Synthesis and identification of metal complexes of E-1-(benzo[d]thiazol-2-yl)-2-(1-(2-methoxyphenyl)ethylidene) hydrazine with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)

ABSTRACT

The reactions of the Schiff base E-1-(benzo[d]thiazol-2-yl)-2-(1-(2-methoxyphenyl) ethylidene)hydrazine (HL), with metal transition ions (Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)), afforded one type of complex formulated as $[M(HL)(Solv)_2Cl]^+(Cl^-)$. These compounds have been characterized by elemental analysis, UV-Vis, FTIR, ^1H and ^{13}C NMR spectroscopies, molar conductivity and room temperature magnetic measurements. The structure of nickel (II) complex has been determined by X-ray crystallography. The complex crystallizes in the monoclinic system space group $P2_1/n$ with a = 16.1761 (8) Å, b = 8.3212 (4) Å, c = 18.6013 (9) Å, b = 105.441 (3)°, V= 2413.4 (2) $Å^3$, Z = 4, R1 = 0.043, and wR2 = 0.123, Dcalc = 1.429 Mgm^{-3}, μ = 1.14 mm^{-1}. The ligand acts in tridentate fashion in its neutral form. Two coordinated alcohol molecules and one chlore atom complete the coordination sphere. The environment around the Ni (II) center is best described as an octahedral geometry. In the crystal structure of the Schiff base ligand, the existence of a strong intramolecular O-H•••Cl hydrogen bonding are observed.

Key words: Transition metal complex; Spectroscopy; Molar conductance; Crystal structure.

1. INTRODUCTION

Over the last decades, coordination chemistry has fully evolved. Complexes have been developed with ligands containing oxygen, nitrogen, phosphorous and/or sulfur atoms[1]. Precursors such as hydrazinobenzothiazole and ketone derivatives are used in condensation reaction to generate ligands which can coordinate metal ions with five- or six-membered rings[2]. Several benzothiazole derivatives are used in the search for new therapeutic agents[3-6]. Indeed, antioxidant[7], anticancer and antibacterial[8]moleculescontaining benzothiazole exist[9,10]. The Schiff bases of general formula R_1-CH=NR_2, obtained by condensation reaction are generally solid and crystalline ligands[11,12]. Their transition metal or rare earth complexes are usedsuch as pigments[10], catalysts but also polymer stabilizers. They are also used in the synthesis of high-performance heterocyclic dyes[13]. Benzothiazole-based ligands are used in coordination chemistry due to the availability of coordination sites[14]. The complexes obtained based on hydrazinobenzothiazole have interesting properties particularly in biology[15], in photophysics[16,17], as antimicrobial[18], anticancer[19], antituberculosis[20] or antiviral agents[21]. Ligands containing the benzothiazole motif can act in various ways depending on their coordination mode, which is often dependent on the synthesis procedures used. We were interested in aryl-NH-N=CH-aryl type structures, in particular those which contain motifs derived from benzaldehyde or methoxybenzaldehyde.The objective of this study is to synthetize and characterize by methods spectroscopic the ligand *E*-1-(benzo[d]thiazol-2-yl)-2-(1-(2-methoxyphenyl)ethylidene)hydrazine and its complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). Among the five complexes, only the complex $[Ni(HL)(EtOH)_2(Cl)]^+ \cdot Cl^-$ has crystallized and its structure has been determined by X -ray diffraction.

2. EXPERIMENTAL

2.1 Materials and Procedures

2-hydrazinobenzothiazole, 2-methoxyacetophenone, manganese (II) chloride tetrahydrate, cobalt (II) chloride hexahydrate, nickel(II) chloride hexahydrate, copper (II) chloride dihydrate and zinc (II) chloride salts were commercial products (from Aldrich) and were used without further purifications. The methanol and ethanolsolvents were reagent grade and were purified by usual methods. Elemental analyses were carried out using a VxRio EL Instrument. The IR spectra were recorded on a FTIR Spectrum Two of Perkin Elmer (4000–400 cm^{-1}). The UV–Vis spectra were run on a Perkin-Elmer UV/Visible spectrophotometer Lambda 365 (1000–200 nm). The ^1H and ^{13}C NMR spectra of the Schiff base were recorded in DMSO-d_6 on a BRUKER AC-300 spectrometer at room temperature using TMS as an internal reference. The molar conductance of 10^{-3} M solutions of the metal complexes in DMF was measured at 25 °C using a WTW LF-330 conductivity meter with a

WTW conductivity cell.Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Mattey scientific magnetic susceptibility balance {calibrant $Hg[Co(SCN)_4]$}. Melting points were recorded on a Büchi apparatus and are uncorrected.

