Polyhedron 205 (2021) 115296

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and characterization of four new azo-Schiff base and their nickel(II) complexes

Saeid Menati [a,*], Reza Azadbakht [b], Hadi Amiri Rudbari [c], Giuseppe Bruno [d]

[a] Department of Chemistry, Khorramabad Branch, Islamic Azad University, Khorramabad, Iran
[b] Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran
[c] Department of Chemistry, University of Isfahan, 81746-73441 Isfahan, Iran
[d] Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Viale Ferdinando Stagno D'Alcontres 31, I-98166 Messina, Italy

ARTICLE INFO

Article history:
Received 12 April 2021
Accepted 25 May 2021
Available online 29 May 2021

Keywords:
Azo compounds
Schiff base complexes
Square-planar structures
X-ray crystal structure
Nickel(II) complexes

ABSTRACT

Four new azo-Schiff base ligands were prepared (H_2L_a-H_2L_d) via condensation of Methyl-2-{*N*-(2′-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) with derivatives of (E)-2-hydroxy-5-(phenyldiazenyl)benzaldehyde. The corresponding nickel(II) complexes were also synthesized. The structures of the azo-Schiff base ligands and the complexes were characterized by elemental analyses, UV–Vis, IR and ^{1}HNMR spectroscopies. The structures of [NiL_a] and [NiL_c] complexes have been determined by X-ray crystallography. The Ni(II) metal complexes are formed by the coordination of the N, S and O atoms of the ligands. The X-ray results confirm that the geometry of the Ni(II) metal complexes are slightly distorted square-planar structures.

1. Introduction

Schiff base compounds are widely used as chelating ligands in coordination chemistry [1]. They are also useful in catalysis, medicine as antibiotics, antiallergic and antitumor agents [2]. Azo compounds have extensively been studied because of various applications in organic synthesis and high technology areas such as inkjet printers, liquid crystalline displays and laser [3–5]. Azo dyes have excellent optical switching among the organic photoactive materials [6–10]. Furthermore, azo metal complexes are used in many biological process such as inhibition of RNA, DNA, and biological activity against fungi and bacteria [11,12]. Azo-Schiff base ligands and their metal complexes have been extensively studied over past few decades. It has been found that azo Schiff base compounds have a widespread application both in biological activities and in organic synthesis. They are increasingly employed in plastic, leather and textile industries [13]. Azo Schiff bases have been shown to coordinate with many metal ions and give stable complexes. The coordination compounds of the azo Schiff bases are used in medicine, for corrosion prevention, metal recovery as well as to treat nuclear wastes [14]. Methyl-2-{N-(2′-aminoethane)}-amino-1-cyclopentenedithiocarboxilate (Hcden) is a convenient starting material for the synthesis of asymmetric ligands containing NNOS coordination spheres.

The synthesis of Ni(II) complexes containing N and S donor atoms is an important area of study with implications in bioinorganic chemistry, catalysis, and medical chemistry [15–17]. Nickel is present in the active sites of several important classes of metalloproteins, such as urease and Ni/Fe hydrogenases [16]. The nickel coordination sphere in both of these metalloenzyme systems contains N and S donor sets. These features led to increased interest in the synthesis of nickel(II) complexes with mixed N, S donating chelates as structural and spectroscopic models of the active sites [17].

In this work, four new azo-Schiff base ligands were synthesized (H_2L_a-H_2L_d) via condensation of Methyl-2-{*N*-(2′-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) with derivatives of (E)-2-hydroxy-5-(phenyldiazenyl)benzaldehyde. The corresponding nickel(II) complexes were also synthesized and the crystal structures of [NiL_a] and [NiL_c] complexes have been determined by X-ray crystallography.

2. Experimental

2.1. Reagents and solvents

All solvents were purchased commercially. Carbon disulfide, cyclopentanone, dimethylsulfate, 1,2-ethylendiamine, 2,4-dichloroaniline, 3,4-dichloroaniline, 2-nitroaniline, 3-nitroaniline,

---

* Corresponding author.
E-mail address: saiedmenati@gmail.com (S. Menati).

https://doi.org/10.1016/j.poly.2021.115296
0277-5387/© 2021 Published by Elsevier Ltd.

sodium carbonate, sodium nitrite, nickel(II) chloride hexahydrate and salicylaldehyde were obtained from Merck and Fluka and were used without further purification.

2.2. Instrumentation

The NMR spectra were obtained in a Brucker Avace DPZ-500 MHz spectrometer. IR spectra were recorded by Perkin Elmer RX1 FT-IR infrared spectrophotometer, Elemental analyses (C, H and N) were measured with a Termo Finnigan-Flash 1200 analyzer and UV–Vis measurements were recorded on a Jenus 5606 UV–Vis spectrophotometer. Uv–Vis absorption spectra were obtained on a Varian Cary Eclipse 300.

2.3. Synthesis

2.3.1. Synthesis of Methyl-2-{N-(2-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden)

Methyl-2-{N-(2-aminoethane)}-amino-1-cyclopentenedithiocarboxylate was prepared by published method [18].

2.3.2. Preparation of Azo-aldehyde compounds (a-d)

Azo-aldehydes (a-d) were synthesized according to the literature procedure [18]. A mixture of aniline derivatives (10 mmol, 1.38 g of 2-nitroaniline and/or 3-nitroaniline, 1.62 g of 2,4-dichloroaniline and/or 3,4-dicheloroaniline) in hydrochloric acid (36 mL), and water (16 mL) were heated. The solutions were poured into an ice-water mixture, and were diazotized between 0 °C and 5 °C with sodium nitrite (10 mmol, 0. 69 g) dissolved in water (5 mL). The cold diazo solutions were added to a solution of salicylaldehyde (10 mmol, 1.29 g) in water (19 mL) containing sodium hydroxide (10 mmol, 0.4 g) and sodium carbonate (40 mmol, 4.24 g) during the period of 30 min at 0 °C. The products were collected by filtration and washed with NaCl solution (100 mL, 10% aq.) under vacuum. Then, the solids were dried under vacuum at 80 °C overnight. The purity of the compounds were controlled by TLC (*n*-hexane:ethylacetate/60:40).

