

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)

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New unsymmetric thioether Schiff base amine, 2-(2-aminoethylthio)-*N*-(thiophene-2-ylmethylene)aniline was prepared by reaction of 2-aminothiophenol with *N*-(2-bromoethyl)phthalimide and then by thiophene-2-carbaldehyde. Then, the phthalimide group converted to the amine by hydrazine hydrate. The new potentially pentadentate N₃S₂ donor unsymmetrical Schiff base ligand, 2-(2-(pyridine-2-ylmethyleneamino)ethylthio)-*N*-(thiophene-2-ylmethylene)aniline (L) was prepared via [1 + 1] condensation of pyridine-2-carbaldehyde with this amine. Manganese(II), nickel(II), copper(II), zinc(II) and cadmium(II) complexes of this ligand were prepared by adding metal salts to an ethanolic solution in this ligand. The thioether amine, ligand (L) and unsymmetric Schiff base complexes are characterized by the appropriate spectroscopic methods such as infrared (IR), UV-Vis, ¹H nuclear magnetic resonance (NMR), ¹³C NMR studies, X-ray, microanalysis and mass spectrometry.

Keywords: N₃S₂ donor, pentadentate ligand, unsymmetrical ligand, Schiff base complexes, thioether ligand

Introduction

Transition metal complexes with thioether Schiff base ligands have been prepared since the beginning of the development of coordination chemistry and there is continuing interest in these complexes.^{1,2} Sulfur atom coordinates to the metals through one (terminal) or both (bridging) of the lone pairs, the latter being less common. They usually form strong bonds with soft metals and more rarely with hard ones. They are considered both poor σ -donor and poor π -acceptor ligands, the latter involving the σ^* orbitals of the S–X bonds. This π -acceptor character can contribute to the M–S bond strength.³ The synthesis of transition metal complexes of unsymmetrical Schiff bases ligands with the hard and soft atom is an important area of study with implications in bioinorganic chemistry,⁴⁻⁶ catalysis⁷ and medical chemistry.⁸ Most of these unsymmetrical ligands and related complexes are Schiff bases obtained by the condensation of different types of amines with various ketones and aldehydes, and many of these in turn are multidentate ligands.^{5,9-13} Unsymmetrical linear pentadentate Schiff base ligands that have N₃S₂

donors or have thiophene and pyridine groups in their structure are very rare.

Here we report the synthesis of new unsymmetric linear pentadentate Schiff base ligand and their chelates with some transition metal ions, e.g., manganese(II), nickel(II), copper(II), zinc(II) and cadmium(II).

Experimental

Chemical and starting materials

2-Aminothiophenol, pyridine-2-carbaldehyde and thiophene-2-carbaldehyde were purchased from Merck and used as received. Other reagents and solvents were of analytical grade and purchased commercially.

Instrumentation

Elemental analyses were performed in a CHNS-O-2400 II PerkinElmer. Infrared spectra were recorded in ATR, using a Bruker FT-IR Equinax-55 spectrophotometer (4000-400 cm⁻¹). Mass spectrometry (MS) spectra were obtained using a QP-1100EX Shimadzu GC-MS (EI at 70 eV). ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were taken in CDCl₃ or DMSO-*d*₆

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on a Bruker NMR 500 and 400 MHz spectrometer using $\text{Si}(\text{CH}_3)_4$ as an internal standard. The electronic spectra were taken in GBC UV-Visible Cintra 101 spectrophotometer with 1 cm quartz, in the range of 200-1100 nm at 25 °C.

X-ray crystal structure determination

Single crystal of 2-(2-(2-((thiophene-2-yl)methyleneamino)phenylthio)ethyl) isoindoline-1,3-dione suitable for X-ray analyses was obtained by evaporation of ethanolic solution of the reaction mixture at 298 K. The details of the X-ray crystal data and of the structure solution and refinement are given in Table 1. The X-ray diffraction measurements were made on a STOE IPDS-2T diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 4873 unique reflections. The structure was solved by direct methods and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were located in their calculated positions and refined using a riding model.