2.2Synthesis of ligand

In a 250 mL flask containing 30 mL of methanol, 2.000 g (0.012 mmol) of 2-hydrazinobenzothiazole and 1.820 g (0.012 mmol) of 2-methoxyacetophenone were introduced[22]. Two drops of glacial acetic acid were added to the mixture which was refluxed for eight hours. The yellow solution was evaporated to dryness. The solid red-wine compound recovered was washed with 20mL of hexane before being dried in a desiccator. Yield 93%. M.p. 119 °C. Anal. Calc (%) for $C_{16}H_{15}N_3OS$: C, 64.62, H, 5.08, N, 14.13, S, 10.78. Found (%): C, 64.58, H, 5.04, N, 14.36, S, 10.78. FTIR (ν, cm^{-1}): 3060 (NH), 1601 (C=N), 1552 (C=N), 1271 ($C\text{-}O_{ether}$), 1025 (N-N), 1488, 1444, 1435 ($C_{Ar}=C_{Ar}$), 881, 814, 747, 727 ($C\text{-}H_{Ar}$). NMR ^1H (dmso-d_6, d (ppm)): 11.51(s, NH, 1H), [7.05-7.70] (m, H_{arom}, 8H), 3.78 (s, $-OCH_3$, 3H), 2.29 (s, $-CH_3$, 3H). NMR ^{13}C (dmso-d_6, d (ppm)): 157.6 (C=N), 155.91 $(C=N)_{cycle}$, 134.29 (C_{Ar}), 133.98 (C_{Ar}), 130.55 (C_{Ar}), 129.90 (C_{Ar}), 126.34 (C_{Ar}), 121.87 (C_{Ar}), 120.83 (C_{Ar}), 112.22 (C_{Ar}), 56.03 ($-OCH_3$), 18.91 ($-CH_3$).

2.3 General procedure for the synthesis of the complexes.

To ethanolic solution (20 mL) of the ligand HL 0.560 g (1 mmol) a solution of the $MCl_2{\cdot}nH_2O$ salt (1 mmol) (M = Mn, Co, Ni, Cu or Zn) in ethanol (10 mL) was added. The solution was stirred for two hours. The clear solution obtained was filtered and left to slow evaporation. After three days, green crystals suitable for X-ray analysis were collected for the nickel (II) complex. The cobalt(II) and manganese (II) complexes were obtained as red and brown powders, respectively. On the other hand, copper(II) and zinc(II) complexes were green and red-wine respectively.

