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Note

Synthesis, spectral and structural studies of novel binuclear Ni(II) complex of salicylaldehyde 3-azacyclothiosemicarbazone

Leji Latheef, E.B. Seena, M.R. Prathapachandra Kurup *

Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, 682 022 Kerala, India

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ABSTRACT

A novel binuclear Ni(II) complex of salicylaldehyde 3-azacyclothiosemicarbazone (H_2L) has been synthesized and characterized by elemental analysis, IR and UV–Vis spectroscopy. The single crystal X-ray structure of the complex shows that bridging occurs through thiolato sulfur and phenolic oxygen atoms. Nickel centers in the complex have square planar and octahedral geometries.

1. Introduction

There has been a continuing interest in the coordination chemistry of thiosemicarbazones particularly on tridentate compounds containing a donor atom, besides the thiosemicarbazone moiety, azomethine nitrogen and thione/thiol sulfur atoms [1,2]. An important feature in the chemistry of thiosemicarbazones and their metal complexes is the acid character of the ^{2}NH; this allows for either neutral or anionic ligands. When coordinated as anionic ligands, the conjugation is extended to include the thiosemicarbazone moiety (i.e., $C{=}N{-}N{=}C{-}S^{(-)}{-}N$). It has been proposed that this conjugation system enhanced biological activity of these compounds [3]. We have previously reported structural and spectral studies of the mono and binuclear transition metal complexes of N(4)-substituted thiosemicarbazones [4–8]. One of the most remarkable facts about the stereochemistry of Ni(II) complexes is that equilibrium between different structural types exist in solution and these equilibria are temperature dependent also. Nickel atom present in the active sites of several dehydrogenases and the chemistry of divalent and trivalent nickel complexes with nitrogen–sulfur donor ligands have received much attention [9,10]. There is currently intense interest in dinickel thiolate-bridged complexes as first-generation models for the active site in [Ni, Fe] hydrogenases, yet only a handful of such complexes have been isolated and fully characterized [11]. Here we report the synthesis and crystal structure of new binuclear Ni(II) complex of salicylaldehyde 3-azacyclothiosemicarbazone ligand.

2. Experimental

2.1. Instruments and reagents

Elemental analyses were performed on a Vario ELIII elemental analyzer. Magnetic susceptibility measurements were performed on a Vibrating Sample Magnetometer using $Hg[Co(SCN)_4]$ as a calibrant. The IR spectrum was recorded on a Thermo Nicolet AVATAR 370 DTGS FTIR spectrometer using KBr pellets in the range 4000–400 cm^{-1} and far IR spectrum was recorded in the range 500–50 cm^{-1} on a Nicolet Magna 550 FT-IR spectrophotometer using polyethylene pellets. Electronic spectra were recorded on a GENESYS^{TM} 10 Series spectrophotometer in DMF solvent. Single crystal X-ray diffraction studies were carried out using CrysAlis CCD diffractometer. $Ni(OAc)_2 \cdot 4H_2O$ (Central drug house) and 1,10-phenanthroline (phen) (Ranbaxy fine chemicals) were used. Solvents were purified by distillation.

2.2. Synthesis of [Ni_2L_2phen]

The ligand H_2L (Fig. 1) was synthesized as reported by us [12,13]. To a hot ethanolic solution of the ligand H_2L (1 mmol, 0.277 g), added hot methanolic solution of $Ni(OAc)_2 \cdot 4H_2O$ (1 mmol, 0.248 g) with constant stirring. This was followed by the addition of the base 1,10-phenanthroline (0.5 mmol, 0.099 g) in the solid form. The above brown solution was refluxed for about

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* Corresponding author. Tel.: +91 484 2575804; fax: +91 484 2577595.
E-mail addresses: mrp@cusat.ac.in, mrp_k@yahoo.com (M.R. Prathapachandra Kurup).

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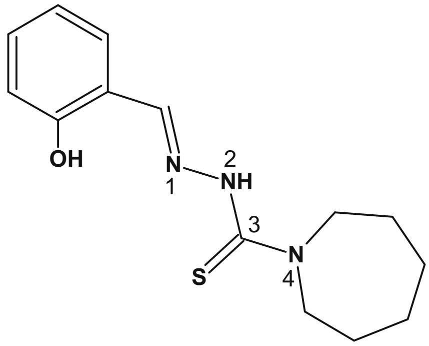


Fig. 1. Formula of H_2L.

3 h and allowed to cool, when brown crystalline compound was formed (Scheme 1). The complex formed was filtered, washed with ethanol and ether and dried in vacuo over P_4O_{10}. Elemental *Anal.* Calc.: C, 56.63; H, 4.99; N, 13.21. Found: C, 56.32; H, 5.29; N, 13.16. μ (B.M.) = 2.08.

