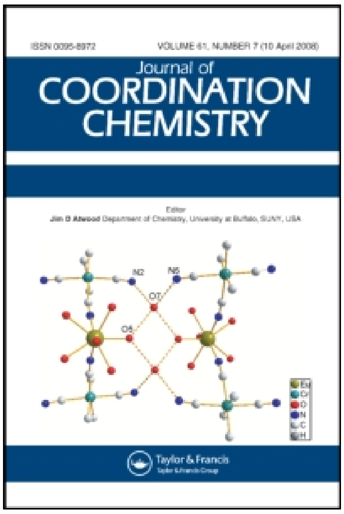

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of heterocyclic Schiff base and its complexes with Cu(II), Ni(II), Co(II), Zn(II), and Cd(II)

Mehmet Sönmez[a]; M. Refik Bayram[a]; Metın Çelebı[a]
[a] Faculty of Science & Arts, Department of Chemistry, Yüzüncü Yıl University, Van, Turkey

To cite this Article Sönmez, Mehmet , Bayram, M. Refik and Çelebı, Metın(2009) 'Synthesis and characterization of heterocyclic Schiff base and its complexes with Cu(II), Ni(II), Co(II), Zn(II), and Cd(II)', Journal of Coordination Chemistry, 62: 16, 2728 — 2735, First published on: 24 May 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970902915582

URL: http://dx.doi.org/10.1080/00958970902915582

Journal of Coordination Chemistry
Vol. 62, No. 16, 20 August 2009, 2728–2735

Synthesis and characterization of heterocyclic Schiff base and its complexes with Cu(II), Ni(II), Co(II), Zn(II), and Cd(II)

MEHMET SÖNMEZ*, M. REFİK BAYRAM and METİN ÇELEBİ

Faculty of Science & Arts, Department of Chemistry, Yüzüncü Yıl University,
65080, Van, Turkey

(*Received 3 December 2008; in final form 12 January 2009*)

A new Schiff base, {1-[(2-hydroxy-naphthalen-1-ylmethylene)-amino]-4-phenyl-2-thioxo-1,2-dihydro-pyrimidin-5-yl}-phenyl-methanone, has been synthesized from *N*-amino pyrimidine-2-thione and 2-hydroxynaphthaldehyde. Metal complexes of the Schiff base were prepared from acetate/chloride salts of Cu(II), Co(II), Ni(II), Zn(II), and Cd(II) in methanol. The chemical structures of the Schiff-base ligand and its metal complexes were confirmed by elemental analyses, IR, ^{13}C-NMR, ^{1}H-NMR, API-ES, UV-Visible spectroscopy, magnetic susceptibility, and thermogravimetric analyses. The electronic spectral data and magnetic moment measurements suggest mononuclear octahedral and mononuclear or binuclear square planar structures for the metal complexes. In light of these results, it was suggested that this ligand coordinates to each metal atom by hydroxyl oxygen, azomethine nitrogen, and thione sulfur to form octahedral complexes with Cd(II) and Zn(II).

Keywords: *N*-aminopyrimidine-2-thione; heterocyclic Schiff base; Complexes

1. Introduction

Pyrimidines have broad spectrum biological activities with antitumor [1], antiviral [2], anti-inflammatory [3], antipyretic [4], antimicrobial [5], and antifungal [6] properties. These observations prompted us to synthesize heterocyclic compounds containing a thione, thiolato moiety fused with pyrimidine to evaluate their biological activity. Heterocyclic thiones forming the backbone of more complicated organic ligands using other sites for their attachment to the metal will not be considered along with specific types of molecules having a thioketo group like 1,3-dithiole-2-thiones which form a vast and expanding field of research with technological applications and merit separate treatment [7]. Numerous pyrimidine derivative Schiff bases and their transition complexes have been investigated [8].

This article describes the synthesis of a new Schiff base (figure 1) containing a pyrimidine ring and its metal complexes. Spectral and magnetic studies have been used to characterize the structures of the complexes. IR, ^{1}H-NMR, and ^{13}C-NMR spectra were obtained to determine the structure of HL.