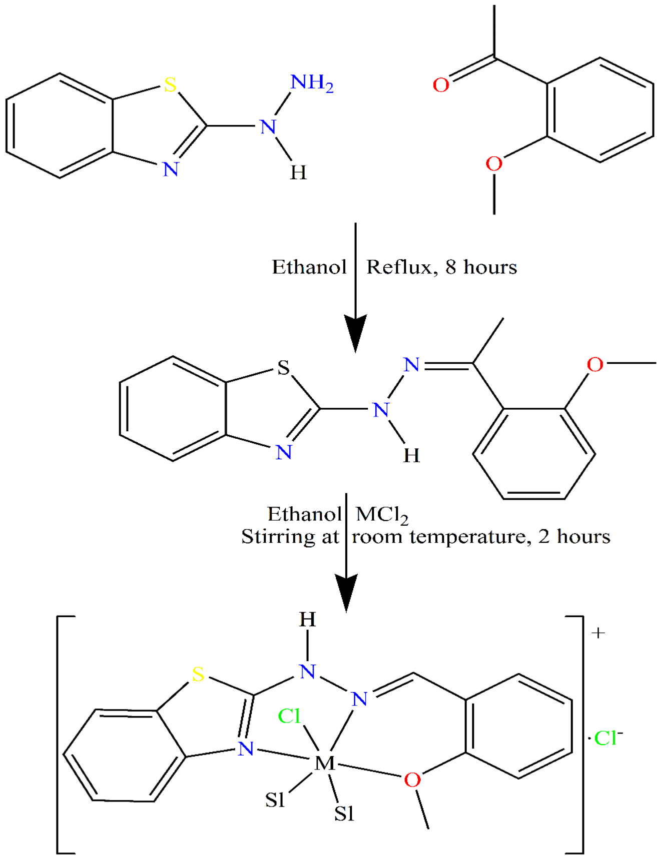
{$[MnCl(C_{16}H_{15}N_3SO)(H_2O)_2]{\cdot}Cl$} (**1**). Yield: 60%. M.P. 90°C. Anal. Calc. (%) for $C_{16}H_{19}Cl_2MnN_3O_3S$, C, 41.84, H, 4.17, N, 9.15, S, 6.98. Found: C, 41.78, H, 4.21, N, 9.18, S, 6.87. FTIR (KBr, (ν, cm^{-1})): 3464, 3317, 3217, 2937, 1592, 1551, 1489, 1444, 1386, 1292, 1276, 1237, 1114, 1018, 751, 725, 677. Λ (Ω^{-1} cm^2 mol^{-1}, DMF): 68. UV-vis (DMF, λ(nm)): 362, 422, 494, 576, 614. μ_{eff} at room temperature is 4.6 MB.

{$[CoCl(C_{16}H_{15}N_3SO)(H_2O)_2]{\cdot}Cl$} (**2**). Yield: 75%. M.P. 120°C. Anal. Calc. (%) for $C_{16}H_{19}Cl_2N_3O_3SCo$: C, 41.48, H, 4.13, N, 9.07, S, 6.92. Found:C, 41.52, H, 4.16, N, 9.12, S, 6.85. FTIR (KBr, (ν, cm^{-1})): 3350, 2970, 1597, 1577, 1555, 1532, 1490, 1455, 1435, 1268 and 1241. Λ (Ω^{-1} cm^2 mol^{-1}, DMF): 72. UV-vis (DMF, λ(nm)) : 365, 419, 606, 665. μ_{eff} at room temperature is 4.1 MB.

{$[NiCl(C_{16}H_{15}N_3SO)(CH_3CH_2OH)_2]{\cdot}Cl$} (**3**). Yield: 65 %. M.P. > 240 °C. Anal. Calc. (%) for $C_{20}H_{27}Cl_2N_3NiO_3S$, C, 44.21, H, 4.33, N, 8.59, S, 6.56. Found:C, 44.31, H, 4.37, N, 8.63, S, 6.58. FTIR (KBr, (ν, cm^{-1})): 3141, 2902, 1589, 1578, 1508, 1434, 1326, 1265, 1233, 1179, 1149, 1095, 1017, 1000, 945, 840, 804, 764, 679, 645 and 575. Λ (Ω^{-1} cm^2 mol^{-1}, DMF): 80.UV-vis (DMF, λ (nm)): 364, 378, 427, 480, 499, 668, 711.μ_{eff} at room temperature is 2.69 MB.

{$[CuCl(C_{16}H_{15}N_3SO)(H_2O)_2]{\cdot}Cl$} (**4**). Yield: 65%. M.P. > 240 °C. Anal. Calc. (%) for$C_{16}H_{19}Cl_2N_3O_3SCu$: C, 41.07, H, 4.09, N, 8.98, S, 6.85. Found (%): C, 40.97, H, 4.19, N, 8.78, S, 6.95. FTIR (KBr, (ν, cm^{-1})): 3450, 3225, 1718, 1585, 1524, 1483, 1455, 1368, 1289, 1164, 1130, 1074, 1009, 749, 713, 611, 558 and 527. Λ ($\Omega^{-1}cm^2mol^{-1}$, DMF): 80.UV-vis (DMF, λ(nm)): 303, 444, 550, 870.μ_{eff} at room temperature is 1.79 MB.