2.3.2.1. (E)-2-hydroxy-5-((2-nitrophenyl)diazenyl)benzaldehyde (a). Yield: 86%. m.p 131 °C. IR (KBr, cm^{-1}): 3193 ν(O—H), 1668 ν (C=O), 1615 ν(C=C), 1579 and 1486 ν(-N=N-, *cis* and *trans*), 1348 and 1532 ν(NO_2), 1290 ν(C—O). ^{1}H NMR δ (500 MHz; $CDCl_3$): 11.48 (OH, s), 10.08 (s, CHO), 8.41 (t, 2H, J = 8.00 Hz), 8.31 (s, 1H), 8.24 (d, 1H, J = 7.83 Hz), 8.04 (d, 2H, J = 8.02 Hz), 7.19 (d, 1H, J = 7.28 Hz), *Anal.* Calc. for $C_{13}H_9O_4N_3$: C, 57.56; H, 3.32; N, 15.50. Found: C, 57.09; H, 3.47; N, 15.08%.

2.3.2.2. (E)-2-hydroxy-5-((3-nitrophenyl)diazenyl)benzaldehyde (b). Yield: 91%. m.p 143 °C. IR (KBr, cm^{-1}): 3103 ν(O—H), 1662 ν(C=O), 1612 ν(C=C), 1579 and 1486 ν(-N=N-, *cis* and *trans*), 1343 and 1528 ν(NO_2), 1290 ν(C—O). ^{1}H NMR δ (500 MHz; $CDCl_3$): 11.49 (s, OH), 10.10 (s, CHO), 8.43 (t, 2H, J = 7.76 Hz), 8.31 (s, 1H), 8.20 (d, 1H, J = 8.68 Hz), 8.09 (d, 2H, J = 7.82 Hz), 7.13 (d, 1H, J = 8.17 Hz), *Anal.* Calc. for $C_{13}H_9O_4N_3$: C, 57.56; H, 3.32; N, 15.50. Found: C, 57.25; H, 3.16; N, 15.19%.

2.3.2.3. (E)-5-((2,4-dichlorophenyl)diazenyl)-2-hydroxybenzaldehyde (c). Yield: 81%. m.p 128 °C. IR (KBr, cm^{-1}): 3086 ν(O—H), 1667 ν (C=O), 1620 ν(C=C), 1577 and 1483 ν(-N=N-, *cis* and *trans*), 1285 ν(C—O). ^{1}H NMR δ (500 MHz; $CDCl_3$): 11.48 (s, OH), 10.08 (s, CHO), 8.42 (d, 1H, J = 8.85 Hz), 8.36 (s, 1H), 8.31 (s, 1H), 8.17 (d, 1H, J = 8.48 Hz), 8.01 (d, 1H, J = 7.91 Hz), 7.21 (d, 1H, J = 8.52 Hz), *Anal.* Calc. for $C_{13}H_8O_2N_2Cl_2$: C, 52.88; H, 2.71; N, 9.49 Found: C, 52.21; H, 2.31; N, 9.04%.

2.3.2.4. (E)-5-((3,4-dichlorophenyl)diazenyl)-2-hydroxybenzaldehyde (d). Yield: 70%. m.p 147 °C. IR (KBr, cm^{-1}): 3045 ν(O—H), 1670 ν (C=O), 1619 ν(C=C), 1571 and 1481 ν(—N=N—, *cis* and *trans*), 1284 ν(C—O). ^{1}H NMR δ (500 MHz; $CDCl_3$): 11.46 (s, OH), 10.06 (s, CHO), 8.23 (s, 1H), 8.19 (d, 1H, J = 8.01 Hz), 8.02 (s, 1H), 7.79 (d, 1H, J = 7.33 Hz), 7.62 (d, 1H, J = 7.58 Hz), 7.15 (d, 1H, J = 7.19 Hz), *Anal.* Calc. for $C_{13}H_8O_2N_2Cl_2$: C, 52.88; H, 2.71; N, 9.49 Found: C, 52.44; H, 2.58; N, 9.17%.

2.3.3. Synthesis of Schiff bases ligands (H_2L_a-H_2L_d)

Schiff base ligands (H_2L_a-H_2L_d) were prepared by addition of a-d compounds (1 mmol, 0.271 g of a and/or b, 0.295 g of c and/or d) in methanol (20 mL) to a methanolic solution of Hcden (1 mmol, 0.216 g). The mixtures were stirred for about 20 min and allowed to react at room temperature for about 24 h. The color powders were recrystallized by chloroform/methanol (1:1) v/v solution (Scheme 1).

2.3.3.1. Methyl 2-((2-((E)-2-hydroxy-5-((E)-2-nitrophenyl)diazenyl) benzylidene)amino)ethyl)ami-no)cyclopent-1-enecarbodithioate (H_2-L_a). Yield: 88%. m.p: 179 °C. IR (KBr, cm^{-1}): 1636 ν(C=N), 1589 ν (N=N), 1478 (Phenol ring), 1335 ν(NO_2), 1275 ν(C—O), 1102, 852, 603. ^{1}H NMR δ (500 MHz; $CDCl_3$): 13.35 (s, 1H, OH), 12.17 (s, 1H, NH), 8.39 (s, 1H, CH = N), 7–8.3 (Phenol ring), 3.82 (t, 2H, J = 8.23 Hz), 3.72 (t, 2H, J = 8.18 Hz), 2.73 (m, 6H), 2.53 (s, -SCH_3). *Anal.* Calc. for $C_{22}H_{23}N_5O_3S_2$: C, 52.21; H, 4.58; N, 14.93. Found: C, 52.61; H, 4.19; N, 14.42%.