Synthesis of the 2-(2-aminoethylthio)-*N*-(thiophene-2-ylmethylene)aniline

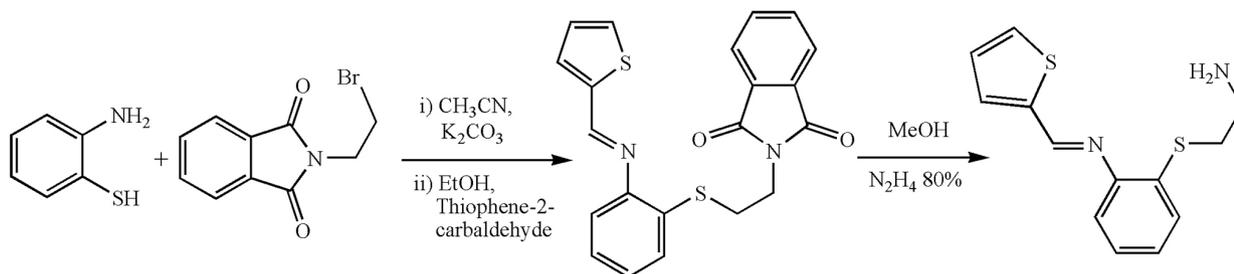
2-Aminothiophenol (6.25 g, 50 mmol) was dissolved in acetonitrile (40 mL) and K_2CO_3 (6.9 g, 50 mmol) was added. The mixture was refluxed and then a solution of *N*-(2-bromoethyl)phthalimide (12.65 g, 50 mmol) in acetonitrile (40 mL) was added. The mixture was refluxed for 8 h and then filtered hot.⁹ The filtrate was reduced to dryness by rotary evaporation. The resulting product was dissolved in ethanol (40 mL) and thiophene-2-carbaldehyde (5.6 g, 50 mmol) was added. After this time the solution was slowly evaporated to small volume (ca. 5 mL) and cooled in refrigerator for several hours. The crystals of 2-(2-(2-((thiophene-2-yl)methyleneamino)phenylthio)ethyl)isoindoline-1,3-dione were filtered off (Scheme 1). Infrared (IR) (ATR) ν / cm^{-1} 1769, 1707, 1610, 751. Then the methanol (50 mL) and hydrazine hydrate 80% (4 mL) was added. The mixture was refluxed for 8 h and cooled in refrigerator for several hours and then filtered. The methanol were removed by rotary evaporation to leave brown oil (Scheme 1). Yield: 7.3 g (56%). IR (ATR) ν / cm^{-1} 3340, 3172, 1607, 750; ^1H NMR (400.1 MHz, CDCl_3) δ 2.86 (s, 4H, CH_2CH_2), 2.9-3.2 (br, 2H, NH_2), 6.68-7.82 (m, 7H, Ar-H), 8.79 (s, 1H, $\text{CH}=\text{N}$); ^{13}C NMR (400.1 MHz, CDCl_3) δ 38.1, 40.8, 115.1, 115.2, 116.8, 118.6, 127.9, 130.1, 130.9, 131.7, 132.6, 148.5, 155.8; EI-MS m/z , calcd. for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{S}_2$ $[\text{M}]^+$: 262.39, found: 262.

Table 1. Crystal data and structure refinement for 2-(2-(2-((thiophene-2-yl)methyleneamino)phenylthio)ethyl)isoindoline-1,3-dione

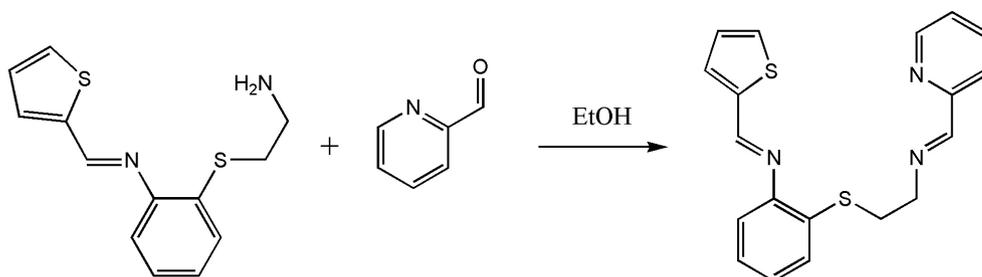
Empirical formula	$\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S}_2$
Formula weight	392.50
Temperature / K	120(2)
Wavelength / \AA	0.71073
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	$a = 7.4333(15) \text{ \AA}$ $\alpha = 90^\circ$ $b = 10.782(2) \text{ \AA}$ $\beta = 94.57(3)^\circ$ $c = 22.656(5) \text{ \AA}$ $\gamma = 90^\circ$
Volume / \AA^3	1810.0(6)
Z, calculated density / (mg m^{-3})	4, 1.440
Absorption coefficient / mm^{-1}	0.314
$F(000)$	816
Crystal size / mm	$0.43 \times 0.4 \times 0.2$
Theta range for data collection / degree	2.09 to 29.15
Limiting indices	$-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-31 \leq l \leq 30$
Reflections collected/unique	20259/4873
$R(\text{int})$	0.0705
Completeness to theta 29.15 / %	99.8
Absorption correction	none
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4873/0/262
Goodness-of-fit on F^2	1.107
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0550$, $wR_2 = 0.0964$
R indices (all data)	$R_1 = 0.0762$, $wR_2 = 0.1029$
Largest diff. peak and hole / (e. \AA^{-3})	0.298 and -0.302