---

*Corresponding author. Email: vansonmez@hotmail.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902915582

2. Experimental

2.1. *Material and methods*

Elemental analyses (C, H, and N) were performed using a Leco CHNS model 932 elemental analyzer. IR spectra were obtained using KBr discs (4000–400 cm^{-1}) on a Bio-Rad-Win-IR spectrophotometer. Electronic spectra in the range of 200–900 nm were obtained in DMF on a Unicam UV2-100 UV-Visible spectrophotometer. Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Molar conductances of the Schiff-base ligand and transition metal complexes were determined in DMF at room temperature using a Jenway model 4070 conductivity meter. The ^{1}H-NMR and ^{13}C-NMR spectra of the Schiff base were recorded with a Bruker 300 MHz Ultrashield TM NMR instrument. LC/MS-API-ES mass spectra were recorded using an Agilent model 1100 MSD mass spectrophotometer. TGA measurements were carried out on a Shimadzu-50 thermal analyzer. 1-Amino-5-benzoyl-4-phenyl-1*H*-pyrimidine-2-thione was prepared according to the method given in [9]. All other reagents and solvents were of reagent-grade quality from commercial suppliers.

2.2. *Synthesis of Schiff base (HL)*

The Schiff base was prepared by condensation of 1-amino-5-benzoyl-4-phenyl-1-H-pyrimidine-2-thione (0.461 g, 1 mmol) with 2-hydroxynaphthaldehyde (0.172 g, 1 mmol) in toluene (40 mL) in the presence of a catalytic amount of (+)-camphorsulfonic acid achieved by boiling the mixture under reflux for 20 min. The precipitated ligand was filtered off, recrystallized from acetonitrile, and dried in a vacuum dessicator. Yield was 0.302 g (68%), m.p. 217°C. Anal. Calcd for $C_{28}H_{19}N_3O_2S$ (461): C, 72.87; H, 4.15; N, 9.10; S, 6.95. Found: C, 72.88; H, 4.18; N, 9.15; S, 7.21%. Selected IR data, ν (cm^{-1}): 3336 (O–H), 3059 (C–H), 1657 (C=O), 1623 (C=N), 1315 (C–O), 1245, 738 (C=S). UV-Vis [λ (nm), ε (M^{-1} cm^{-1})]: 268 (39410), 316 (34621), 363 (23345). ^{1}H-NMR (δ): 7.28–7.95 (m, xH, ArH), 9.26 (s, H, C(4)pyrim.), 9.77 (s, 1H, HC=N–), 11.99 (s, 1H, OH). ^{13}C-NMR (δ) 192.02 (–CO–Ph), 176.56 (C=S), 166.02 (Ph–C–pyrim.), 164.29 (–HC=N–), 160.95 (napht–C–OH), 146.52 (HC–pyrim.), 136.91–118.55 (aromatic C). API-ES: 460 [M]$^+$.

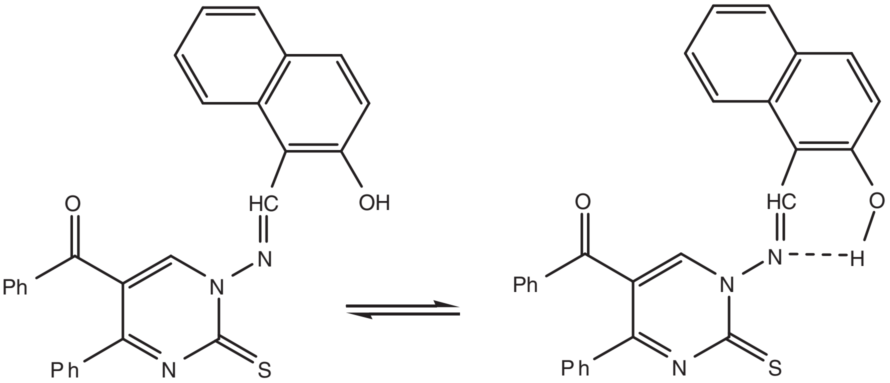

Figure 1. Structure of the Schiff base.

