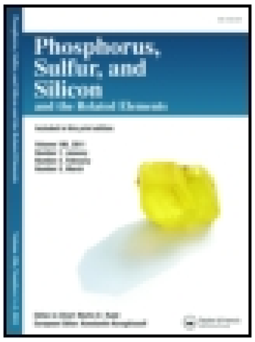


Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: https://www.tandfonline.com/loi/gpss20

Metal complexes with thioether containing unsymmetrical N_2S donor Schiff base ligand: Crystal and molecular structure of nickel(II) complex

Ahmad Ali Dehghani-Firouzabadi, Farzaneh Morovati & Behrouz Notash

To cite this article: Ahmad Ali Dehghani-Firouzabadi, Farzaneh Morovati & Behrouz Notash (2020): Metal complexes with thioether containing unsymmetrical N_2S donor Schiff base ligand: Crystal and molecular structure of nickel(II) complex, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2019.1709458

To link to this article: https://doi.org/10.1080/10426507.2019.1709458

PHOSPHORUS, SULFUR, AND SILICON AND THE RELATED ELEMENTS
https://doi.org/10.1080/10426507.2019.1709458

Metal complexes with thioether containing unsymmetrical N_2S donor Schiff base ligand: Crystal and molecular structure of nickel(II) complex

Ahmad Ali Dehghani-Firouzabadi[a], Farzaneh Morovati[a], and Behrouz Notash[b]

[a]Department of Chemistry, Faculty of Science, Yazd University, Yazd, Iran; [b]Chemistry Department, Shahid Beheshti University, G. C., Evin, Tehran, Iran

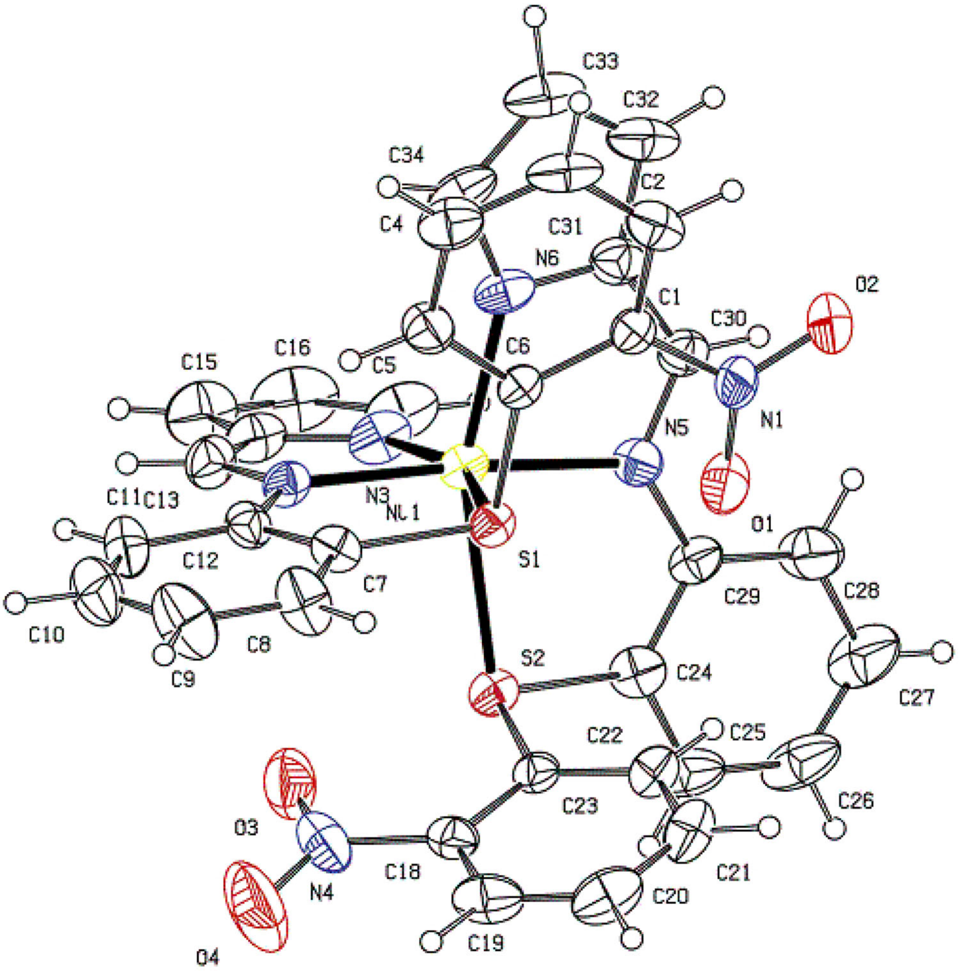
ABSTRACT

A thioether unsymmetrical N_2S donor Schiff base ligand, N-2-((2-nitrophenyl)thio)phenyl)-1-(pyrrole-2-yl)methanimine (HL) and its five complexes $[NiL_2]$, $[CuL_2]$, $[ZnHL(H_2O)_2(OAc)_2]$, $[CdHL(H_2O)_2(OAc)_2]\cdot 2H_2O$ and $[MnHL(H_2O)_2(OAc)_2]\cdot 2H_2O$ were synthesized. The ligand and metal complexes were characterized by spectroscopic methods (FT-IR, ^1H and ^{13}C NMR, UV–Vis), elemental analyses, mass spectrometry, and conductance measurements. Of these complexes, $[NiL_2]$ was structurally characterized by single-crystal X-ray crystallography. In this complex, two ligands function as monobasic N_2S tridentate and coordinate through pyrrole-N, thioether-S, and azomethine-N, and the nickel(II) is in distorted octahedral environments.

ARTICLE HISTORY
Received 13 August 2019
Accepted 23 December 2019

KEYWORDS
Tridentate ligand; NNS donor; unsymmetrical ligand; pyrrole-2-carboxaldehyde; Schiff base complexes

GRAPHICAL ABSTRACT



CONTACT Ahmad Ali Dehghani-Firouzabadi aadehghani@yazd.ac.ir Department of Chemistry, Faculty of Science, Yazd University, 89195-741 Yazd, Iran.
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gpss.
Supplemental data for this article is available online at https://doi.org/10.1080/10426507.2019.1709458.