Synthesis of 2-(2-(pyridine-2-ylmethyleneamino)ethylthio)-*N*-(thiophene-2-ylmethylene)aniline (L)

A solution of 2-(2-aminoethylthio)-*N*-(thiophene-2-ylmethylene)aniline (2.62 g, 10 mmol) in ethanol (30 mL) was added dropwise to a refluxing solution of pyridine-2-carbaldehyde (1.07 g, 10 mmol) in the same solvent (20 mL). After refluxing for 3 h the solution was vacuum evaporated to yield the crude product as a yellow oil. A small volume of petroleum ether was added to the residue remaining in the flask and rubbed. Then liquid was decanted and residue was evaporated until a yellow oil remained (Scheme 2). Yield: 2.95 g (84%). λ (DMF) / nm 314 ($\log \epsilon = 4.05$), 327 ($\log \epsilon = 4.02$); IR (ATR) ν / cm^{-1} 1647, 1610, 748; ^1H NMR (400.1 MHz, CDCl_3) δ 3.12 (t, 2H, CH_2), 3.81 (t, 2H, CH_2), 6.53-8.39 (m, 11H, Ar-H), 8.63 (s, 1H, $\text{CH}=\text{N}$), 8.74 (s, 1H, $\text{CH}=\text{N}$); ^{13}C NMR (400.1 MHz, CDCl_3) δ 35.4, 60.4, 115.0, 118.4, 120.8, 121.6, 122.6, 123.6, 124.9, 125.3, 125.7, 126.3, 129.8, 136.2, 136.7, 149.5, 149.7, 154.2, 163.2; EI-MS m/z , calcd. for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{S}_2$ $[\text{M}]^+$: 351.49, found: 351.



Scheme 1. Syntheses of the 2-(2-(2-((thiophene-2-yl)methyleneamino)phenylthio)ethyl) isoindoline-1,3-dione and the 2-(2-aminoethylthio)-*N*-(thiophen-2-ylmethylene)aniline.



Scheme 2. Synthesis of the ligand (L).

General synthesis of the complexes

2-(2-(Pyridine-2-ylmethyleneamino)ethylthio)-*N*-(thiophene-2-ylmethylene)aniline (L) (0.351 g, 1 mmol) was dissolved in ethanol (10 mL) and then a solution of metal ion (1 mmol) in ethanol (20 mL) was added and the reaction mixture was refluxed for 1 h. The solution was then concentrated in a rotary evaporator to ca. 5–10 mL. The complexes were filtered off, washed with cold ethanol and air-dried (Scheme 3).

[MnL]Cl₂·EtOH

Yield: 392 mg (75%). Anal. calcd. for C₂₁H₂₃Cl₂MnN₃OS₂: C, 48.19; H, 4.43; N, 8.03%. Found: C, 47.36; H, 4.33; N, 8.63%; λ (DMF) / nm 309 (log ε = 3.04); IR (ATR) ν / cm⁻¹ 1609, 751.

[NiL]Cl₂

Yield: 375 mg (78%). Anal. calcd. for C₁₉H₁₇Cl₂N₃NiS₂: C, 47.43; H, 3.56; N, 8.73%. Found: C, 46.54;

H, 2.98; N, 9.04%; λ (DMF) / nm 325 (log ε = 4.21), 533 (log ε = 1.90); IR (ATR) ν / cm⁻¹ 1608, 759.