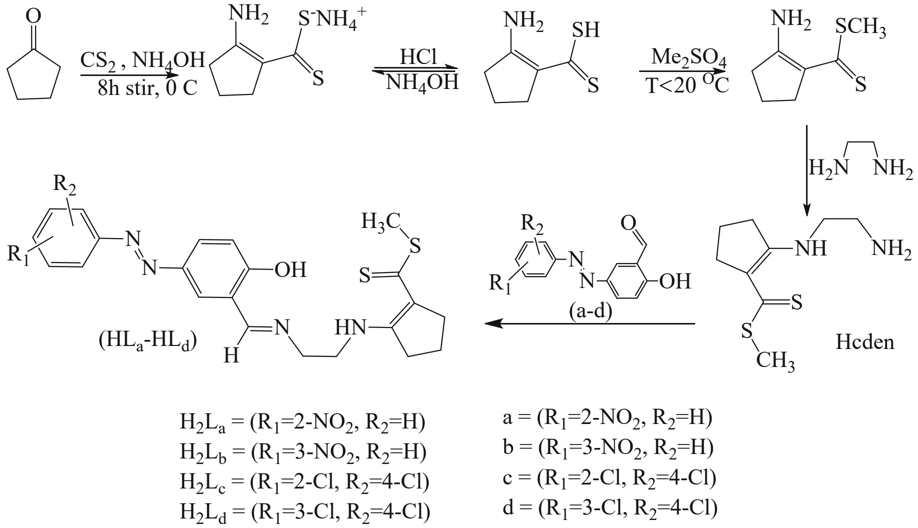
2.3.3.2. Methyl 2-((2-((E)-2-hydroxy-5-((E)-(3-nitrophenyl)diazenyl) benzyledeneamino)ethyl)ami-no)cyclopent-1-enecarbodithioate (H_2-L_b). Yield: 93%. m.p: 188 °C. IR (KBr, cm^{-1}): 1628 ν(C=N), 1583 ν (N=N), 1477 (Phenol ring), 1339 ν(NO_2), 1278 ν(C—O), 1109, 848, 610. ^{1}H NMR δ (500 MHz; $CDCl_3$): 13.40 (s, 1H, OH), 12.43 (s, 1H, NH), 8.57 (s, 1H, CH=N), 7–8 (Phenol ring), 3.82 (t, 2H, J = 8.23 Hz), 3.72 (t, 2H, J = 8.18 Hz), 2.73 (m, 6H), 2.53 (s, —SCH_3). *Anal.* Calc. for $C_{22}H_{23}N_5O_3S_2$: C, 52.21; H, 4.58; N, 14.93. Found: C, 52.61; H, 4.19; N, 14.42%.

2.3.3.3. Methyl 2-((2-((E)-5-((E)-(2,4-dichlorophenyl)diazenyl)-2-hydroxybenzylidene)amino)eth-yl)amino)cyclopent-1-enecarbod-ithioate (H_2L_c). Yield: 79%. m.p: 170 °C. IR (KBr, cm^{-1}): 1633 ν (C=N), 1582 ν(N=N), 1485 (Phenol ring), 1288 ν(C—O), 1103, 841, 613. ^{1}H NMR δ (500 MHz; $CDCl_3$): 13.51 (s, 1H, OH), 12.35 (s, 1H, NH), 8.45 (s, 1H, CH=N), 7–8.2 (Phenol ring), 3.86 (t, 2H, J = 8.20 Hz), 3.75 (t, 2H, J = 8.31 Hz), 2.73 (m, 6H), 2.51 (s, —SCH_3), *Anal.* Calc. for $C_{22}H_{22}N_4OS_2Cl_2$: C, 57.26; H, 4.77; N, 12.15. Found: C, 56.87; H, 4.28; N, 11.79%.

2.3.3.4. Methyl 2-((2-((E)-5-((E)-(3,4-dichlorophenyl)diazenyl)-2-hydroxybenzylidene)amino)eth-yl)amino)cyclopent-1-enecarbod-ithioate (H_2L_d). Yield: 68%. m.p: 187 °C. IR (KBr, cm^{-1}): 1635 ν (C=N), 1577 ν(N=N), 1479 (Phenol ring), 1283 ν(C—O), 1107, 839, 610. ^{1}H NMR δ (500 MHz; $CDCl_3$): 13.48 (s, 1H, OH), 12.27 (s, 1H, NH), 8.49 (s, 1H, CH=N), 7–8 (Phenol ring), 3.86 (t, 2H, J = 8.20 Hz), 3.75 (t, 2H, J = 8.31 Hz), 2.73 (m, 6H), 2.51 (s, —SCH_3). *Anal.* Calc. for $C_{22}H_{22}N_4OS_2Cl_2$: C, 57.26; H, 4.77; N, 12.15. Found: C, 56.63; H, 4.45; N, 11.81%.