{$[ZnCl(C_{16}H_{15}N_3SO)(H_2O)_2]{\cdot}Cl$}(**5**). Yield: 80%. M.P. > 240 °C. Anal. Calc. (%) for $C_{16}H_{19}Cl_2N_3O_3SZn$: C, 40.91, H, 4.08, N, 8.95, S, 6.83. Found (%): C, 40.95, H, 4.11, N, 8.98, S, 6.88. FTIR (KBr, (ν, cm^{-1})): 3469, 3175, 1596, 1556, 1489, 1455, 1438, 1366, 1300, 1240, 1106, 1045, 1021, 935, 893, 815, 748, 594, 559 and 504. Point de fusion > 240°C. Λ (Ω^{-1} cm^2 mol^{-1}, DMF): 80.UV-vis (DMF, λ(nm)) : 311, 574, 615. Diamagnetic.



Sl = H_2O for M = Co, Mn, Cu or Zn and Sl = EtOH for M = Ni

Scheme 1. Synthetic procedure of the ligand and itsMn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}.

2.4 X-ray data collection, structure determination and refinement

Crystals suitable for X-diffraction, of the reported compound, were grown by slow evaporation of EtOH solution of the complex. Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a Bruker APEX-II CCD diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. The structures were solved by direct methods that revealed the position of all non-hydrogen atoms. All structures were refined on F^2 by a full-matrix least-squares method using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms are located using the Fourier difference and refined with the AFIX instruction. Molecular graphs were generated using ORTEP[23].

Table 1. Crystal data, X-ray data collection, data reduction and structure refinement for the nickel (II) complex.

Chemical formula	$C_{20}H_{27}N_3O_3Cl_2NiS$
M_r	519.11
Crystal system	monoclinic
Space group	$P2_1/n$
Temperature (K)	173
a (Å)	16.1761 (8)
b (Å)	8.3212 (4)
c (Å)	18.6013 (9)
β (°)	105.441 (3)
V (Å^3)	2413.4 (2)

Z	4
Radiation type	Mo $K\alpha$
m(mm^{-1})	1.14
F(000)	1080
Crystal size (mm)	0.20 × 0.15 × 0.14
θ range for data collection (°)	2.6– 26.8
R_{int}	0.050
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.123, 1.04
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å^{-3})	1.55−0.37
No. of reflections	5820
No. of parameters	277

3. RESULTS AND DISCUSSION

3.1 General studies

The synthesis of the acyclic Schiff base HL (*E*-1-(benzo[d]thiazol-2-yl)-2-(1-(2-methoxyphenyl)ethylidene)hydrazine) is achieved in a one-step procedure using the direct condensation of the 2-hydrazinobenzothiazole and 2-methoxyacetophenone in 1/1 ratio. The coordination abilities of the HL with transition metal (II) chloride salt was investigated in 1:1 ligand/metal ratio in ethanol solutions (Scheme 1). The infrared spectrum of the ligandshows in the high frequency zone a weak band at 3060 cm^{-1} , it is attributed to then (NH) vibrations of hydrazine[21]. The strong band at 1696 cm^{-1} is attributed to theν(C=N) vibration of the azomethine group. The band of the $\nu_{C=N}$ function of the benzothiazole group is pointed at 1601 cm^{-1}. The absence of the characteristic bands ν_{NH_2} and $\nu_{C=O}$ expected, respectively, around 3300 cm^{-1} and 1720 cm^{-1} and the appearance of the band attributed to the vibration $\nu_{C=N}$ are indicative of success of the condensation reaction[8]. Bands attributable to the $\nu_{C=C}$ bonds of the aromatic rings appear in the range 1601-1444 cm^{-1}. The medium intense bands at *ca*. 1025 and 1271 cm^{-1} are attributed respectively to $\nu_{N—N}$and $\nu_{C—O}$ vibrations. The ^{1}H and ^{13}CNMR spectra of the ligand were recorded in a solution of d$_6$-dmso. The ^{1}H NMR spectrumof the ligand exhibits multiplets between 7.05 and 7.7 ppm attributed the eight aromatic protons. The signals singlets at 2.29 ppm and 3.78 ppm are attributed, respectively, to the methyl and the methoxy protons.The signal pointed at 11.51 ppm is attributed to the proton of the N—H group**.** The ^{13}C NMR spectrum reveals a signal at 157.6 ppm attributed to theazomethine carbon atom[24]. The signal observed at 155.91 ppm is attributed to the azomethine carbon atom of the benzothiazole ring. The methyl carbon atoms are observed at 18.91 and 56.03 ppm, respectively, while the carbon atoms of the aromatic groups appear in the range 134.29-112.22 ppm.