[CuL]Cl₂·CuCl₂

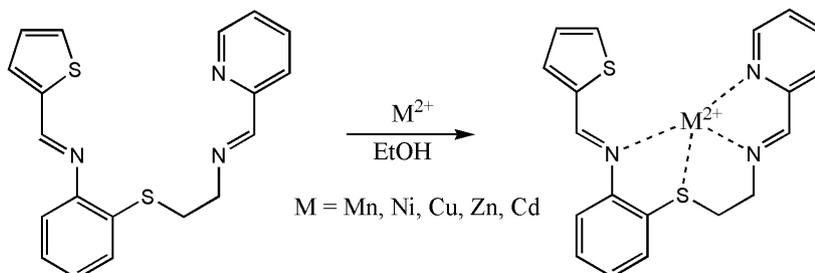
Yield: 366 mg (59%). Anal. calcd. for C₁₉H₁₇Cl₄Cu₂N₃S₂: C, 36.78; H, 2.76; N, 6.77%. Found: C, 36.43; H, 2.81; N, 6.92%; λ (DMF) / nm 312 (log ε = 3.91), 550 (log ε = 2.77); IR (ATR) ν / cm⁻¹ 1609, 752.

[ZnL]Cl₂·1.5H₂O

Yield: 330 mg (64%). Anal. calcd. for C₁₉H₂₀Cl₂N₃O_{1.5}S₂Zn: C, 44.33; H, 3.92; N, 8.16%. Found: C, 43.93; H, 3.59; N, 8.99%; λ (DMF) / nm 308 (log ε = 4.09); IR (ATR) ν / cm⁻¹ 3405, 1627, 1650, 776.

[CdL]Cl₂·H₂O

Yield: 470 mg (85%). Anal. calcd. for C₁₉H₁₉CdCl₂N₃OS₂: C, 41.28; H, 3.46; N, 7.60%. Found: C, 41.30; H, 3.80; N, 7.48%; λ (DMF) / nm 313 (log ε = 3.99); IR (ATR) ν / cm⁻¹ 3443, 1605, 1649, 778; ¹H NMR (500.1 MHz, DMSO-*d*₆)



Scheme 3. Synthesis of the complexes.

δ 3.15 (t, 2H, J 6.1 Hz, CH₂), 3.79 (t, 2H, J 6.1 Hz, CH₂), 5.32 (s, 2H, H₂O), 6.55 (t, 1H, J 7.4 Hz, Ar-H), 6.74 (d, 1H, J 8.0 Hz, Ar-H), 7.04 (t, 1H, J 7.3 Hz, Ar-H), 7.29 (d, 1H, J 7.5 Hz, Ar-H), 7.81 (t, 1H, J 6.1 Hz, Ar-H), 7.99 (d, 1H, J 7.5 Hz, Ar-H), 8.22 (t, 1H, J 7.4 Hz, Ar-H), 8.57 (s, 1H, CH=N), 8.80 (d, 2H, J 4.3 Hz, Ar-H), 7.25 (J 4.1 Hz) and 7.58 (J 7.2 Hz) (t, 1H, Ar-H), 7.71 (J 3.2 Hz) and 7.87 (J 4.8 Hz) (d, 1H, Ar-H), 8.07 (J 7.7 Hz) and 8.76 (J 4.2 Hz) (d, 1H, Ar-H), 8.63 and 9.06 (s, 1H, CH=N). ¹³C NMR (500.1 MHz, DMSO-*d*₆) δ 34.0, 58.3, 115.4, 115.7, 117.5, 128.6, 129.1, 130.2, 135.9, 141.2, 150.2, 150.6, 162.5.

Results and Discussion

The IR spectrum for 2-(2-(2-((thiophene-2-yl)methyleneamino)phenylthio)ethyl) isoindoline-1,3-dione shows bands at 1769 and 1707 cm⁻¹ assignable to the carbonyl groups (C=O) in phthalimide, band at 1610 cm⁻¹ assignable to the imine stretch and a band at 751 cm⁻¹ due to the thioethers stretch. The IR spectrum for 2-(2-aminoethylthio)-*N*-(thiophene-2-ylmethylene)aniline shows bands at 3340 and 3172 cm⁻¹ assignable to the aliphatic primary amine vibrations (NH₂), band at 1607 cm⁻¹ assignable to the imine stretch and a band at 750 cm⁻¹ due to the thioethers stretch. The IR spectrum for the ligand (L) confirms the presence of two different imines (1647 and 1608 cm⁻¹) and the absence of carbonyl and amine functional groups of the starting materials. In these compounds, the imine stretch band shifts to lower wave number (1607-1610 cm⁻¹) which supports overlapped resonances of the imine bond with the phenyl and thiophene rings. The vibration peak of C-S is observed in 748 cm⁻¹. In the IR spectra of manganese(II), nickel(II) and copper(II) complexes, the band at about 1608 or 1609 cm⁻¹ and in the IR spectra of zinc(II) and cadmium(II) complexes, the bands in the range of 1605-650 cm⁻¹ are associated with ν (C=N) vibration and the vibration peaks of C-S are observed in the range of 751-778 cm⁻¹. The vibration peaks of C=N and C-S are shifted relative to the similar bands of the ligand that show the imine nitrogen atoms and the thioether sulfur atom coordinated to the metal ions.¹⁴⁻¹⁶