2.3.4. General procedure for the synthesis of the complexes ([NiL_a] – [NiL_d])

To a solution of the appropriate (H_2L_a-H_2L_d) ligands (0.5 mmol, 0.235 g of H_2L_a and/or H_2L_b, 0.247 g of H_2L_c and/or H_2L_d) in cholo-form/methanol (2:1 v/v) (30 mL), were added a solution of nickel (II) chloride hexahydrate (0.5 mmol, 0.119 g) in methanol (20 mL). The solutions were stirred for 30 min and then allowed



Scheme 1. Syntheses of the azo-dye ligands (H$_2$L$_a$-H$_2$L$_d$).

to stand at room temperature for 24 h. The resulting powders were filtered and recrystallized from chloroform/methanol (1:1 v/v) solution (Scheme 2).

2.3.4.1. [NiL$_a$] complex. Yield: 67%. m.p: 267 °C. IR (KBr, cm^{-1}): 1618 ν(C=N), 1462 ν(Phenol ring), 1281 ν(C—O), 489–558 ν(Ni—N), 413–448 ν(Ni—O). ^{1}H NMR δ (500 MHz; CDCl$_3$): 7.61 (s, 1H, CH=N), 7–7.9 (Phenol ring), 3.80 (t, 2H, J = 7.59 Hz), 3.70 (t, 2H, J = 8.18 Hz), 2.81 (m, 6H), 2.62 (s, SCH$_3$). *Anal.* Calc. for $C_{22}H_{21}N_5O_3S_2Ni$: C, 53.52; H, 4.29; N, 14.19. Found: C, 53.39; H, 4.31; N, 14.25%.

2.3.4.2. [NiL$_b$] complex. Yield: 58%. m.p: 242 °C. IR (KBr, cm^{-1}): 1619 ν(C=N), 1458 ν(Phenol ring), 1280 ν(C—O), 496–564 ν (Ni—N), 405–435 ν(Ni—O). ^{1}H NMR δ (500 MHz; CDCl$_3$): 8.02 (s, 1H, CH=N), 7–7.9 (Phenol ring), 3.69 (t, 2H, J = 8.55 Hz), 3.61 (t, 2H, J = 8.41 Hz), 2.49 (m, 6H), 2.53 (s, -SCH$_3$), *Anal.* Calc. for $C_{22}H_{21}N_5O_3S_2Ni$: C, 53.52; H, 4.29; N, 14.19. Found: C, 53.18; H, 4.17; N, 13.93%.

2.3.4.3. [NiL$_c$] complex. Yield: 70%. m.p: 241 °C. IR (KBr, cm^{-1}): 1621 ν(C=N), 1473 ν(Phenol ring), 1278 ν(C—O), 496–564 ν(Ni—N), 415–435 ν(Ni—O). ^{1}H NMR δ (500 MHz; CDCl$_3$): 7.98 (s, 1H, CH=N), 7–7.9 (Phenol ring), 3.76 (t, 2H, J = 8.01 Hz), 3.55 (t, 2H, J = 7.78 Hz), 2.65 (m, 6H), 2.62 (s, —SCH$_3$), 2.43 (q, —CH$_2$, J = 8.24 Hz), 1.54 (t, —CH$_3$, J = 8.45 Hz). *Anal.* Calc. for $C_{22}H_{20}N_4OS_2Cl_2Ni$: C, 48.03; H, 3.66; N, 10.18. Found: C, 47.81; H, 3.72; N, 10.49%.

2.3.4.4. [NiL$_d$] complex. Yield: 80%. m.p: 276 °C. IR (KBr, cm^{-1}): 1626 ν(C=N), 1469 ν(Phenol ring), 1271 ν(C—O), 496–564 ν (Ni—N), 438 ν(Ni—O). ^{1}H NMR δ (500 MHz; CDCl$_3$): 7.67 (s, 1H, CH=N), 7–7.9 (Phenol ring), 3.65 (t, 2H, J = 7.41 Hz), 3.26 (t, 2H, J = 7.72 Hz), 2.64 (m, 6H), 2.61 (s, —SCH$_3$). *Anal.* Calc. for $C_{22}H_{20}N_4OS_2Cl_2Ni$: C, 48.03; H, 3.66; N, 10.18. Found: C, 48.15; H, 3.34; N, 10.33%.

2.4. X-ray crystallography

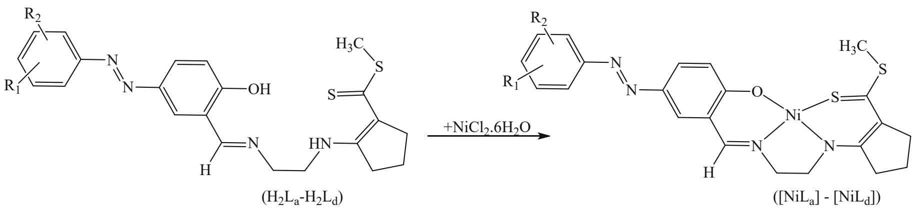
X-ray data for *[NiL$_a$] complex* and *[NiL$_c$] complex* were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo Kα radiation (k = 0.71073 Å). Data collection, cell refinement, data reduction and absorption correction were performed using multiscan methods with BRUKER software [19]. The structures were solved by direct methods using SIR2004 [20]. The non-hydrogen atoms were refined anisotropically by the full matrix least squares method on F^2 using SHELXL [21]. All the hydrogen (H) atoms were placed at the calculated positions and constrained to ride on their parent atoms. Details concerning collection and analysis are reported in Table 1.

For structure [NiL$_a$], all obtained crystals of the compound had low quality and also were weakly diffracting, with very broad diffraction peaks. We collected the dataset but obtained data are still insufficient for proper refinement. Weak data also led to a number of additional problems. In spite of this, however, all the non-H atoms could easily be located in the electron difference map, and the overall shape of the molecule can be considered to be reasonably determined.