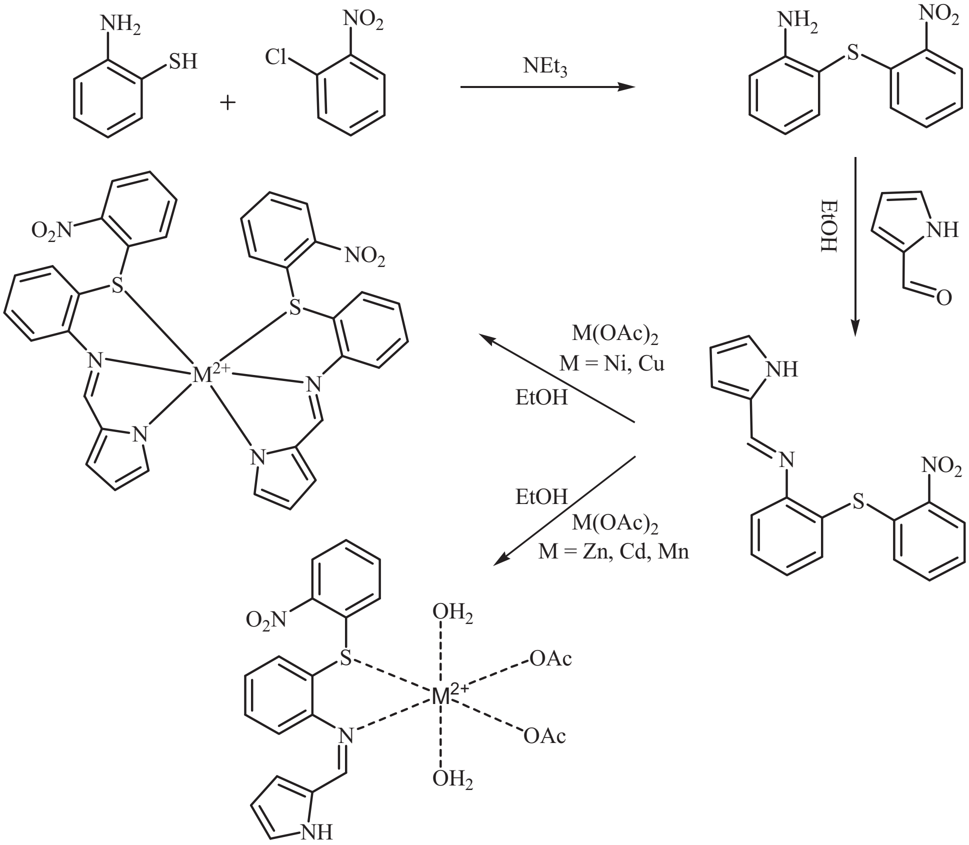
Introduction

One of the traditional methods of synthesizing ligands and their complexes is the Schiff base method, and Schiff bases have been known since 1864 when Hugo Schiff reported the condensation of primary amines with carbonyl compounds.[1,2] By this method, ligands and complexes can be synthesized in different classes, such as macrocyclic and macroacyclic, symmetrical and unsymmetrical, neutral and ionic, hard and soft and hard-soft donors, flexible and nonflexible and di- up to multi-dentate.[3–13] The synthesis of ligands containing a Schiff base and their complexes is very broad due in part to their potential interest for the chemistry, biochemistry, material science and hydrometallurgy, activation and catalysis.[14,15] Also, syntheses of Schiff base ligands with specific properties as mentioned above are important in bioinorganic chemistry, catalysis, and medical chemistry.[16–18] Interest in thioether tridentate unsymmetrical Schiff base ligands with flexibility and hard-soft donating sites in coordination chemistry has increased. The reason for this increase is due to their ability to form stable four-, five-, and six-coordinated complexes and they have been found to possess a wide range of biological properties.[19–25] Tridentate ligands L can provide metal complexes with ML or ML_2 stoichiometry. Also, tridentate ligands can bind to metal centers in complexes through two or three donor atoms per metal center (bidentate or tridentate).[21,22,25] We report here the preparation and characterization of a new unsymmetrical and flexible tridentate N_2S donor Schiff base ligand derived from pyrrole-2-carboxaldehyde, 2-mercaptoaniline, and 2-nitrochlorobenzene. Ni(II), Cu(II), Zn(II), Cd(II) and Mn(II) complexes of this ligand were synthesized and characterized. The complexation reaction of manganese(II), cadmium(II) and zinc(II) acetate with this N_2S ligand gave complexes with a metal:ligand ratio 1:1, whereas nickel(II) and copper(II) acetate with this ligand gave a complex with a metal:ligand ratio 1:2. Of these complexes, $[NiL_2]$ was structurally characterized by single-crystal X-ray crystallography. In this complex, two ligands function as monobasic N_2S tridentate and coordinate through pyrrole-N, thioether-S, and azomethine-N. The single-crystal X-ray structure of $[NiL_2]$ shows the nickel ion to be in a distorted octahedral N_4S_2 environment.

Results and discussion

Synthesis

The 2-((nitrophenyl)thio)aniline was obtained according to Scheme 1 in 92% yield, using triethylamine as a base, by a modification of a method previously reported for this synthesis.[11,12] The Schiff base ligand, N-2-((2-nitrophenyl)thio)phenyl)-1-(pyrrole-2-yl)methanimine (HL) was prepared from condensation of 2-((nitrophenyl)thio)aniline and pyrole-2-carbaldehyde. Since the formation of the Schiff base is a reversible reaction and these are sensitive to moisture and decompose when exposed to air and water, this ligand (HL) is unstable (sensitive to moisture) and return to the initial material. The syntheses of complexes $[NiL_2]$ and $[CuL_2]$ were carried out *via* [1 + 2] condensation of HL with



Scheme 1. Synthesis of the ligand (HL) and related complexes.