2.3. X-ray crystallography

Single crystals of [Ni_2L_2phen] suitable for X-ray diffraction studies were grown from its solution in a mixture of dimethylformamide and methanol (1:1) by slow evaporation at room temperature in air. A single crystal of dimensions 0.33 × 0.16 × 0.11 mm^3 with $P\bar{1}$ symmetry was selected and mounted on a CrysAlis CCD diffractometer, equipped with an enhance (Mo) X-ray source. The compound was diffracted by CrysAlis CCD, Oxford Diffraction Ltd. with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The trial structure was solved by direct methods with the program SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97 [14]. The crystal data and structure refinement parameters for [Ni_2L_2phen] are given in Table 1.

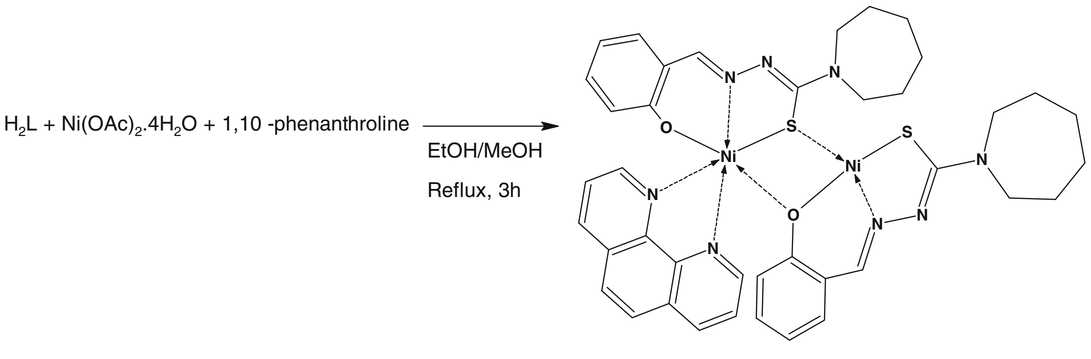
3. Results and discussion

The IR spectrum of free ligand exhibits a medium band at 3109 cm^{-1}, which is assigned to $\nu(^2N–H)$ vibration. The absence of $\nu(^2N–H)$ band in the spectrum of complex provides a strong evidence for the ligand coordination around Ni(II) ion in its deprotonated form. On coordination of azomethine nitrogen, ν(C=N) shifts to lower wavenumbers by 10–20 cm^{-1}, as the band shifts from 1612 cm^{-1} in the uncomplexed thiosemicarbazone spectrum to 1597 cm^{-1} in the spectrum of the Ni(II) complex. Coordination of azomethine nitrogen is confirmed with the presence of new band at 470 cm^{-1}, assignable to ν(Ni–N) [15,16]. The decrease in the stretching frequency of ν(CS) band from 792 cm^{-1} in the thiosemicarbazone to 757 cm^{-1} upon complexation indicates coordination *via* its thiolato sulfur. Coordination of thiolato sulfur is confirmed with the presence of new band at 340 cm^{-1}, assignable to ν(Ni–S) [17,18]. In Ni(II) complex, phenolate oxygen is coordinated to nickel by loss of the –OH proton. A new band at 425 cm^{-1} in the spectrum of the complex is assignable to ν(Ni–O) [19].

Table 1
Crystal data and structure refinement parameters for [Ni_2L_2phen].

Empirical formula	$C_{40}H_{42}Ni_2N_8O_2S_2$
Formula weight	848.35
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	12.3730(12)
b (Å)	12.573(2)
c (Å)	14.181(2)
α (°)	73.639(15)
β (°)	79.832(11)
γ (°)	63.324(14)
Volume (Å^3)	1888.2(5)
Z	2
D_{calc} (Mg/m^3)	1.492
Absorption coefficient (mm^{-1})	1.156
F(000)	884
Crystal size (mm^3)	0.33 × 0.16 × 0.11
θ Range for data collection (°)	25
Index ranges	$-14 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 16$
Reflections collected	14670
Independent reflections (R_{int})	6350 (0.0423)
Refinement method	full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.110
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0565, wR_2 = 0.1341
R indices (all data)	R_1 = 0.0773, wR_2 = 0.1425

The thiosemicarbazone (H_2L) has a ring $\pi \rightarrow \pi^*$ band at 36110 cm^{-1} and a band at 29500 cm^{-1} due to $n \rightarrow \pi^*$ transition associated with the azomethine linkage. These bands suffer marginal shifts on complexation. The broad band at 31250 cm^{-1} in the spectrum of the Ni(II) complex is assigned for $n \rightarrow \pi^*$ transition [20]. The shift of the $\pi \rightarrow \pi$ band to the longer wavelength region in the complex is the result of the C=S band being weakened and conjugation system being enhanced after the formation of the complex [21]. Two ligand to metal charge transfer bands are found at 26810 and 23150 cm^{-1} regions. In accordance with studies of previous Cu(II) and Ni(II) thiosemicarbazone complexes [22,20], higher energy band at 26810 cm^{-1} is assigned to S → Ni^{II} transitions. The band at 23150 cm^{-1} is assignable to phenoxy O → Ni^{II} transitions.