3. Results and discussion

3.1. Synthesis

The azo-Schiff base ligands were prepared by direct reaction of the azo-aldehydes (a-d) and Hcden in methanol. The infrared spectrum of the azo-Schiff base ligands exhibited a strong band at



Scheme 2. General procedure for syntheses of Ni(II) complexes (*([NiL$_a$] – [NiL$_d$])*).

Table 1
Crystal and structure data for the nickel complexes for [NiL_a] and [NiL_c].

Complex	*[NiL_a]*	*[NiL_c]*
Formula	$C_{46}H_{42}N_{10}Ni_2O_7S_4S_2$	$C_{22}H_{20}Cl_2N_4NiOS_2$
Formula weight	1092.55	566.15
Temperature/K	298(2)	298(2)
Wavelength λ/Å	0.71073	0.71073
Crystal system	*Monoclinic*	*Monoclinic*
Space Group	$C2/c$	$P2_1/c$
a/Å	18.0096(13)	13.5298(4)
b/Å	8.4055(6)	23.1664(7)
c/Å	32.631(2)	7.7186(2)
β/°	91.18(4)	96.172(2)
Volume/Å^3	4938.6(6)	2405.27(12)
Z	4	4
Density (calc.)/g cm^{-1}	1.469	1.563
θ ranges for data collection	1.248–29.721°	1.514–30.852
$F(000)$	2256	1160
Absorption coefficient	0.992	1.230
Index ranges	$-24 \le h \le 24$ $-11 \le k \le 11$ $-45 \le l \le 45$	$-19 \le h \le 19$ $-33 \le k \le 33$ $-11 \le l \le 10$
Reflections collected/unique	36,025/6940 [$R_{(int)}$ = 0.0952]	55,183/7415 [$R_{(int)}$ = 0.0574]
Data/restraints/parameters	6940/2/311	7415/0/301
Goodness-of-fit on F^2[a]	1.513	1.175
R_1/wR_2 [$I > 2\sigma (I)$][b]	0.1433, 0.4189	0.0752, 0.2266
R_1/wR_2 (all data)[b]	0.2269, 0.4565	0.1387, 0.2951
Max./min. $\Delta\rho$ (e. Å^{-3})[c]	1.889 and −1.143	2.501 and −0.871

[a] Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.
[b] $R_1 = [\sum(||F_o| - |F_c||)/\sum|F_o|]$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.
[c] Largest difference peak and hole.

about 1633 cm^{-1}, corresponding to the imine stretching vibration, while there were no bands that could be attributed to the carbonyl and primary amine groups, indicating that condensation of the amine with the aldehyde, to form the azo-Schiff base ligands, has completely occurred. FTIR spectrum of ligands did not show the stretching frequency of phenolic (O—H) because of its involvement in hydrogen bonding (Intra-ligand hydrogen bond) with lone electron pair of azo-Schiff base nitrogen atom (O—H……N). The nickel complexes were synthesized by direct reaction between azo-Schiff base ligands with nickel(II) chloride hexahydrate in methanol.

The stretching frequency of azo-Schiff base in metal complexes shifted to lower frequencies (10–12 cm^{-1}) compared with free ligands. This confirms the participation of this group in coordination with metal ions. The stretching frequency of phenolic (C—O) bond has been shifted by 14–20 cm^{-1} to lower wave numbers in spectra of prepared complexes. This also indicated the participation of phenolic oxygen atom in coordination with nickel ions after losing its proton. New vibration bands have been noticed in spectra of prepared complexes at wave number ranges 564–572 cm^{-1} and 433–439 cm^{-1} assigned to υ(M—O) and υ(M—N) vibrations, respectively.

The NMR data are in agreement with the structures of the azo-aldehydes. In the ^{1}H NMR spectrum of azo-aldehydes, the presence of the peaks related to imine protons at 8.39, 8.57, 8.45 and 8.49 ppm for a, b, c and d, respectively, and the related peaks to other groups at the appropriate values are exactly matched with the structure of the azo-aldehydes.

3.2. Structures of the complexes

The X-ray structure determinations confirmed that the complexes show the expected molecular structure. For complexes [NiL_a] and [NiL_c], the Ni(II) is bonded to the two imine nitrogen atoms, to the sulfur atom from the methyl dithiocarboxylate residue and to the phenolic oxygen atom of the ligand, assuming a cis configuration. The ligands are Schiff bases that are formed with a fragment derived from the 2-((methylimino)methyl)phenolate and another one derived from the 2-aminocyclopentenedithiocarboxylate methyl ester. The complexes have an ethylenic diimine chain. The structures of complexes are depicted in Fig. 1. The analysis of the bond length within the metallocyclic part of the molecule is indicative of a strong delocalization of the p-electron density through the six member rings. For the cyclopentene fragments of the [NiL_a] and [NiL_c] complexes, the mean value for the S1—C1 bond lengths are 1.702(7) and 1.703(8)Å, respectively, which is considerably lower than what is usually found for a single S—C_{sp3} bond, 1.808(10) Å, and similar to the 1.712(17) Å attributed to the S—C_{sp2} bond in thiophene, showing a high delocalization of the p-electron density in this part of the molecules [22]; in addition, the distances found between the C3-C4 carbon atoms of the cyclopentene rings of the [NiL_a] and [NiL_c] complexes have a mean value 1.427(7) and 1.433(6) Å, respectively, that is similar to the mean value for the C_{sp2}—C_{sp2} bond in conjugated systems [22]. Finally, the similarity of the N1—C4 and N2—C7 bond length values is indicative that this fragment coordinates in a Schiff base mode. This electronic delocalization was reported for complexes containing this type of ligand with other metals [23,24] and for complexes of related ligands [25,26]. The complexes show a square planar geometry but with different degrees of tetrahedral distortion. The degree of the distortion will be quantified by measuring the dihedral angle, h, between planes formed by the N/Cu/O and N/Cu/S atoms of the two semi-coordination spheres.