Upon complexation of the metal ions by the ligand, the $\nu_{C=N}$ vibration bands of the azomethine group of the complexes are slightly shifted to low frequencies and appears in the range [1600-1597 cm^{-1}]. This fact is indicative of the involvement of azomethine nitrogen atom in the coordination sphere of each of the metals[25]. The broad bands pointed on the spectra of the complexes are due to the vibration bands of the $\nu_{O—H}$ bonds of ethanol and/or coordinated water. The shift of the $\nu_{C=N}$ of the benzothiazole ring upon coordination indicates the participation of the nitrogen atom in metal the coordination[26]. The shift to low frequencies of the vibration bands of the $\nu_{C—O}$ of the methoxy group, which are located in the range [1241-1265 cm^{-1}] for the complexes, attests the involvement of the methoxy oxygen atom in the coordination. The conductance measurements in fresh solution and two weeks later give values which indicate that the complexes are 1:1 electrolytes and are stable in DMF solution. The complex (**1**) gives a value which undergoes a slight increase two weeks later. This increase may be due to substitution of coordinated water molecules by DMF molecules. This fact is not observed in the complexes (**2**) and (**3**). Based on an analysis of coordinated ligand exchanges, it is reported that coordinated alcohol molecules are more stable than water molecules. The substitution power of DMF on an aqua complex is more marked than on alcohol complexes[27]. UV–visible spectra of the complexes, recorded in DMF solution, show bands in the (362–378) nm regions which are due to n → π* transitions within the ligand[28].

The ligand→metal charge transfer bands are observed in the (419-480) nm range. Bands absorption towards high frequencies on the spectra of the complexes, are due to d→d[29]. Conductimetric measurements taken in DMF in fresh solution and fifteen days later give values consistent with 1:1 type electrolytes[30]. Magnetic moment values are close to those observed for free metal ions[31]. The data are reported in Table 2.

Table 2. Electronic, magnetic moments and conductance data of the complexes.

	IR				**UV-vis DMF**		
	$\nu_{C=N}$	ν_{N-N}	$\nu_{C=Ncycl}$	ν_{C-O}	**λ(nm)**	**Λ ($\Omega^1 cm^2 mol^{-1}$)**	**μ_{eff} (M_B)**
HL	1601	1025	1552	1271	-		
1	1592	1095	1529	1265	364, 378, 427, 480, 499, 668, 711	80	4.6
2	1585	1072	1551	1237	362, 422, 494, 576, 614	68	4.1
3	1597	1099	1532	1241	365, 419, 606, 665	72	2,69
4	1585	1074	1524	1289	303, 444, 550, 870	67	1.79
5	1596	1045	1556	1240	311, 574, 615	76	0