[Ni_2L_2phen]

Scheme 1. Synthesis route for [Ni_2L_2phen].

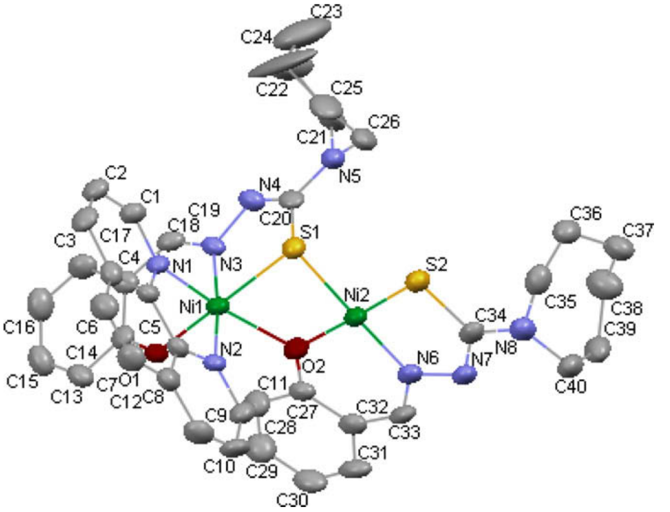


Fig. 2. Structure and labeling diagram for [Ni_2L_2phen]. Selected bond lengths (Å): Ni(1)–N(3) 2.006(4), Ni(1)–O(1) 2.006(3), Ni(1)–N(2) 2.082(4), Ni(1)–N(1) 2.124(4), Ni(1)–O(2) 2.236(3), Ni(1)–S(1) 2.3876(13), Ni(2)–N(6) 1.882(4), Ni(2)–O(2) 1.910(3), Ni(2)–S(2) 2.1520(14), Ni(2)–S(1) 2.2424(13). Selected bond angles (°): N(3)–Ni(1)–O(1) 91.91(14), N(3)–Ni(1)–N(2) 173.28(14), O(1)–Ni(1)–N(2) 88.05(14), N(3)–Ni(1)–N(1) 93.93(15), O(1)–Ni(1)–N(1) 92.47(13), N(3)–Ni(1)–O(2) 95.32(13), O(1)–Ni(1)–O(2) 100.59(12), N(2)–Ni(1)–O(2) 91.29(13), N(1)–Ni(1)–O(2) 163.70(13), N(3)–Ni(1)–S(1) 83.62(11), O(1)–Ni(1)–S(1) 174.51(10), N(2)–Ni(1)–S(1) 96.77(11), O(2)–Ni(1)–S(1) 76.73(9), N(6)–Ni(2)–O(2) 95.80(15), N(6)–Ni(2)–S(2) 87.18(13), O(2)–Ni(2)–S(2) 174.88(11), N(6)–Ni(2)–S(1) 176.54(13), O(2)–Ni(2)–S(1) 87.14(9), S(2)–Ni(2)–S(1) 89.74(5).