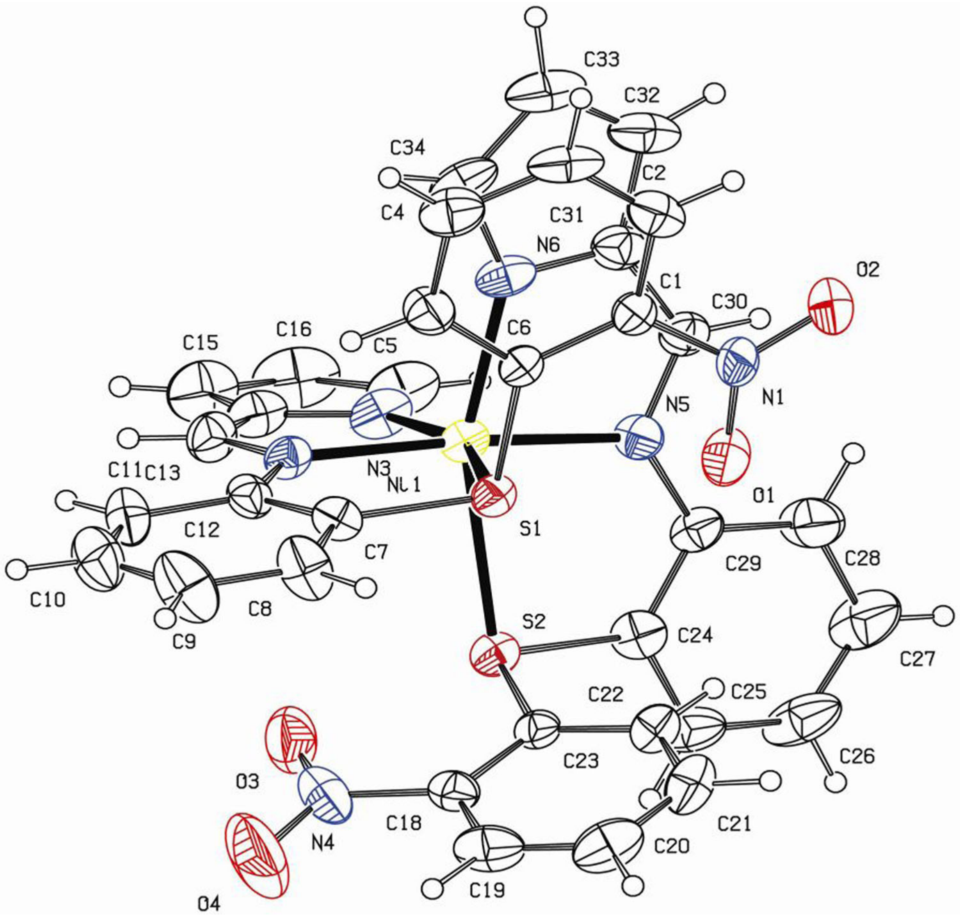


Figure 1. Molecular structure of [NiL_2] showing 50% displacement ellipsoids.

nickel(II) and/or copper(II) acetate in ethanol. Other complexes were carried out via [1 + 1] condensation of HL with metal(II) acetate in ethanol. The Schiff base ligand and complexes have been characterized by appropriate spectroscopic methods such as elemental analyses, IR and EI mass spectrometry. These complexes are air stable solids and have elemental analyses consistent with the formulations given in the Experimental section.

FT-IR spectra

In the FT-IR spectrum for the ligand (HL), a broad peak at 3374 cm^{-1}, strong peaks at 1610, 729 cm^{-1} and 1509, 1300 cm^{-1} are assigned to the N-H, C = N, C-S and NO_2 stretching vibration respectively. In the FT-IR spectra of Ni(II), Cu(II), Zn(II), Cd(II) and Mn(II) complexes, the bands in the range of 1591–1613 cm^{-1} are associated with the imine vibration. Also, the vibration peaks of the nitro group are observed in the range of 1506–1509 cm^{-1} and 1299–1303 cm^{-1}. The shifted $\nu_{\text{C-S}}$ of the corresponding ligands in complexes, found in the ranges 741–755 cm^{-1}, indicate the thioether S coordinated to the metal ions.[11] In the IR spectra of Zn(II), Cd(II), and Mn(II) complexes, the vibration peaks of H_2O (3470, 3480, 3440 cm^{-1}, respectively, and broad peak at 3000–3500 cm^{-1} for Cd(II) and Mn(II)), N-H (3369–3373 cm^{-1}) and acetate ion (1409–1411, 1647–1649 cm^{-1}) are observed. In the Zn(II) Cd(II) and Mn(II) complexes, the $\Delta\nu$ for the acetate (ν_{asym}(COO)-ν_{sym}(COO)) is more than 200 cm^{-1}, indicating that the acetate is a unidentate ligand.[26]

NMR studies

The ^{1}H NMR and ^{13}C NMR data of the ligand (HL) dissolved in $CDCl_3$ is shown in the Experimental Section. Due to the instability of the ligand (HL) and decomposition to the initial material (sensitive to moisture), the ^{1}H and ^{13}C NMR spectra are accompanied by impurities. The ^{1}H NMR spectrum of the ligand (HL) exhibit a singlet resonance at 8.06 ppm, which has been assigned to the imine resonance. The aromatic rings protons appeared in the region of 6.82–8.25 ppm and the significant signal with 4.52 ppm is assigned to the NH group. In the ^{13}C NMR spectrum of the ligand (HL), the HC = N carbon resonance is observed in the 154.8 ppm and the resonances for the aromatic carbons are observed in the region 119.3–150.9 ppm.

Electronic and mass spectra

The UV-Vis spectrum for 0.001 M solutions of the ligand (HL) in DMF exhibits two absorption bands at 280 nm and 350 nm, which these bands can be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.[27] The UV-Vis spectra for 0.001 M solutions of complexes in DMF exhibit bands at 280 to 285 nm

Table 1. Crystallographic and structure refinements data for [NiL_2].