3.2.1. [NiL_a]

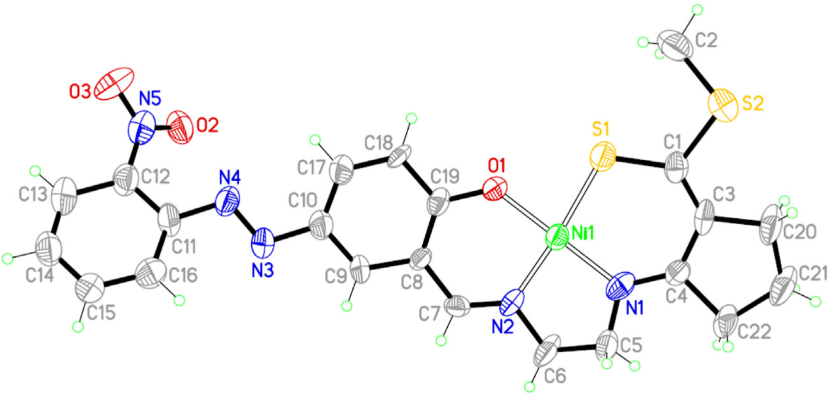
The ORTEP representation of the structure of [NiL_a] complex, including the atom numbering scheme is shown in Fig. 1. Selected bond lengths and angles are given in Table 2. The crystal structure determination revealed the existence of two independent molecules in the asymmetric unit. The complex has tetrahedral distortion relative to the square-planar geometry. The [NiL_a] complex presents a dihedral angle of 2.58(17). The geometry around the coordination center is more planar than that in the homologous N2S2 complex. The main bond lengths for the complexes studied as well as for the homologous compounds with a symilar coordination sphere, are shown in Table 3. The bond lengths are within the expected range for Nickel (II) complexes with Schiff base ligands [27]. [Ni(cden)] that presents a dihedral angle of about 20 Å [27]. On the other hand, the analogous N_2O_2 [Ni(napen)] seems to be more planar with h = 8Å [28]. The minimum distance between the copper atoms is 3.661A ° which rules out the existence of an interaction between them. The sum of the angles subtended by the donor atoms at Ni(II) for [NiL_a] is 360.10°. The plane containing S1, N1, N2, O1 has r.m.s. values of 0.03803 Å. The nickel atom for [NiL_a] is close to co-planarity, being only 0.004 Å out of the plane containing S1, N1, N2, O1.

3.2.2. [NiL_c]

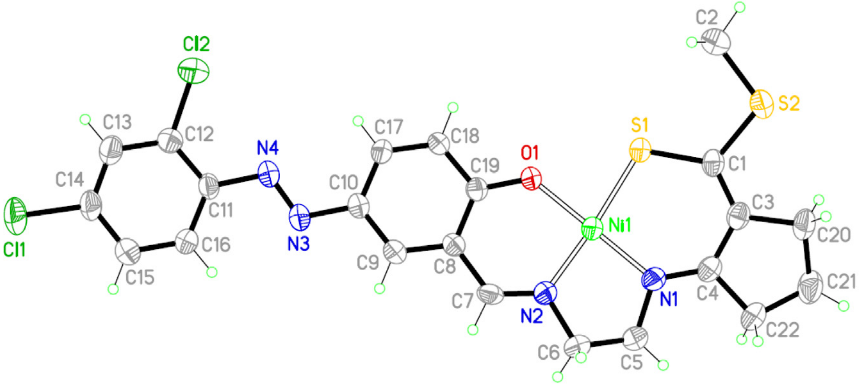
The molecular diagram of the complex, together with the atom numbering scheme is depicted in Fig. 1. Selected bond lengths and angles are given in Table 2. The molecular structure revealed that the geometry around the coordination center is a square planar one with a tetrahedral distortion. The dihedral angle is 3.80 (25), higher than that observed for [NiL_a]. The sum of the angles subtended by the donor atoms at Ni(II) for [NiL_c] is 360.14°. The plane containing S1, N1, N2, O1 has r.m.s. values of 0.04803 Å. The nickel atom for [NiL_c] is close to co-planarity, being only 0.008 Å out of the plane containing S1, N1, N2, O1.

3.3. IR spectra

In the IR spectra of Ni(II) complexes, strong bands around 1618–26 cm^{-1} were observed, which assigned to the ν(C=N) band [33],



(a) [NiL$_a$]



(b) [NiL$_c$]

Fig. 1. ORTEP representation of (a) [NiL$_a$] and (b) [NiL$_c$]. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Table 2
Selected bond distance (Å) and bond angles (°) for *[NiL$_a$]* and *[NiL$_c$]* and related complexes.