The molecular structure of [Ni_2L_2phen] along with atom numbering scheme is given in Fig. 2. In the title compound, nickel centers adopt two different coordination environments. Ni1 adopts a distorted octahedral geometry defined by the tridentate ONS donor dianionic ligand, neutral bidentate phenanthroline ligand and one of the oxygen O2 coordinated to the second nickel center, which bridge to occupy the sixth coordination site. The Ni–O, Ni–N and Ni–S bond lengths [Ni1–O1, 2.006(3); Ni1–O2, 2.236(3); Ni1–N1, 2.124(4); Ni1–N2, 2.082(4); Ni1–N3, 2.006(4); Ni1–S1, 2.3876(13)] are in agreement with those found in the related Ni(II) complexes [11,23]. The Ni1–O1 bond length is shorter than Ni1–O2 indicates that the phenoxy oxygen O1 coordinates more strongly to the Ni1 center than the bridging phenoxy oxygen O2. The high spin nature of Ni1 is nicely reflected by its comparatively long bond distances to S1 and N3. For example, the "intramolecular" distance of Ni1–S1 even exceeds the "intermolecular" distance of Ni2–S1 [24]. The planes defined by atoms Ni1–O2–Ni2 and Ni1–S2–Ni2 intersect at an angle of 156.54(10)°. This structural feature is due to the greater steric effect between the phenyl rings of the monomeric subunit bound to Ni1, sp^3 like character of O2 and S1 and also due to the coordination of the bulkier phenanthroline coligand. The bond angles O1–Ni1–S1 = 174.51(10)° and O1–Ni1–N2 = 88.05(14)° indicate distortion from octahedral geometry. Ni2 adopts a square-planar geometry in which coordination occurs through deprotonated ligand and the fourth position by bridging sulphur S1. The Ni2 deviates from the basal plane N6–O2–S2–S1 by 0.0559 Å. The Ni2–S2 bond length is 2.1520(14) Å which is slightly shorter than Ni2–S1 suggests the weakening of sulphur bridging. The O2–Ni2–S2 bond angle in [Ni_2L_2phen] is 174.88(11)° is a measure of distortion from regular stereochemistry for complexes with tridentate thiosemicarbazonato ligands. These angles are comparable to [$Ni(Ap4DM)]_2$, 174.3(1) [25], [$Ni(DMAp4DM)]_2$, 173.5(1), 173.1(1) [25] found for nickel(II) complexes with ONS tridentate thiosemicarbazones. The distance between the two Ni atoms in the complex is 3.247 Å, which is greater than the 2.721(1) Å found for [$Ni(Ap4DM)]_2$, 2.728(1) Å found for [$Ni(5Map4DM)]_2$ and 2.729 Å found for [$Ni(tmtssA)]_2$ [25]. The four membered metal chelate ring Cg(1) [Ni1–S1–Ni2–O2] having a maximum deviation of 0.4507 Å at O2. This indicates large tetrahedral distortion in this complex.

One intermolecular hydrogen bonding interactions is observed between C7–H7 and N7 [$D\cdots H = 0.930(6)$ Å, $H\cdots A = 2.612(5)$ Å, $D\cdots A = 3.487(8)$ Å, $D–H\cdots A = 157.02°$]. The molecules are packed in an opposite manner within the unit cell when viewed along the *b* axis (Fig. 3). The assemblage of molecules in the respective manner in the unit cell is resulted by the diverse π–π stacking of ring Cg(6) with Cg(11) [$D_{(Cg-Cg)} = 3.4932$ Å; Cg(6) = Ni2, O2, C27, C32, C33, N6; Cg(11) = C27, C28, C29, C30, C31, C32; Symmetry code = x, y, z] and ring-metal interactions of Cg(11) with Ni2 [$D_{(Cg-M)} = 3.969$ (Å); Symmetry code = $-x$, $1-y$, $-z$]. In addition to this, the C–H$\cdots\pi$ interactions of C6–H6 of phenanthroline with phenyl ring Cg(10) [Cg(10) = C13, C14, C15, C16, C17, C18; Symmetry code = x, y, z] of the neighbouring molecule is at a distance of 3.4513 Å and angle of 172° also contribute stability to the unit cell packing.

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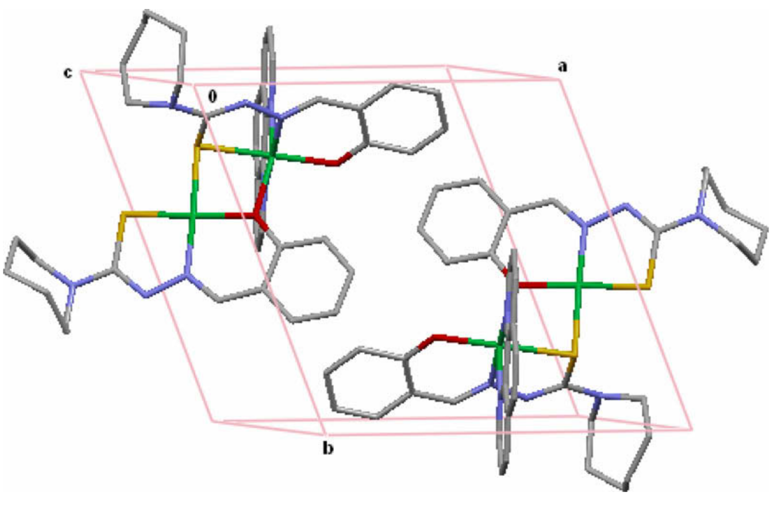

Fig. 3. Unit cell packing diagram for the compound [Ni_2L_2phen].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.10.012.

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