (°) for non hydrogen atoms (e.s.d.'s are given in parentheses)

Bond lengths, Å		Bond angles, °	
Ni-N1	2.117(5)	N1-Ni-N1 ⁱ	180.0(1)
Ni-S1	2.448(2)	N1-Ni-S2	88.5(1)
Ni-S2	2.442(2)	N1-Ni-S1	89.9(1)
C6-O1	1.317(7)	N1 ⁱ -Ni-S2	91.5 (1)
O1-C7	1.438(9)	N1-Ni-S2 ⁱ	91.5 (1)
S1-C6	1.681(7)	N1 ⁱ -Ni-S2 ⁱ	88.5(1)
S2-C6	1.684(7)	C5-N1-Ni	120.6 (4)
Br1-C4	1.887(6)	C1-N1-C5	118.0(5)
		C1-N1-Ni	121.4(4)

The short value of bond distance for O1–C6 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.²¹ The Br–C4 bond length of 1.887(6) Å is comparable with those reported for related structures.^{22,23} The amyl chain attached to the dithiocarbonato group contains disorder over two sets of sites with occupancy ratios of 0.683: 0.317.

The crystal structure is stabilized by weak C-H... π interactions. Details of the geometry of C-H... π interactions are given in Table 3. Crystal packing viewed down the a-axis (Figure 3) shows that the molecules are stacked in parallel layers forming a zig-zag pattern along bc-plane.

Table 3. Geometry of intra and inter molecular hydrogen bonds

D-H...A	D-H, Å	H...A, Å	D...A, Å	θ [DH...A], °
C8-H8B...Cg1 ⁱ	0.97	3.031	3.764	133

Symmetry codes: (i) $1/2+x, 1/2-y, -z$; Cg1 represents center of gravity of pyridine ring (N1/C1/C2/C3/C5/C5)

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