Complex	[NiL_2]
Empirical formula	$C_{34}H_{24}N_6NiO_4S_2$
Formula weight	703.40
Temperature (K)	298(2)
Wavelength λ (Å)	0.71073
Crystal system	Monoclinic
Space group	P 21/n
a (Å)	10.753(2)
b (Å)	18.552(4)
c (Å)	16.158(3)
α (°)	90
β (°)	99.45(3)
γ (°)	90
Volume (Å)^3	3179.6(11)
Z, Calculated density (Mg/m^3)	4, 1.469
Absorption coefficient (mm^{-1})	0.791
F(000)	1448
Crystal size (mm)	0.50 × 0.25 × 0.15
Theta range for data collection (°)	2.39 to 25.00
Limiting indices	$-11 \leq h \leq 12$ $-22 \leq k \leq 22$ $-19 \leq l \leq 19$
Reflections collected/unique	16593/5592 [R(int) = 0.1303]
Completeness to theta	99.9%
Absorption correction	Numerical
Max. and min. transmission	0.8906 and 0.6932
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5592/0/424
Goodness-of-fit on F^2	0.974
Final R indices [I > 2sigma(I)]	R1 = 0.0639, wR2 = 0.1146
R indices (all data)	R1 = 0.1345, wR2 = 0.1389
Largest diff. peak and hole (eÅ^{-3})	0.345 and −0.307

corresponding to $\pi \rightarrow \pi^*$ transitions and show bands at 345 to 375 nm corresponding $n \rightarrow \pi^*$ and/or charge transfer transitions. In general, the electronic transitions for Zn(II), Cd(II) (d^{10}) and Mn(II) (d^5 high spin) complexes are spin-forbidden and hence cannot be observed. Complex Cu(II) shows only one band at 650 nm and the Ni(II) complex shows bands at 580 nm and 720 nm corresponds to $d \rightarrow d$ transition.[11,28]

The EI mass spectrum of the ligand (HL), provide strong evidence for the formation of this compound and exhibit peak at the higher molecular weight. The molecular weights peak in the spectra of ligand (HL), Ni(II) and Cu(II) complexes are observed at m/z 323, 703 and 707, respectively. The peaks in the spectra of the Zn(II) and Cd(II) complexes are observed at m/z 537 and 592 corresponding to $[ZnHL(H_2O)_2(OAc)_2\text{-}4H]^+$ and $[CdHL(H_2O)_2(OAc)_2{+}H]^+$, respectively. The spectra for the Zn(II), Cd(II) and Mn(II) complexes contains peaks due to different fragmentation species, including 464 $[ZnHL(H_2O)(OAc)]^+$, 423 $[ZnHL(H_2O)_2]^+$, 555 $[CdHL(OAc)_2]^+$, 473$[CdHL(H_2O)_2]^+$, 496 $[MnHL(OAc)_2]^+$, 437 $[MnHL(OAc)]^+$, 414 $[MnHL(H_2O)_2]^+$.

Conductance measurements and elemental analysis

Table 2. Hydrogen bonds (Å and deg) for [NiL_2].

D-H … A	d(H … A) (Å)	d(D … A) (Å)	<(DHA) (deg)
C(11)-H(11) … O(3)	2.488	3.315	148.2
C(16)-H(16) … O(1)	2.668	3.557	160.1
C(16)-H(16) … O(2)	2.696	3.545	152.3

Molar conductivity data for ligand (HL) and complexes measured at room temperature using DMF as solvent (1×10^{-3} mol dm^{-3}) fall in the range 2.7–28.1 Ω^{-1} cm^2 mol^{-1}. These obtained values of the molar conductance are well within the expected range for non-electrolytes.[29] Also, the elemental analysis data for these complexes were accord in all cases in good agreement with the above molecular formula. These values are indicative of the different coordinative capacity. In Ni(II) and Cu(II) complexes, it showed that the Schiff base ligand acts as monobasic and NNS-tridentate in the 1:2 complex. Also, in the Zn(II), Cd(II) and Mn(II) complexes, it showed that the Schiff base ligand acts as neutral and NS-bidentate in the 1:1 complex.

X-ray crystallography

Single crystals of nickel(II) complex were prepared by slow evaporation of a dichloromethane/acetonitrile (1:1) solution of this complex. Then, the structure of Ni(II) complex was determined by single crystal X-ray diffraction method. The thermal ellipsoid plot of [NiL_2] is shown in Figure 1. The details of the X-ray crystal data, and the structure resolution and refinement, are given in Table 1. Selected bond lengths and bond angles are shown in supplemental materials Table S1. The complex [NiL_2] is monoclinic and crystallizes in the space group P 21/n with Z = 4 (supplemental materials Figure S1). The molecular structure of the complex has a distorted octahedral geometry around the Ni(II) center, as can be judged from spread in its observed angles [78.41(13)–104.20(14)°] and the trans angles [159.49(16)–174.28(17)°], by two Schiff base anion ligands. Each of the Schiff base ligands loses one hydrogen atom and coordinates to the metal ion through the imine N atom, the pyrrole N and the thioether S atom. The bond lengths found in the structure are within the normal ranges for this geometry (longest bond length of Ni-S 2.5919(16) Å and Ni-N 2.061(4) Å). In this complex, the pyrrole N atom of the Schiff base ligand and the thioether S atom of another Schiff base ligand are trans coordinated with a bond angle of 159.49(16) and 159.65(16)° and the imine N atoms of both Schiff base ligands are trans coordinated with a bond angle of 174.28(17)°. The Ni(1)-N(3) and Ni(1)-N(6) (the pyrrole N atom) bond lengths [2.015(5) Å and 2.017(5) Å, respectively] are shorter than Ni(1)-N(2) and Ni(1)-N(5) (the imine N atom) bond lengths [2.055(5) Å and 2.061(4) Å, respectively]. Crystal packing structure of the complex is stabilized by intermolecular hydrogen-hydrogen, hydrogen-carbon, and hydrogen bonding interactions. Each molecule in [NiL_2] is involved in intermolecular hydrogen bonding interactions between the hydrogens of the aromatic carbon atoms (H11 and H16) of a molecule with the NO_2 groups (O1, O2, O3) of another molecules [H(11) … O(3), 2.488 Å, H(16) … O(1), 2.668 Å, H(16) … O(2), 2.696 Å] (Table 2 and Figure 2).