¹H and ¹³C NMR results obtained for prepared compounds at ambient temperature in CDCl₃ and DMSO-*d*₆, respectively, are presented in Experimental section. The ¹H and ¹³C NMR spectra of the 2-(2-aminoethylthio)-*N*-(thiophene-2-ylmethylene)aniline indicate that this compound has synthesized. The slightly broad signal at 2.9-3.2 ppm in the ¹H NMR spectrum of this Schiff base amine is assigned to the NH₂ protons and the ν (CH=N) proton exhibits a singlet resonance at 8.79 ppm.

The ¹H NMR spectrum exhibits a singlet at 2.86 ppm corresponding to the methylene protons and the resonances for the aromatic rings (phenyl and thiophene) protons are observed in the region of 6.68-7.82 ppm. In the ¹³C NMR spectrum of this Schiff base amine, azomethine carbon resonance is observed in the 155.8 ppm and the resonances for the aliphatic C-N and C-S carbon atoms are observed in the 38.1 and 40.8 ppm, respectively. The aromatic carbons of the benzyl and thiophene rings are observed in the 115.1-148.5 ppm range. The ¹H NMR spectrum of ligand (L) (¹H and ¹³C NMR spectra of ligand show amount of impurity due to its instability), shows the aliphatic protons in the region of 3.12-3.81 ppm, the aromatic ring protons in the region of 6.53-8.39 ppm and the ν (CH=N) protons in the 8.63 and 8.74 ppm. The ¹³C NMR spectrum of ligand features 2 signals for the aliphatic carbon atoms and 15 signals for the aromatic carbon atoms in the region of 35.4-149.7 ppm. In this spectrum, azomethine carbons are observed in the 154.2 and 163.2 ppm.

For the cadmium(II) complex, we propose two conformation isomer Z and E for this complex (Figure 1). Z and E configurations would be expected to lead to two separate resonances in the ¹H NMR spectrum for the thiophene ring and imine group attached to it. The ¹H NMR spectrum (Figure 2) of the cadmium(II) complex confirm this two isomer in E/Z ratio approximately 70/30. The ¹H NMR spectrum of this complex shows two signals at 7.71 and 7.81 ppm corresponding to the imine proton (H_i in Z and E). The thiophene protons appear as two triplets at 7.25, 7.58 ppm (H_n in Z and E) and four doublets at 7.71, 7.87 ppm (H_m in Z and E) and 8.07, 8.76 ppm (H_o in Z and E). It was not possible to assign these resonances unambiguously to individual two-conformation isomer Z and E for this complex directly from the spectrum. However, it should be noted, that the sulfur atom of thiophene in conformation isomer E can be coordinated to the Cd and the resulted signals (thiophene ring and imine group attached to it) moved downfield. Also, the ¹H NMR spectrum of this complex shows two triplet signals due to the methylene protons (H_f and H_g) at 3.15 and 3.79 ppm, and also shows a signal at 5.32 ppm, corresponding to coordinated H₂O.¹⁷ The pyridine protons appear as two triplets at 7.81, 8.22 ppm (H_b, H_c) and two doublets at 7.99, 8.80 ppm (H_d, H_a), and the benzene ring protons appear as two triplets and two doublets at 6.55, 7.04 ppm (H_j, H_i) and 6.74, 7.29 ppm (H_k, H_h), respectively. The singlet at 8.57 ppm (which is shifted upfield) corresponds to the imine proton (H_o).¹⁸ In the ¹³C NMR spectrum of [CdL]²⁺, azomethine carbon resonances are observed at 150.2 and 162.5 ppm. Two methylene carbon atoms present in complex exhibited signals at 34.0 and 58.3 ppm and the