	[NiL$_a$]	*[NiL$_c$]*
Ni1—O1	1.854(8)	1.851(4)
Ni1—S1	2.147(4)	2.1577(17)
Ni1—N1	1.864(9)	1.867(5)
Ni1—N2	1.899(10)	1.880(5)
N2—C7	1.288(14)	1.283(7)
N1—C4	1.305(15)	1.318(7)
O1—C19	1.330(13)	1.302(6)
S1—C1	1.704(11)	1.716(6)
O1—Ni1—S1	81.6(3)	82.12(13)
N1—Ni1—S1	97.8(3)	98.21(15)
N1—Ni1—N2	86.7(4)	86.4(2)
O1—Ni1—N2	93.9(4)	93.39(19)
O1—Ni1—N1	178.1(4)	177.6(2)
S1—Ni1—N2	175.1(3)	174.46(15)

and the bands at 1230–1296 cm^{-1} range are attributed to the phenolic (C—O) group vibrations [34,35]. The vibrations of C═S were in the region of 1440–1496 cm^{-1} [36]. The bands in the range 700–800 cm^{-1} belongs to stretching vibrations of (C—S) and the bands between 1103 and 1190 cm^{-1} are due to the coupling of ν(C—S) + ν(C—N) [37–39]. These data were compared with the related ligands, indicate that the ν(C═N), ν(C—O) and ν(C═S) bands are shifted to lower energy. These results show that Ni(II) ion is coordinated through the nitrogen atoms of the imine group, oxygen atom of the phenolic group and sulfur of the (C═S) group for Ni(II) complexes.

3.4. ^{1}H NMR spectra

The ^{1}H NMR spectra of the ligand (H_2L_a-H_2L_d) and the nickel complex are mentioned in the experimental section. The resonance

Table 3
Selected geometric parameters for some nickel (II) complexes with Schiff base ligands.

Complex	Ni—N	Ni—O	Ni—S	S—C	O—C	Reference
[Ni(cd5Clsalen)]	1.872 (10), 1.875(9)	1.867(8)	2.166(3)	1.714(11)	1.307(14)	[29]
[Ni(cdsalen)]	1.872(5), 1.867(5)	1.860(4)	2.163(3)	1.725(6)	1.311(7)	[30]
[Ni(cd2en)]	1.893(6), 1.902(11)		2.174(4), 2.170(2)			[29]
[Ni(salen)]	1.853(2), 1.843(2)	1.850(2), 1.855(2)				[29]
[Ni(cdMeOsalen)]	1.867(4),1.871(3)	1.863(3)	2.155(12)	1.709(5)	1.297(5)	[30]
[Ni(cdnapen)]	1.863(3), 1.856(3)	1.853(2)	2.156(2)	1.707(7)	1.308(4)	[30]
[Ni(cdsalpd)]	1.904.1(2), 1.930(2)	1.887(2)	2.187.1(1)	1.736(2)	1.312(2)	[31]
[Ni(t-salpd)]	1.909(2), 1.916)		2.1454(8), 2.1733(80)	1.708(3), 1.731(3)		[32]
[NiLa]	1.864(9), 1.899(10)	1.854(8)	2.147(4)	1.704(11)	1.330(13)	This work
[NiLc]	1.867(5), 1.880(5)	1.851(4)	2.1577(17)	1.716(6)	1.302(6)	This work

Table 4
UV–Vis spectral date of the ligands and Ni(II) complexes.

compound	(MLCT)	(n → π*)	(π → π*)
H2La		398	266
H2Lb		400	272
H2Lc		395	280
H2Ld		394	274
[NiLa]	375	305	273
[NiLb]	385	320	275
[NiLc]	420	350	264
[NiLd]	438	288	262

of azomethine proton (CH=N) in the ligands (8.39–8.57 ppm), is shifted to higher field in the Ni(II) complex (7.61–8.02 ppm), confirming the coordination of the metal ion to azomethine group. In the ^{1}H NMR spectra of the free ligands, OH and NH exhibit single resonance at δ = 13.35–13.51 ppm, and δ = 12.17–12.43 ppm, respectively, which have disappeared in the nickel(II) complexes, indicating that the OH and NH groups have been deprotonated and bonded to the Ni(II) ion.

3.5. The electronic spectra

The electronic spectra of the ligands in DMF show a low intensity band at 270 nm, which is assigned to $\pi \rightarrow \pi^*$ transition, and a relatively intense band in the 391–400 nm region, which is due to $n \rightarrow \pi^*$ excitation. The complexes have a band in the region of 260–280 nm attributed to the $\pi \rightarrow \pi^*$ transition. In the complexes, $n \rightarrow \pi^*$ transitions were shifted to 430 nm. The complexes have a band between 375 and 400 nm, which may be assigned to O(phenolate) ↔ Ni(II) LMCT or MLCT. The d-d bands were not observed due to the low concentration (~10^{-4} M) of the solution. These bands should be low in intensity in the region of 500–600 nm. UV–Vis spectra data of ligand and complexes are given Table 4.

4. Conclusions

In the present work, four asymmetric tetradentate ligand was synthesized by condensation reaction of Methyl-2-{N-(2′-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) with derivatives of (E)-2-hydroxy-5-(phenyldiazenyl)benzaldehyde that are favorable to formation of the complexes with Ni(II) ions. IR, ^{1}H NMR and UV–Vis spectra of the nickel(II) complexes were recorded and compared with together. The crystal structures analysis of *[NiL$_a$]* and *[NiL$_c$]* by using X-ray crystallography confirmed the complexes are slightly distorted square-planar structure based on experimental studies.

CRediT authorship contribution statement

Saeid Menati: Writing - original draft, Conceptualization, Data curation. **Reza Azadbakht:** Investigation. **Hadi Amiri Rudbari:** Methodology, Project administration. **Giuseppe Bruno:** Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

CCDC 2046105 and 2046106 contains the supplementary crystallographic data for [NiLa] and [NiLc] complexes, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2021.115296.