2.3. *Synthesis of compounds 1–5*

Total of 0.922 g (2.00 mmol) of the ligand was dissolved in 30 mL of chloroform, and a solution of 1.00 mmol of the metal salt [$Cu(AcO)_2 \cdot H_2O$ (0.20 g), $Co(AcO)_2 \cdot 4H_2O$ (0.25 g), $CdCl_2 \cdot 2H_2O$, $Zn(AcO)_2 \cdot 2H_2O$ (0.22 g), and $NiCl_2 \cdot 6H_2O$ (0.24 g)] in 15 mL methanol was added dropwise with continuous stirring. The mixture was stirred for 1.5–2.5 h at 80°C and the precipitated solid was then filtered off, washed with diethyl ether, cold methanol, and dried in a vacuum desiccator.

2.3.1. [Ni(L)$_2$]·2H$_2$O (1). Yield 73%, m.p. 221°C. Anal. Calcd for $C_{56}H_{40}N_6NiO_6S_2$ (1014): C, 66.22; H, 3.97; N, 8.27; S, 6.31. Found: C, 66.38; H, 3.88; N, 8.57; S, 6.14%. Selected IR data, ν (cm^{-1}): 3435 (OH/H$_2$O), 3057 (C–H), 1666 (C=O), 1615 (C=N), 1346 (C–O), 1247, 740 (C=S), 426 (M–N), 510 (M–O). UV-Vis [λ (nm), ε (M^{-1} cm^{-1})]: 269 (27830), 313 (20810), 454 (507), 525 (8680). μ_{eff}, Dia., Λ_o (S cm^2 mol^{-1}): 10.5. API-ES, *m*/*z*: 978 [2L + ^{58}Ni]$^+$.

2.3.2. [Co(L)$_2$]·3H$_2$O (2). Yield 65%, m.p. 242°C. Anal. Calcd for $C_{56}H_{42}CoN_6O_7S_2$ (1033): C, 65.05; H, 4.09; N, 8.13; S, 6.20. Found: C, 64.58; H, 3.85; N, 8.55; S, 6.18%. Selected IR data, ν (cm^{-1}): 3436 (OH/H$_2$O), 3053 (C–H), 1666 (C=O), 1614 (C=N), 1340 (C–O), 1248, 740 (C=S), 426 (M–N), 488 (M–O). UV-Vis [λ (nm), ε (M^{-1} cm^{-1})]: 277 (37630), 308 (23760), 474 (8590), 610 (86). μ_{eff}, 1.66 BM, Λ_o (S cm^2 mol^{-1}) 22.4. API-ES, *m*/*z*: 1014 [2L + ^{59}Co + 2H$_2$O]$^+$.

2.3.3. [Cd(L)$_2$]·4H$_2$O (3). Yield 47%, m.p. 251°C. Anal. Calcd for $C_{56}H_{44}CdN_6O_8S_2$ (1106): C, 60.84; H, 4.01; N, 7.60; S, 5.80. Found: C, 60.64; H, 3.87; N, 7.93; S, 6.13%. Selected IR data, ν (cm^{-1}): 3434 (OH/H$_2$O), 3059 (C–H), 1676 (C=O), 1616 (C=N), 1350 (C–O), 1252, 745 (C=S), 465 (M–N), 548 (M–O). UV-Vis [λ (nm), ε (M^{-1} cm^{-1})]: 264 (36,200), 308 (30,720), 468 (5420). ^{1}H-NMR (δ): 6.49–8.09 (m, *x*H, ArH), 9.41 (s, H, C(4)pyrim.), 9.58 (s, 1H, HC=N–), 3.35 (s, 8H, H$_2$O). ^{13}C-NMR (δ) 191.55 (–CO–Ph), 163.40 (C=S), 147.89 (–HC=N–), 137.44 (HC–pyrim.), 136.54–107.85 (aromatic C). μ_{eff}, Dia., Λ_o (S cm^2 mol^{-1}): 17.6. API-ES, *m*/*z*: 1051 [2L + ^{113}Cd + H$_2$O]$^+$.