3.2 Structure description of the complex$C_{20}H_{27}Cl_2N_3NiO_3S$

Suitable single crystals for X-ray diffraction of the nickel(II) complex were obtained by slow solvent evaporation at room temperature. Crystal data, collection and refinement parameters are listed in Table 1. Selected bond lengths and angles are summarized in Table 3. Hydrogen bond data for the complex are gathered in Table 4. The Ni(II) complex crystallizes in the monoclinic system with space group $P2_1$ /n. An ORTEP view of the structure is shown in Figure 1.The asymmetric unit is composed by one Ni(II) metal cation, one ligand molecule, one coordinated chloride anion, two coordinated ethanol molecules and one free chloride anion. The ligand acts in tridentate fashion through one azomethine nitrogen atom, one nitrogen atom from the benzothiazole ring and one methoxy oxygen atom. Thus, the Ni(II) metal center is hexacoordinated. The equatorial plane around the Ni(II) ion is occupied by the oxygen atom of the methoxy group of the ligand, the coordinated chloride cation and two nitrogen atoms belonging to the iminic groups of the ligand. The apical positions are occupied by the oxygen atoms of two ethanol molecules with the angle value of 171.29(8)° [O2—Ni1—O3]. The *cissoid* angles [N1—Ni1—N3], [N3—Ni1—O1], [N1—Ni1—Cl1] and [O1—Ni1—Cl1] have value of 79.66(8)°, 81.99(8)°, 102.17(6)° and 95.87(6)°, respectively. The sum of the *cissoid* angles values is equal 359.69° and is very close to the expected value of 360°. The *transoid* angles values [N1—Ni1—O1] and [N3—Ni1—Cl1] are 160.17(9)° and 176.98(7)°, respectively. The geometry around the Ni(II) ion is best described as a distorted octahedronas shown by the deviation of the angle values from the ideal values of 90° and 180° for an ideal octahedron. Upon coordination to the metal ion one six-membered ring [Ni1O1C11C10C8N3] and one five-membered ring [Ni1N1C7N2N3] were formed with bite angles of 81.99 (8)° [N3—Ni1—O1] and 79.66 (8)° [N1—Ni1—N3]. The mean planes of these rings are twisted each other and form a dihedral angle of 12.62°. The bond lengths C11-O1 and O1-C16 which are 1.386 (6) Å and 1.436 (4) Å are characteristic of single bond. The N1-C1 and N3-C8 bonds values of 1.399 (3) Å and 1.295 (3) Å, respectively, correspond to double bonds character. The length of the N2–N3 bond which is 1.384 (3) Å indicates a simple bond. It is almost equal to the value of the same bond observed in the molecule obtained by Sow et *al*[32]. The Ni-N1, Ni-N3 and Ni-O1 bond lengths are 2.065 (2) Å, 2.093 (2) Å and 2.1205 (19) Å, respectively. These lengths are very close to those published by for similar hexacoordinated nickel complexes[33,20,32].Intramolecular hydrogen bonds are observed between a coordinated ethanol molecule oxygen atom which acts as donor and the free chloride cation which is the acceptor: O2B—H2B⋯Cl2 and O3—H3A⋯Cl2. In the intramolecular N—H⋯Cl hydrogen bond, the free chloride ion acts as the acceptor while the donor is the hydrazonyl nitrogen of ligand: N2—H2A⋯Cl2. Additional weak intramolecular hydrogen bonds of type C—H⋯Cl and C—H⋯O [C2—H2⋯Cl1, C14—H14⋯Cl1 and C16—H16B⋯O3] consolidate the structure (Table 4, Figure 2).

Table 3. Selected geometric parameters (Å, º).

Ni1—O2	2.064(2)	Ni1—N3	2.093 (2)
Ni1—N1	2.065 (2)	Ni1—O1	2.1205 (19)
Ni1—O3	2.087(2)	Ni1—Cl1	2.3161 (8)
N1—Ni1—N3	79.66 (8)	N3—Ni1—Cl1	176.98 (7)
N1—Ni1—O1	160.17 (9)	O1—Ni1—Cl1	95.87 (6)

N3—Ni1—O1	81.99 (8)	N1—Ni1—Cl1	102.17 (6)
O2—Ni1—N1	96.46(8)	O2—Ni1—O3	171.30(8)
N1—Ni1—O3	88.42(9)	O2—Ni1—N3	87.67(8)
O2—Ni1—O1	90.21(8)	O3—Ni1—Cl1	91.51(6)
O2—Ni1—Cl1	94.48(6)	O3—Ni1—N3	86.12(8)
O3—Ni1—O1	82.90(8)		

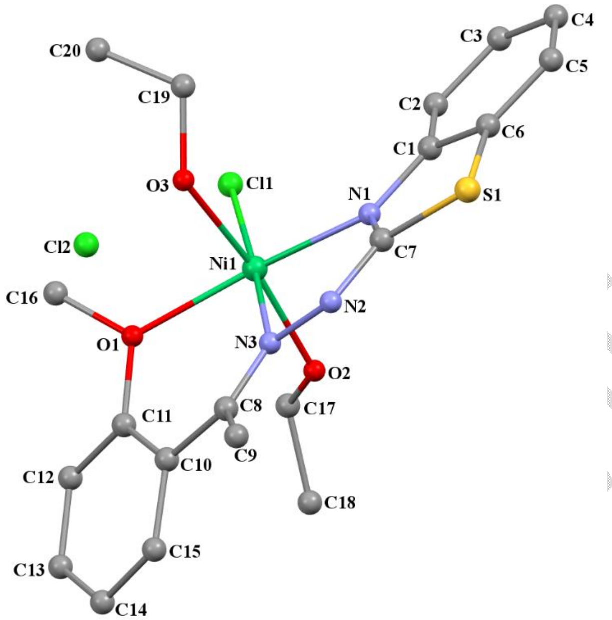


Figure 1. Crystal structure of the nickel(II) complex. H atoms are omitted for clarity.