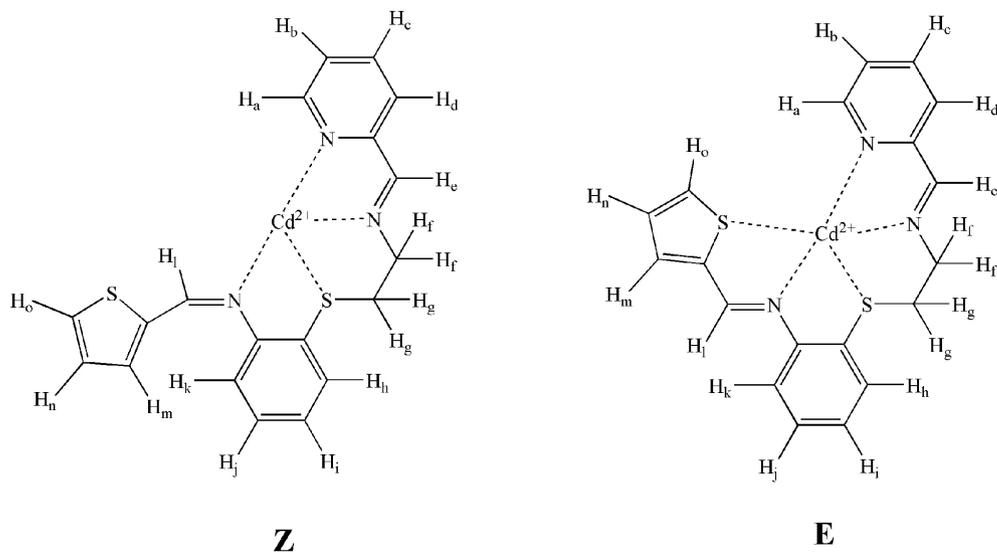


Figure 1. Two conformation isomer Z and E for the cadmium(II) complex.