2.3.4. [Zn(L)$_2$]·3H$_2$O (4). Yield 65%, m.p. 170°C. Anal. Calcd for $C_{56}H_{42}N_6O_7S_2Zn$ (1038): C, 64.64; H, 4.07; N, 8.08; S, 6.16. Found: C, 63.94; H, 3.73; N, 7.94; S, 6.16%. Selected IR data, ν (cm^{-1}): 3436 (OH/H$_2$O), 3057 (C–H), 1659 (C=O), 1616 (C=N), 1351 (C–O), 1255, 744 (C=S), 446 (M–N), 535 (M–O). UV-Vis [λ (nm), ε (M^{-1} cm^{-1})]: 264 (28,340), 309 (21,390), 454 (8850). ^{1}H-NMR (δ): 6.60–8.10 (m, *x*H, ArH), 9.41 (s, H, C(4)pyrim.), 9.13 (s, 1H, HC=N–), 3.36 (s, 6H, H$_2$O). ^{13}C-NMR (δ) 191.57 (–CO–Ph), 174.91 (C=S), 163.78 (Ph–C–pyrim.), 147.39 (–HC=N–), 138.15 (HC–pyrim.), 136.51–107.73 (aromatic C). μ_{eff}, Dia., Λ_o (S cm^2 mol^{-1}) 22.5. API-ES, *m*/*z*: 1001 [2L + ^{63}Zn + H$_2$O]$^+$.

2.3.5. [Cu$_2$(L)$_2$]·(CH$_3$COO)$_2$·H$_2$O (5). Yield 45%, m.p. 231°C. Anal. Calcd for $C_{60}H_{44}Cu_2N_6O_9S_2$ (1183.08): C, 60.85; H, 3.72; N, 7.10; S, 5.41. Found: C, 60.54; H, 3.63; N, 7.70; S, 5.84%. Selected IR data, ν (cm^{-1}): 3435 (OH/H$_2$O), 3059 (C–H), 1677 (C=O), 1615 (C=N), 1351 (C–O), 1260, 749 (C=S), 436 (M–N), 532 (M–O).

UV-Vis [λ (nm), ε ($M^{-1}\,cm^{-1}$)]: 259 (30930), 307 (28,830), 487 (11,490), 638 (240). μ_{eff}, 2.75 BM, Λ_o (S $cm^2\,mol^{-1}$) 160.1. API-ES, *m*/*z*: 1166 $[2L + 2^{64}Cu + 2(CH_3COO)]^+$.

3. Results and discussion

Schiff base HL was synthesized by condensation of *N*-pyrimidine-2-thione with 2-hydroxynaphthaldehyde. The Schiff-base ligand and its complexes are very stable at room temperature in the solid state. The ligand is soluble in common organic solvents, but its metal complexes are generally only soluble in DMF and DMSO. The elemental analytical data of the complexes reveal a metal: ligand stoichiometry of 1 : 2 corresponding to the general formula of $[M(L)_2] \cdot nH_2O$, except for binuclear Cu(II) complex $[Cu_2(L)_2] \cdot 2CH_3COO \cdot H_2O$. These analytical data are in good agreement with the proposed stoichiometry of the complexes (table 1). The molar conductivities of compounds **1**–**4** in DMF at 25°C are in the range of 10.5–22.5 $\Omega^{-1}\,cm^2\,mol^{-1}$, indicating non-electrolytes, except for $[Cu_2(L)_2] \cdot (CH_3COO)_2 \cdot H_2O$ which behaves as a 1: 2 electrolyte ($\Lambda_o = 160.1\ \Omega^{-1}\,cm^2\,mol^{-1}$) [10].

3.1. *Infrared spectral study*

IR spectra of Schiff-base ligand show characteristic bands at 3336 cm^{-1} ν(O–H) [11, 12], 3059 cm^{-1} ν(C–H pyrimidine ring), 1657 cm^{-1} ν(C=O benzoyl), 1623 cm^{-1} ν(C=N azomethine), 1315 cm^{-1} ν(C–O phenolic) [13] and 1245, 738 cm^{-1} ν(C=S) vibrations [14, 15].