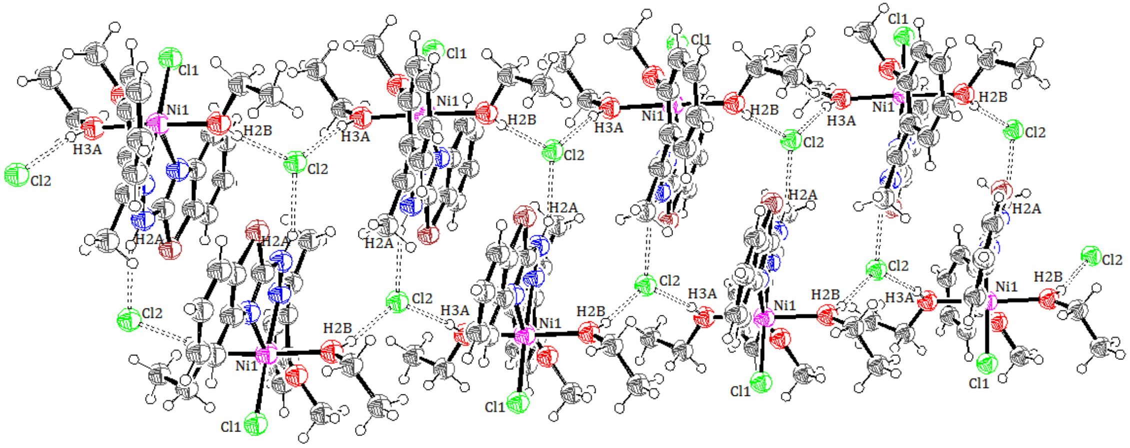


Figure 2. The packing of the compound in the crystal structure and hydrogen bonds

Table 4. Hydrogen-bond geometry (Å, °).

D—H···A	*D*—H	H···A	*D*···A	*D*—H···A
N2—H2A···Cl2	0.88	2.28	3.071(2)	149
O2—H2B···Cl2	0.84	2.23	3.055(2)	168
O3—H3A···Cl2	0.84	2.17	2.993(2)	167

C2—H2⋯Cl1	0.95	2.74	3.509(3)	139
C14—H14⋯Cl1	0.95	2.82	3.754(4)	169
C16—H16B⋯O3	0.98	2.60	3.143(4)	115

4. CONCLUSION

The reported work is concerned with the synthesis and the structural study of mononuclear complexes derived from the organic molecular ligand, *E*-1-(benzo[d]thiazol-2-yl)-2-(1-(2-methoxyphenyl)ethylidene)hydrazine. All the complexes are stable in DMF solution. The powders are characterized using analytical techniques such as elemental analysis, molar conductance, room temperature magnetic susceptibility as well as FTIR and UV-visible spectroscopies. The data obtained show that the complexes are isomorphous. Additionally, the structure of the nickel(II) complex was characterized by single crystal X-ray diffraction technique and the result confirms the structure proposed from analytical and spectroscopic data. In the solid state, the ligand acts in tridentate fashion, yielding an hexacoordinated metal ion. In all the synthetized complexes, the environments around the metal ions are best described as octahedral polyhedron.

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SUPPLEMENTARY MATERIALS

CCDC-2392509 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/ structures/, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (Telephone: +44–01223–762910; Fax: +44–1223–336033; or E-mail: deposit @ccdc.cam.ac.uk).

IN MEMORIAM

Dr. Cheikh Hamidou KANE 1963-2021 and Pr. Mouhamadou Moustapha SOW 1982-2022. KANE and SOW were highly talented and committed chemists. They were very involved in research and in supervising the work of students and PhD students. Their contribution is sorely missed by all our teams. This article is dedicated to their memory.