Experimental

Materials and physical measurements

All the starting materials and solvents for syntheses were used as received from Merck or Aldrich Chemical Co. Inc.

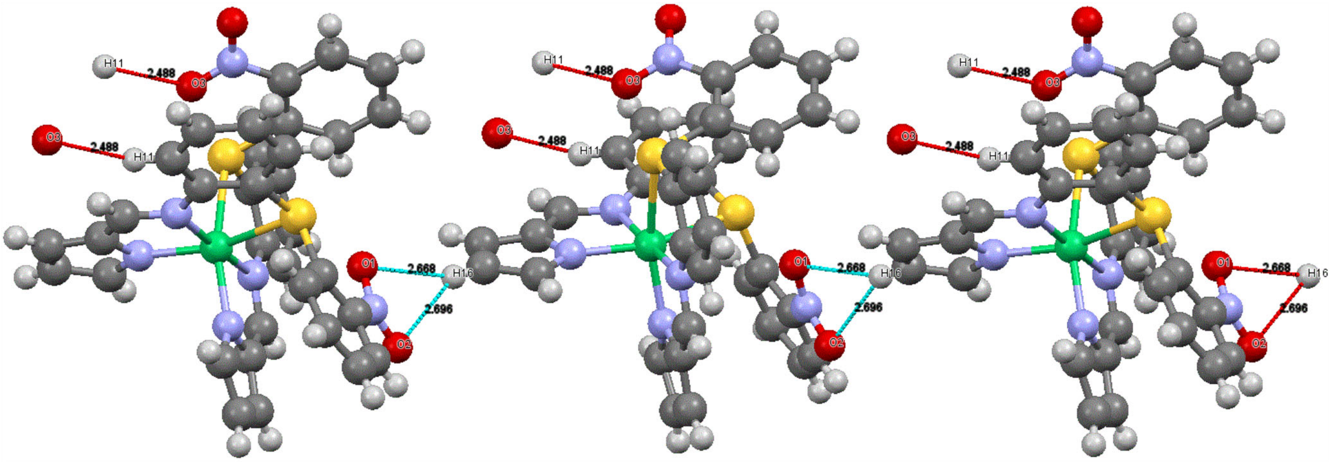


Figure 2. View of the crystal packing of [NiL_2] in the c-direction. Dashed lines indicate hydrogen bonds.

Carbon, Hydrogen, Nitrogen microanalyses were performed in a CHNS-O-2400 II Perkin-Elmer. UV–Vis spectra were measured on a GBC UV-Visible Cintra 101 spectrophotometer and FT-IR spectra were recorded in ATR, with Bruker FT-IR Equinax-55 spectrophotometer (4000–400 cm^{-1}). Mass spectra were obtained using a QP-1100EX Shimadzu GC–MS (EI at 70 eV). The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC-400 NMR spectrometer using TMS as an internal standard. Conductance measurements of ca. 10^{-3} mol dm^{-3} solutions in DMF at 25 °C were measured by means of a Metrohm 660 conductometer

X-ray crystal structure determination

Red crystals of [NiL_2] were obtained by slow evaporation from dichloromethane/acetonitrile (1:1) solution of this complex. The X-ray diffraction data were recorded on an STOE IPDS-II diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A red block shape crystal with dimensions $0.50 \times 0.25 \times 0.15$ mm was applied for data collection. Cell parameters and an orientation matrix for data collection were refined by the least-squares refinement of the diffraction data from 5592 unique reflections. Data were collected at a temperature of 298(2) K to a maximum 2θ value of 50.00° and in a series of ω scans in 1° oscillation and integrated using the Stoe X-AREA software package.[30] The numerical absorption coefficient, μ, for Mo Kα radiation is 0.791 mm^{-1}. Numerical absorption correction was applied using X-RED and X-SHAPE software.[31,32] All data were corrected for Lorentz and polarization effects. The crystal structure was solved by direct methods and subsequent difference Fourier maps and then refined by full-matrix least-squares procedure on F^2 values for all unique data.[33] All non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were included at estimated positions. Subsequent refinement then converged with R factors. Atomic factors are from the International Tables for X-ray Crystallography.[34] All refinements were performed using the X-STEP 32 crystallographic software package.[35] The details of data collection, refinement and crystallographic data are summarized in Table 1.

Synthesis

Synthesis of the N-2-((2-nitrophenyl)thio)phenyl)-1-(pyrrole-2-yl)methanimine (HL)

The 2-((nitrophenyl)thio)aniline was prepared by a modification procedure of our other works.[11,12] The dissolved 2-((nitrophenyl)thio)aniline (1.23 g, 5 mmol) in absolute ethanol (20 mL) was added to a refluxing solution of pyrrole-2-carboxaldehyde (0.48 g, 5 mmol) in the same solvent (5 mL). After refluxing for 8 h, the solution was vacuum evaporated to yield the crude product as a brown oil. The product was rubbed with diethyl ether and n-hexane. The product (HL) was separated in brown oil (Scheme 1). Yield: 1.24 g, 77%; UV-Vis in DMF (λ, nm) 280, 350; IR (ATR, cm^{-1}) 3374 ν(N-H); 1610 ν(C = N); 1509, 1300 $\nu(NO_2)$; 729 ν(C-S); ^{1}H NMR ($CDCl_3$, ppm): δH 4.52 (1H s) 6.82 (1H, d), 6.91 (1H, t), 7.11 (1H, t), 7.15 (1H, d), 7.22 (1H, t), 7.28 (1H, t), 7.34 (1H, d), 7.45 (1H, d), 7.53 (1H, t), 7.61 (1H, d), 8.06 (1H, s), 8.25 (1H, d); ^{13}C NMR ($CDCl_3$, ppm): δC 119.3, 124.1, 125.2, 125.5, 126.2, 127.3, 129.1, 131.8, 132.5, 133.3, 133.9, 136.6, 137.9, 145.1, 149.7, 150.9, 154.8; Anal. Calc. for $C_{17}H_{13}N_3O_2S$: C, 63.14; H, 4.05; N, 12.99%. Found: C, 62.76; H, 4.13; N, 12.75%; EI MS (m/z, M^+): 323 $[HL]^+$; Λ_m (DMF) 2.9 Ω^{-1} cm^2 mol^{-1}.