IR spectra of the complexes are compared with that of the free ligand to show changes during complexation. In the spectra of all the complexes, the phenolic (C–O) band at 1340–1351 cm^{-1} shifts to 25–36 cm^{-1}, the lower frequency supporting bonding of the phenolic OH after deprotonation [16]. The azomethine vibration of the ligand at 1623 cm^{-1} shifts to 1614–1616 cm^{-1} after complexation confirming formation of a bond from the imine nitrogen to the metal [11–13]. The ν(C=S) at 1245, 738 cm^{-1} in the free ligand shifts to higher frequency after complexation, due to coordination of Zn(II), Cd(II), and Cu(II) with nitrogen of azomethine, oxygen of hydroxyl, and sulfur of thione group (figures 2 and 3). The ν(C=S) thione bands in spectra of Co(II) and Ni(II) complexes remain almost at ~1245 and ~738 cm^{-1} suggesting that C=S group does not take part in complexation, indicating bidentate coordination for Schiff base through

Table 1. Physical characterization, analytical, mass spectra, and magnetic susceptibility data of the complexes.

Compound No.	(Calcd) Found (%) C	H	N	S	Formula weight	API-ES	Assignment	μ_{eff} (BM)
1	(66.2) 66.3	(3.9) 3.8	(8.2) 8.5	(6.3) 6.1	1014	978	$Ni(L)_2]^+$	Dia
2	(65.0) 64.6	(4.1) 3.8	(8.1) 8.5	(6.2) 6.2	1033	1014	$[Co(L)_2 + 2H_2O]^+$	1.66
3	(60.8) 60.6	(4.0) 3.9	(7.6) 7.9	(5.8) 6.1	1106	1051	$[Cd(L)_2 + H_2O]^+$	Dia
4	(64.6) 63.9	(4.0) 3.7	(8.0) 7.9	(6.1) 6.1	1038	1001	$[Zn(L)_2 + H_2O]^+$	Dia
5	(60.8) 60.5	(3.7) 3.6	(7.1) 7.7	(5.4) 5.8	1183	1166	$[Cu_2(L)_2 + 2(CH_3COOH)]^+$	2.75

phenolic oxygen and nitrogen of the azomethine to Ni(II) or Co(II) (figure 2). The binuclear Cu(II) complex shows the phenolic ν(C–O) at 1570 cm^{-1}, indicating a bridging phenolic C–O [17].

Bands observed at 426–465 and 488–548 cm^{-1} are due to ν(M–N) and ν(M–O), respectively [11, 12]. Broad bands of the Cu(II), Ni(II), Co(II), and Zn(II) complexes from 3240–3350 cm^{-1} are assigned to ν(OH) of water [18]; water content was also identified by thermal analyses.

3.2. *Proton and carbon nuclear magnetic resonance spectra*

DMSO-d_6 was used as a solvent to measure the ^{1}H-NMR and ^{13}C-NMR spectra of HL and its Zn(II) and Cd(II) complexes.

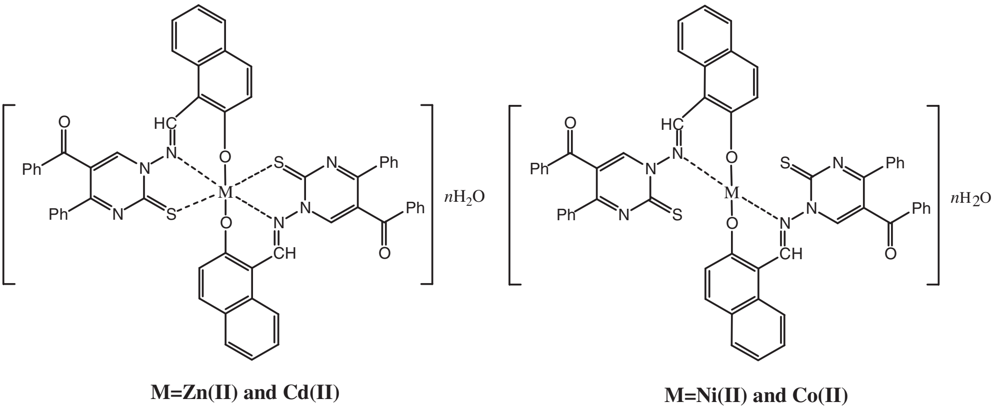

Figure 2. Proposed structure of the metal complexes.