References

[1] Y. Shibuya, K. Nabari, M. Kondo, S. Yasue, K. Maeeda, F. Uchida, H. Kawaguchi, Chem. Lett. 37 (2008) 78–79.
[2] B.J. Gangani, P.H. Parsania, Spectrosc. Lett. 40 (2007) 97–112.
[3] B.K. So, M.C. Jang, J.H. Park, K.S. Lee, H.H. Song, S.M. Lee, Opt. Mater. 21 (2002) 685–689.
[4] Z. Rezvani, B. Divband, A.R. Abbasi, K. Nejati, Polyhedron 25 (2006) 1915–1920.
[5] M.R. Lutfor, G. Hegde, S. Kumar, C. Tschierske, V.G. Chigrinov, Opt. Mater. 32 (2009) 176–183.
[6] H. Dinçalp, S. Yavuz, Ö. Haklı, C. Zafer, C. Özsoy, I. Durucasu, S. Içli, J. Photochem. Photobiol. A 210 (2010) 8–16.
[7] C. Motoc, G. Iacobescu, J. Magn. Magn. Mater. 306 (2006) 103–107.
[8] Z. Zhu, Q. Li, Q. Zeng, Z. Li, Z. Li, J. Qin, C. Ye, Dyes Pigments. 78 (2008) 199–206.
[9] C. Saravnan, P. Kanan, Polym. Degrad. Stab. 94 (2009) 1001–1012.
[10] P.J. Coelho, L.M. Carvalho, A.M.C. Fonseca, M.M.M. Raposo, Tetrahedron Letters 47 (2006) 3711–3714.
[11] S.M. Pradeepa, H.S.B. Naik, B.V. Kumar, K.I. Priyadarsini, A. Barik, M.C. Prabhakara, Spectrochim. Acta A. 141 (2015) 34–42.
[12] M. Odabaşoglu, Ç. Albayrak, R. Özkanca, F.Z. Akyan, P. Lonecke, J. Mol. Struct. 840 (2007) 71–89.
[13] E. Ispir, Dyes Pigments. 82 (2009) 13–19.
[14] S. Issaadi, D. Haffar, T. Douadi, S. Chafaa, D. Seraphin, M.A. Khan, G. Bouet, Synth. React. Inorg. Met-org. Nan. Chem. 35 (2005) 875–882.
[15] F. Czerny, P. Döhlert, M. Weidauer, E. Irran, S. Enthaler, Inorganica Chimica Acta 425 (2015) 118–123.
[16] S. Wang, M.H. Lee, R.P. Hausinger, P.A. Clark, D.E. Wilcox, R.A. Scott, Inorg. Chem. 33 (1994) 1589.
[17] N. Goswami, D.M. Eichhorn, Inorg. Chem. 36 (1999) 4329.
[18] S. Menati, A. Azadbakht, R. Azadbakht, A. Taeb, A. Kakanejadifard, Dyes and Pigments 98 (2013) 499–506.
[19] (a) COSMO, version 1.60; Bruker AXS Inc., Madison, Wisconsin, 2005.; (b) SAINT, version 7.06A; Bruker AXS Inc., Madison, Wisconsin, 2005.; (c) SADABS, version 2.10; Bruker AXS Inc., Madison, Wisconsin, 2005.
[20] M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, J. Appl. Crystallogr. 38 (2005) 381.
[21] G.M. Sheldrick, A short history of SHELX, Acta Crystallogr. Sect. A Found. Crystallogr. 64 (1) (2008) 112–122.
[22] F.H. Allen, O. Kennard, D.G. Watson, G. Orpen, L. Brammer, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (1987) S1.
[23] B. Castro, E. Pereira, L. Gomes, Acta Crystallogr., Sect. C 53 (1997) 572.
[24] E.M. Martin, R.D. Bereman, Inorg. Chim. Acta 188 (1991) 221.
[25] R.D. Beremenn, M.R. Churchill, G. Shields, Inorg. Chem. 18 (1979) 3117.
[26] R.D. Beremenn, J.R. Dorfmann, J. Bordener, D.P. Rillema, P. McCarthy, G.D. Shilds, J. Inorg. Biochem. 16 (1982) 47.
[27] (a) A.D. Garnovskii, A.L. Nivorozhkin, V.I. Minkin, Coord. Chem. Rev. 126 (1993) 1;
(b) S. Mandal, G. Das, R. Singh, K. Bhuradwaj, Coord. Chem. Rev. 160 (1997) 191.
[28] V.C. Freiburg, W. Reicht, W. Melchers, B. Engelen, Acta Crystallogr., Sect. B 36 (1980) 1209.
[29] M. Asadi, K. Mohammadi, S. Esmaielzadeh, B. Etemadi, H.K. Fun, Polyhedron 28 (2009) 1409–1418.
[30] B. Castro, E. Pereira, L. Gomes, Inorg. Chim. Acta 271 (1998) 83.
[31] E. Pereira, L. Gomes, B. de Castro, J. Chem. Soc., Dalton Trans. (1998) 629–636.
[32] L. Gomes, E. Perema, B. De Castro, Acta Cryst. C 55 (1999) 1061–1063.
[33] A. Khandar, B. Shaabani, F. Belaj, A. Bakhtiari, Polyhedron 25 (2006) 1893–1900.
[34] A. Garnovskii, A.L. Nivorozhkin, V.I. Minkin, Coord. Chem. Rev 126 (1993) 1–2.
[35] G.C. Percy, D.A. Thorton, J. Inorg. Nucl. Chem 34 (1972) 3357–3363.
[36] Y. L. Zhang, W. J. Ruan, X. J. Zhao, H. G. Wang, Z. A. Zhu, Polyhedron 20 (2001) OR 22 (2003) 1535-1545.
[37] S. Chandra, A. Rathi, J. Saudi. Chem. Soc. 5 (2001) 175–181.
[38] S. Chandra, U. Kumar, Spectrochim. Acta. Part A 61 (2006) 219–224.
[39] P.R. Blum, S.C. Cummings, R.M.C. Wei, Inorg. Chem. 13 (1974) 450–462.