General synthesis of the complexes

The dissolved 2-((nitrophenyl)thio)aniline (0.49 g, 2 mmol) in absolute ethanol (10 mL) was added to a refluxing solution of pyrrole-2-carboxaldehyde (0.19 g, 2 mmol) in the same solvent (5 mL). After refluxing for 8 h, a solution of $M(OAc)_2$ (M = Ni, Cu, Zn, Cd, Mn) (1 mmol) in ethanol (20 mL) was added dropwise to a refluxing solution, and the reaction mixture was refluxed for 1 h. For the Ni(II) and Cu(II) complexes, the solution was then concentrated in a rotary evaporator to *ca.* 5–10 mL, the solid product filtered off and crystallized in the CH_3CN/CH_2Cl_2 (1:1). For other complexes, the solution was vacuum evaporated to yield the crude product. Petroleum benzene (2×10 mL) was added to the residue remaining in the flask and rubbed. Then, the liquid was decanted, and the residue solution was evaporated until a powder remained (Scheme 1).

[NiL_2]. UV-Vis in DMF (λ, nm) 285, 350, 580, 720; IR (ATR, cm^{-1}) 1591 ν(C = N); 1506, 1303$\nu(NO_2)$; 750 ν(C-S);

EI MS (m/z, M^+): 703 $[NiL_2]^+$; Anal. Calc. for $C_{34}H_{24}N_6NiO_4S_2$: C, 58.00; H, 3.72; N, 11.83%. Found: C, 58.06; H, 3.44; N, 11.95%; Λ_m (DMF) 5.7 Ω^{-1} cm^2 mol^{-1}.

[CuL$_2$]. UV-Vis in DMF (λ, nm) 280, 345, 650; IR (ATR, cm^{-1}) 1613 ν(C=N); 1509, 1302 $\nu(NO_2)$; 747 ν(C-S); EI MS (m/z, M^+): 707 $[CuL_2]^+$; Anal. Calc. for $C_{34}H_{24}CuN_6O_4S_2$: C, 57.64; H, 3.49; N, 11.80%. Found: C, 57.66; H, 3.42; N, 11.87%; Λ_m (DMF) 4.3 Ω^{-1} cm^2 mol^{-1}.

[ZnHL(H$_2$O)$_2$(OAc)$_2$]. UV-Vis in DMF (λ, nm) 280, 345; IR (ATR, cm^{-1}) 3470 $\nu(H_2O)$; 3372 ν(N-H); 1409, 1648 ν(OAc); 1610 ν(C=N); 1509, 1299 $\nu(NO_2)$; 741 ν(C-S); EI MS (m/z, M^+): 537 $[ZnHL(H_2O)_2(OAc)_2\text{-}4H]^+$, 464 $[ZnHL(H_2O)(OAc)]^+$, 423 $[ZnHL(H_2O)_2]^+$; Anal. Calc. for $C_{21}H_{23}N_3O_8SZn$: C, 45.59; H, 4.18; N, 7.25%. Found: C, 46.46; H, 4.27; N, 7.74%; Λ_m (DMF) 2.7 Ω^{-1} cm^2 mol^{-1}.

[CdHL(H$_2$O)$_2$(OAc)$_2$]·2H$_2$O. UV-Vis in DMF (λ, nm) 280, 370; IR (ATR, cm^{-1}) 3480, 3000–3500 $\nu(H_2O)$; 3369 ν(N-H); 1409, 1647 ν(OAc); 1611 ν(C=N); 1508, 1302 $\nu(NO_2)$; 755 ν(C-S); EI MS (m/z, M^+): 592$[CdHL(H_2O)_2(OAc)_2+H]^+$, 555 $[CdHL(OAc)_2]^+$, 473$[CdHL(H_2O)_2]^+$; Anal. Calc. for $C_{21}H_{27}CdN_3O_{10}S$: C, 40.04; H, 3.83; N, 5.70%. Found: C, 40.30; H, 4.35; N, 6.71%; Λ_m (DMF) 3.2 Ω^{-1} cm^2 mol^{-1}.

[MnHL(H$_2$O)$_2$(OAc)$_2$]·2H$_2$O. UV-Vis in DMF (λ, nm) 280, 375; IR (ATR, cm^{-1}) 3440, 3000–3500 $\nu(H_2O)$; 3373 ν(N-H); 1411, 1649 ν(OAc); 1610 ν(C=N); 1508, 1300 $\nu(NO_2)$; 744 ν(C-S); EI MS (m/z, M^+): 496 $[MnHL(OAc)_2]^+$, 437 $[MnHL(OAc)]^+$, 414 $[MnHL(H_2O)_2]^+$; Anal. Calc. for $C_{21}H_{27}MnN_3O_{10}S$: C, 42.51; H, 7.32; N, 4.41%. Found: C, 42.94; H, 7.15; N, 3.95%; Λ_m (DMF) 28.1 Ω^{-1} cm^2 mol^{-1}.

Conclusion

In this paper, we have successfully designed and synthesized the N_2S unsymmetrical tridentate Schiff base ligand (HL) containing NO_2 group and hard-soft donors. This ligand can form neutral and anionic complexes and can be bonded to metal centers in complexes through two or three donor atoms per metal center (bidentate or tridentate). Also, nickel(II), copper(II), zinc(II), cadmium(II) and manganese(II) complexes with this ligand were prepared and characterized by appropriate spectroscopic methods. Molecular structure of $[NiL_2]$ was determined by single crystal X-ray crystallography and showed distorted octahedral geometry about metal center.