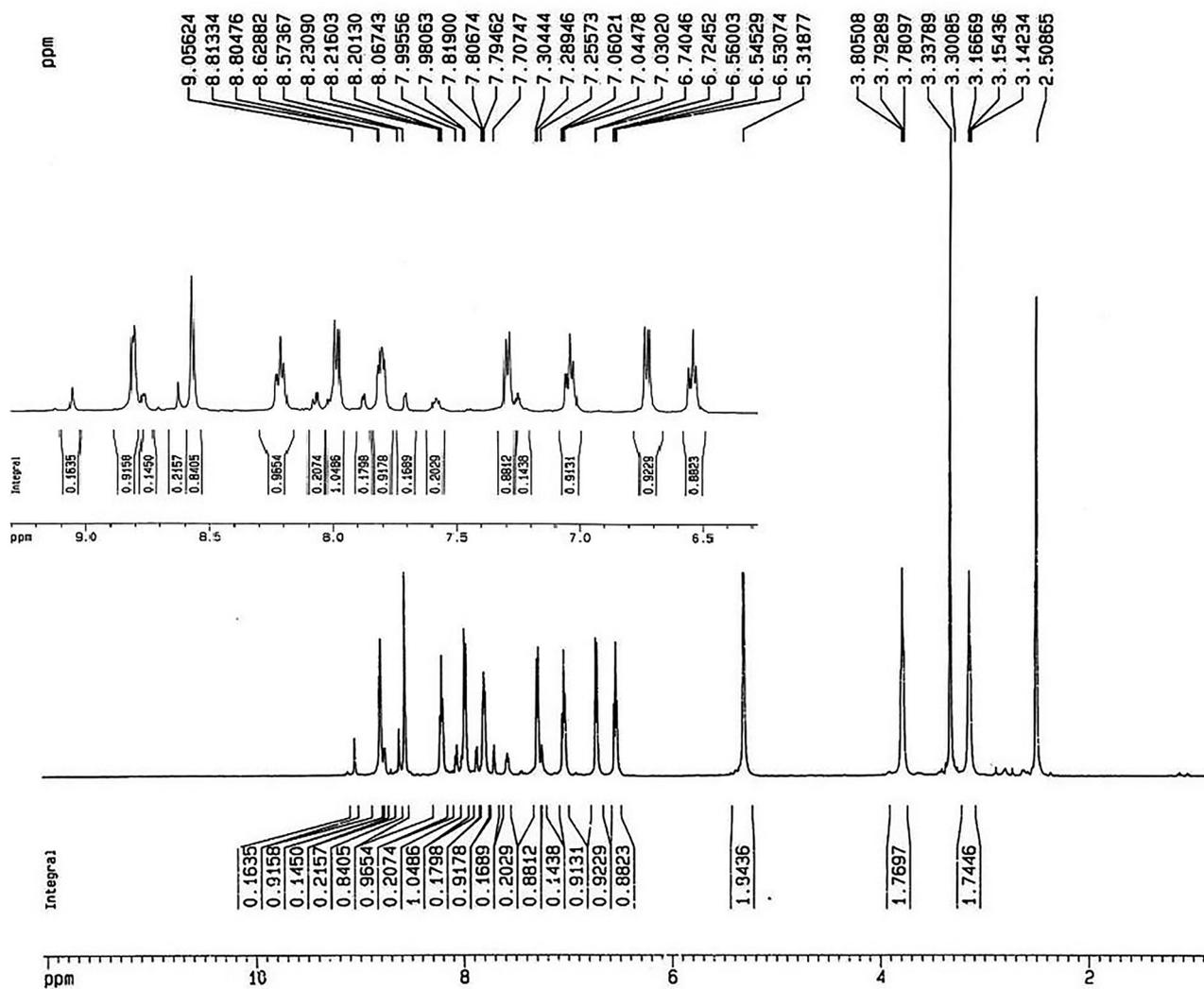


Figure 2. ^1H NMR spectrum of the $[\text{Cd}(\text{L})]\text{Cl}_2 \cdot \text{H}_2\text{O}$ in $\text{DMSO}-d_6$.

resonances for the aromatic rings carbons are observed in the region 115.4-150.2 ppm.

The EI mass spectra of the 2-(2-aminoethylthio)-*N*-(thiophene-2-ylmethylene)aniline and the unsymmetrical Schiff bases ligand (L), provide strong evidence for the formation of these compounds and exhibit peaks at higher molecular weights. The peak in the spectrum of 2-(2-aminoethylthio)-*N*-(thiophene-2-ylmethylene)aniline is observed at m/z 262 and the peak in the spectrum of the ligand is observed at m/z 351 corresponding to $[L]^+$. The absorption spectrum for 0.001 mol L⁻¹ solutions of the ligand (L) in DMF shows two absorption bands at 314 nm ($\log \epsilon = 4.05$) and 327 nm ($\log \epsilon = 4.02$), that these bands can be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.¹⁹ The absorption spectra for 0.001 mol L⁻¹ solutions of complexes in DMF show bands at 308 to 325 nm corresponding to $\pi \rightarrow \pi^*$ transitions. In general, the electronic transitions for zinc(II), cadmium(II) (d¹⁰) and manganese(II) (d⁵ high spin) complexes are spin-forbidden and hence cannot be observed. Complex copper(II) shows only one band at 550 nm ($\log \epsilon = 2.77$) corresponding to $d \rightarrow d$ transition. Complex nickel(II) displayed a less intense band at 550 nm ($\log \epsilon = 1.90$) corresponding to a forbidden $d \rightarrow d$ transition, which is consistent with a square planar geometry.²⁰⁻²² The elemental analyses for these complexes are in good agreement with the above molecular formula. In absence of crystal structures, we must be careful in any attempt to elucidate the coordinative environment of the metal ions on these systems. Taking into account that there are five donor atoms in the ligand, it could be suggested a distorted tetrahedral or square planar environment for each metal or five coordinated geometry for manganese(II) and cadmium(II), which would be in agreement with the UV-Vis data.

Description of the crystal structure

Single crystal of 2-(2-(2-((thiophene-2-yl)methyleneamino)phenylthio)ethyl)isoindoline-1,3-dione were obtained by slow evaporation of an ethanol solution of this compound. Crystal and structure refinement data are given in Table 1, and the molecular structure is shown in Figure 3. This compound crystallizes in monoclinic system in the $P2_1/c$ space group with the disordered thiophene ring (with occupancies of 0.64 and 0.36).²³ The bond lengths and angles are within the expected range of values. Selected bond lengths, bond angles and hydrogen bonds are given in Tables 2 and 3. Among the bond lengths, significant difference is observed between the aliphatic (1.815 Å) and aromatic (1.772 Å) C–S (thioether) bonds. The different bond lengths are observed between C(14)–O(1) (1.218 Å),

C(14)–N(2) (1.389 Å) and C(21)–O(2) (1.211 Å), C(21)–N(2) (1.402 Å). This different bond lengths shows that there is resonance between N(2)–C(14)–O(1) more than between N(2)–C(21)–O(2). The dihedral angles for S(2)–C(11)–C(6)–N(1) and S(2)–C(12)–C(13)–N(2) are 5.1° and 72.45°, respectively. Each unit cell contains four molecules and each molecule is involved in intermolecular hydrogen bonding interactions with C=O groups [H(9)···O(1) #1, 2.60 Å; H(18)···O(2) #2, 2.45 Å (symmetry codes: #1: $-x + 1, -y, -z$; #2: $-x, y + 1/2, -z + 1/2$)].