Funding

We are grateful to the Faculty of Chemistry of Yazd University and the Ministry of Science, Research and Technology of Iran, for financial support.

ORCID

Ahmad Ali Dehghani-Firouzabadi http://orcid.org/0000-0003-1658-4322

References

[1] Schiff, H. A New Series of Organic Bases. *Ann. Chem. Pharm.* **1864**, *131*, 118–119.

[2] Xiang, L.; Jean-Rene, H. Recent Developments in Penta-, Hexa- and Heptadentate Schiff Base Ligands and Their Metal Complexes. *Coord. Chem. Rev.* **2019**, *389*, 94–118. DOI: 10.1016/j.ccr.2019.03.010.

[3] Keypour, H.; Dehghani-Firouzabadi, A. A.; Rezaeivala, M.; Salehzadeh, S. Synthesis of a New Heteropolytopic Cryptand through Schiff Base Condensation in the Presence of Ba (II) Ion. *Synthetic Comm.* **2009**, *39*, 1136–1142. DOI: 10.1080/00397910802513037.

[4] Keypour, H.; Dehghani-Firouzabadi, A. A.; Rezaeivala, M.; Goudarziafshar, H. Synthesis and Characterization of Cd (II) Macrocyclic Schiff Base Complex with Two 2-Aminoethyl Pendant Arms. *JICS.* **2010**, *7*, 820–824. DOI: 10.1007/BF03246074.

[5] Spence, J. T. Modeling the Molybdenum Centers of the Molybdenum Hydroxylases. *Coord. Chem. Rev.* **1983**, *48*, 59–82. DOI: 10.1016/0010-8545(83)85002-4.

[6] Gupta, S.; Barik, A. K.; Pal, S.; Hazra, A.; Roy, S.; Butcher, R. J.; Kar, S. K. Oxomolybdenum (VI) and (IV) Complexes of Pyrazole Derived ONO Donor Ligands–Synthesis, Crystal Structure Studies and Spectroelectrochemical Correlation. *Polyhedron* **2007**, *26*, 133–141. DOI: 10.1016/j.poly.2006.08.001.

[7] Devi, J.; Kumari, S.; Asijaa, S.; Malhotra, R. Synthetic, Spectroscopic, and Biological Aspects of Triorganosilicon (IV) Complexes of Tridentate Schiff Bases. *Phosphorus, Sulfur Silicon Relat. Elem.* **2012**, *187*, 1409–1417. DOI: 10.1080/10426507.2012.686546.

[8] Keypour, H.; Dehghani-Firouzabadi, A. A.; Khavasi, H. R. Synthesis and Characterization of Three Heptaaza Manganese (II) Macrocyclic Schiff Base Complexes Containing Two 2-Pyridylmethyl Pendant Arms. *Transition Met. Chem.* **2011**, *36*, 307–311. DOI: 10.1007/s11243-011-9470-6.

[9] Dehghani-Firouzabadi, A. A.; Kargar, H.; Eslaminejad, S.; Notash, B. Synthesis and Characterization of a Thioether Schiff Base Ligand and Its Metal Complexes and Crystal Structure Determination of the Nickel (II) Complex. *J. Coord. Chem.* **2015**, *68*, 4345–4354. DOI: 10.1080/00958972.2015.1091925.

[10] Dehghani-Firouzabadi, A. A.; Motevaseliyan, F. Synthesis and Characterization of Four New Unsymmetrical Potentially Pentadentate Schiff Base Ligands and Related Zn (II) and Cd (II) Complexes. *Eur. J. Chem.* **2014**, *5*, 635–638. DOI: 10.5155/eurjchem.5.4.635-638.1131.

[11] Dehghani-Firouzabadi, A. A.; Sobhani, M.; Notash, B. Synthesis and Characterization of Metal Complexes with NOS Unsymmetrical Tridentate Schiff Base Ligand. X-Ray Crystal Structures Determination of Nickel(II) and Copper(II) Complexes. *Polyhedron* **2016**, *119*, 49–54. DOI: 10.1016/j.poly.2016.08.021.

[12] Dehghani-Firouzabadi, A. A.; Sepehri, S.; Notash, B. Synthesis and Characterization of Metal Complexes of a New Unsymmetrical Tridentate NNS Schiff Base Ligand: X-Ray Crystal Structure Determination of Nickel(II) Complex. *J. Chin. Chem. Soc.* **2017**, *64*, 1104–1110. DOI: 10.1002/jccs.201700068.

[13] Dehghani-Firouzabadi, A. A.; Firouzmandi, S. Synthesis and Characterization of a New Unsymmetrical Potentially Pentadentate Schiff Base Ligand and Related Complexes with Manganese(II), Nickel(II), Copper(II), Zinc(II) and Cadmium(II). *J. Braz. Chem. Soc.* **2017**, *28*, 768–774. DOI: 10.21577/0103-5053.20160226.

[14] Vigato, P. A.; Tamburini, S. The Challenge of Cyclic and Acyclic Schiff Bases and Related Derivatives. *Coord. Chem. Rev.* **2004**, *248*, 1717–2128. DOI: 10.1016/j.cct.2003.09.003.

[15] Dolega, A. Alcohol Dehydrogenase and Its Simple Inorganic Models. *Coord. Chem. Rev.* **2010**, *254*, 916–937. DOI: 10.1016/j.ccr.2009.12.039.

[16] Harrop, T. C.; Mascharak, P. K. Fe (III) and Co (III) Centers with Carboxamido Nitrogen and Modified Sulfur Coordination:

lessons Learned from Nitrile Hydratase. *Acc. Chem. Res.* **2004**, *37*, 253–260. DOI: 10.1021/ar0301532.