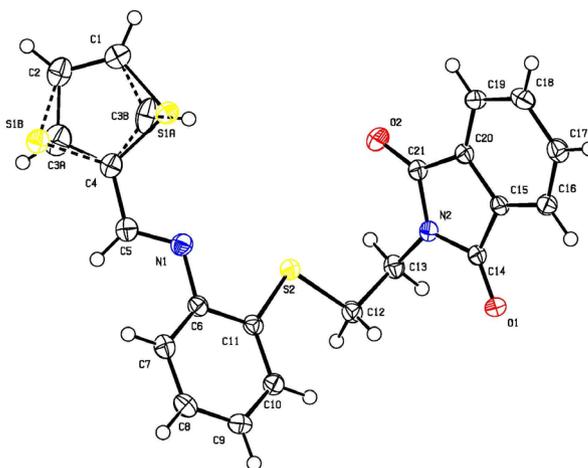


Figure 3. Crystal structure of 2-(2-(2-((thiophene-2-yl)methyleneamino)phenylthio)ethyl)isoindoline-1,3-dione showing 50% displacement ellipsoids.

Table 2. Selected bond lengths and angles for 2-(2-(2-((thiophene-2-yl)methyleneamino)phenylthio)ethyl)isoindoline-1,3-dione

Bond length / Å		Bond angle / degree	
C(11)–S(2)	1.772(2)	H(12B)–C(12)–C(13)–H(13A) ^a	73.17
C(12)–S(2)	1.815(2)	H(12B)–C(12)–C(13)–H(13B) ^a	46.24
C(4)–S(1A) ^a	1.707(3)	S(2)–C(12)–C(13)–N(2)	72.45(18)
C(4)–S(1B) ^a	1.728(4)	S(2)–C(11)–C(6)–N(1)	5.1(2)
C(21)–O(2)	1.211(2)	C(7)–C(6)–N(1)–C(5)	44.9(3)
C(14)–O(1)	1.218(2)	N(1)–C(5)–C(4)–S(1A) ^a	1.1(3)
C(13)–N(2)	1.456(2)	C(12)–S(2)–C(11)–C(10)	5.45(19)
C(14)–N(2)	1.389(2)	C(11)–S(2)–C(12)	102.75(9)
C(21)–N(2)	1.402(2)	C(5)–N(1)–C(6)	120.92(17)
C(6)–N(1)	1.413(3)	C(14)–N(2)–C(21)	112.03(16)
C(5)–N(1)	1.279(3)	O(2)–C(21)–C(20)	129.56(18)

^aOccupancies of A: 0.64 and B: 0.36.

Conclusion

In this work, we designed and prepared the unsymmetrical amine and then unsymmetrical potentially

Table 3. Hydrogen bonds for 2-(2-(2-((thiophene-2-yl)methyleneamino)phenylthio)ethyl)isoindoline-1,3-dione

D–H...A	D–H / Å	H...A / Å	D...A / Å	∠DHA / degree
C(9)–H(9)...O(1) #1	0.93	2.60	3.272(3)	129.8
C(18)–H(18)...O(2) #2	0.93	2.45	3.117(3)	128.3

Symmetry codes: #1: $-x + 1, -y, -z$; #2: $-x, y + 1/2, -z + 1/2$.

pentadentate Schiff base ligand (L) containing the pyridine and thiophene moieties and/or hard-soft donors (N_3S_2). Then five complexes of manganese(II), nickel(II), copper(II), zinc(II) and cadmium(II) from ligand were synthesized and characterized by various spectroscopic methods. Taking into account that there are five donor atoms in the ligand, it was found that only N3S donor set has bonding interaction (in agreement with the UV-Vis data). In the absence of crystal structures, it could be suggested a distorted tetrahedral or square planar environment for each metal or five coordinated geometry for manganese(II) and cadmium(II).

Supplementary Information

Supplementary data (FTIR, 1H NMR and ^{13}C NMR spectra) are available free of charge at <http://jbcbs.sbcq.org.br> as PDF file. CCDC 916929 contains the supplementary crystallographic data for 2-(2-(2-((thiophene-2-yl)methyleneamino)phenylthio)ethyl)isoindoline-1,3-dione. 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.

Acknowledgments

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

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Submitted: June 30, 2016

Published online: August 3, 2016