[17] Kwong, H. L.; Yeung, H. L.; Yeung, C. T.; Lee, W. S.; Lee, C. S.; Wong, W. L. Chiral Pyridine-Containing Ligands in Asymmetric Catalysis. *Coord. Chem. Rev.* **2007**, *251*, 2188–2222. DOI: 10.1016/j.ccr.2007.03.010.

[18] Saghatforoush, L. A.; Chalabian, F.; Aminkhani, A.; Karimnezhad, G.; Ershad, S. Synthesis, Spectroscopic Characterization and Antibacterial Activity of New Cobalt (II) Complexes of Unsymmetrical Tetradentate (OSN_2) Schiff Base Ligands. *Eur. J. Med. Chem.* **2009**, *44*, 4490–4495. DOI: 10.1016/j.ejmech.2009.06.015.

[19] Brand, U.; Vahrenkamp, H. Zinc Complexes of the New N, N, S Ligand N-(2-Mercaptoisobutyl)(Picolyl) Amine. *Inorg. Chim. Acta* **2000**, *308*, 97–102. DOI: 10.1016/S0020-1693(00)00220-6.

[20] Zhang, C.; Guzei, I. A.; Espenson, J. H. Synthesis, Structure, and Catalytic Reactivity of N, N, S-and O, N, S-Tridentate Oxorhenium (V) complexes. *Inorg. Chem.* **2001**, *40*, 2437–2438. DOI: 10.1021/ic001087s.

[21] Balamurugan, R.; Palaniandavar, M.; Stoeckli-Evans, H.; Neuburger, M. Axial versus Equatorial Coordination of Thioether Sulfur: Mixed Ligand Copper(II) Complexes of 2-pyridyl-N-(2′-Methylthiophenyl)-Methyleneimine with Bidentate Diimine Ligands. *Inorg. Chim. Acta* **2006**, *359*, 1103–1113. DOI: 10.1016/j.ica.2005.09.062.

[22] Alaghaz, A. M. A.; Zayed, M. E.; Alharbi, S. A.; Ammar, R. A. A.; Chinnathambi, A. Synthesis, Spectroscopic Identification, Thermal, Potentiometric and Antibacterial Activity Studies of 4-Amino-5-mercapto-S-Triazole Schiff's Base Complexes. *J. Mol. Struct.* **2015**, *1087*, 60–67. DOI: 10.1016/j.molstruc.2015.01.035.

[23] Zimmerman, J. R.; Smucker, B. W.; Dain, R. P.; Van Stipdonk, M. J.; Eichhorn, D. M. Tridentate N2S Ligand from 2,2′-Dithiodibenzaldehyde and N,N-Dimethylethylenediamine: Synthesis, Structure, and Characterization of a Ni(II) Complex with Relevance to Ni Superoxide Dismutase. *Inorg. Chim. Acta* **2011**, *373*, 54–61. DOI: 10.1016/j.ica.2011.03.052.

[24] Ghosh, M.; Layek, M.; Fleck, M.; Saha, R.; Bandyopadhyay, D. Synthesis, Crystal Structure and Antibacterial Activities of Mixed Ligand Copper (II) and Cobalt (II) Complexes of a NNS Schiff Base. *Polyhedron* **2015**, *85*, 312–319. DOI: 10.1016/j.poly.2014.08.014.

[25] Biswas, S.; Sarkar, D.; Kundu, S.; Roy, P.; Mondal, T. K. Rhodium (III)-Triphenylphosphine Complex with NNS Donor Thioether Containing Schiff Base Ligand: Synthesis, Spectra, Electrochemistry and Catalytic Activity. *J. Mol. Struct.* **2015**, *1099*, 297–303. DOI: 10.1016/j.molstruc.2015.06.065.

[26] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; John Wiley & Sons: New York, **1978**. DOI: 10.1002/0470027320.s4104.

[27] Khandar, A. A.; Cardin, C.; Hosseini-Yazdi, S. A.; McGrady, J.; Abedi, M.; Zarei, S. A.; Gan, Y. Nickel(II) and Copper(II) Complexes of Schiff Base Ligands Containing N_4O_2 and N_4S_2 Donors with Pyrrole Terminal Binding Groups: Synthesis, Characterization, X-Ray Structures, DFT and Electrochemical Studies. *Inorg. Chim. Acta* **2010**, *363*, 4080–4087. DOI: 10.1016/j.ica.2010.08.019.

[28] Chatterjee, S. K.; Roy, S.; Barman, S. K.; Maji, R. C.; Olmstead, M. M.; Patra, A. K. Shuttling of Nickel Oxidation States in N_4S_2 Coordination Geometry versus Donor Strength of Tridentate N_2S Donor Ligands. *Inorg. Chem.* **2012**, *51*, 7625–7635. DOI: 10.1021/ic300606g.

[29] Geary, W. J. The Use of Conductivity Measurements in Organic Solvents for the Characterisation of Coordination Compounds. *Coord. Chem. Rev.* **1971**, *7*, 81–122. DOI: 10.1016/S0010-8545(00)80009-0.

[30] Stoe & Cie, X-AREA, Version 1.30: *Program for the Acquisition and Analysis of Data*; Stoe & Cie GmbH: Darmstadt, Germany, **2005**.

[31] Stoe & Cie, X-RED, Version 1.28b: *Program for Data Reduction and Absorption Correction*; Stoe & Cie GmbH: Darmstadt, Germany, **2005**.

[32] Stoe & Cie, X-SHAPE, Version 2.05: *Program for Crystal Optimization for Numerical Absorption Correction*; Stoe & Cie GmbH: Darmstadt, Germany, **2004**.

[33] Sheldrick, G. M, SHELX-97: *Program for Crystal Structure Solution and Refinement*; University of Göttingen: Göttingen, Germany, **1997**.

[34] Lonsdale, K. *International Tables for X-Ray Crystallography*; Vol. C; Kluwer Academic Publisher: Doordrecht, The Netherlands, **1995**.

[35] Stoe&Cie, X-STEP32, Version 1.07b: *Crystallographic Package*; Stoe&Cie GmbH: Darmstadt, Germany, **2000**.