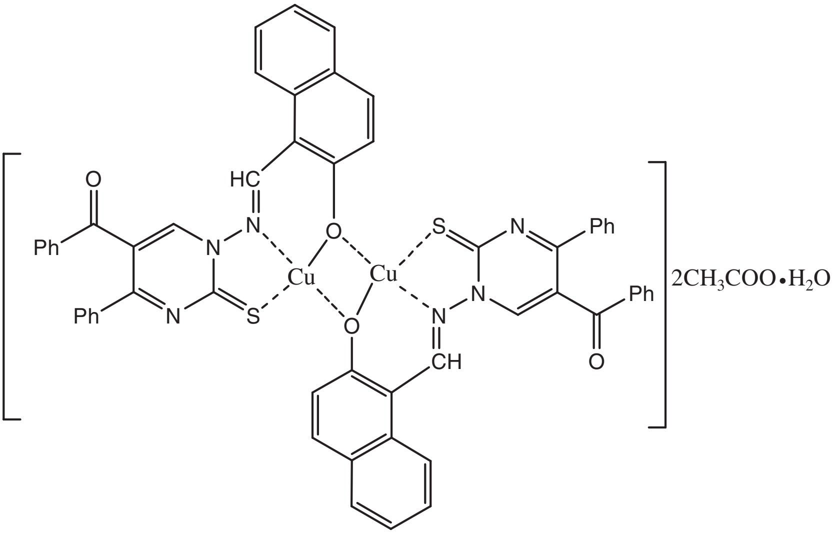

Figure 3. Structure of $[\mathrm{Cu}_2(\mathrm{L})_2]\cdot 2\mathrm{CH}_3\mathrm{COO}\cdot \mathrm{H}_2\mathrm{O}$.

^{1}H-NMR spectra of the ligand (Supplementary material) do not show a signal corresponding to the primary amine, supporting complete condensation and formation of Schiff base. The signal due to imine group at δ 9.77 ppm (s, 1H) provides evidence for formation of Schiff base [19]. Sharp singlets at δ 11.99 and 9.26 ppm are due to enolic proton and C_6(H)–pyrimidine proton of the ligand; the naphthyl and phenyl multiplets were between δ 7.28–7.95 ppm [20]. The ^{13}C-NMR spectrum of the ligand has a cluster of peaks at δ 192.02 and 176.56 ppm due to benzoyl and thione carbons. The peak at δ 164.29 ppm may be attributed to CH=N. Peaks in the region δ 118.55–136.91 ppm are due to aromatic carbons.

In the ^{1}H-NMR spectra of Zn(II) and Cd(II) complexes, the enolic OH signal is absent, confirming deprotonation. The signals for the azomethine proton in the complexes appear at 9.58 and 9.13 ppm, respectively, shifted downfield, indicating the metal–nitrogen bond is retained in the solution [21]. The aromatic protons due to phenyl rings resonate in the region δ 6.50–8.10 in the Cd(II) and Zn(II) complexes.

3.3. *Electronic spectra and magnetic measurements*

Electronic spectra were recorded in DMF. In the Schiff base, the band at 363 nm is attributed to $\pi \rightarrow \pi^*$ of the azomethine. Bands at 316 and 268 nm are associated with naphthalene and pyrimidine $\pi \rightarrow \pi^*$ transitions. In spectra of the complexes, the $\pi \rightarrow \pi^*$ of the azomethine is shifted to 370 nm, indicating that the imino nitrogen is involved in coordination. The electronic spectra of the Zn(II) and Cd(II) complexes have bands in the range 309–264 nm due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the naphthalene, pyrimidine, and azomethine.

The binuclear $[Cu_2(L)_2] \cdot (CH_3COO)_2 \cdot H_2O$ complex is expected to be square planar, confirmed by characteristic absorption bands at 487 and 638 nm assignable to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ [22]. Magnetic measurements at room temperature with a value of 2.70 B.M. for **5** [23] points to antiferromagnetic interactions between the two copper(II) ions bridged by a phenol [24].

The diamagnetic behavior of $[Ni(L)_2] \cdot 2H_2O$ reveals a square planar structure. Two bands in electronic spectrum of Ni(II) complex (Supplementary material) at 454 and 525 nm are due to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1B_{2g}$ transitions, confirming square planar geometry [25].

The Co(II) complex shows a magnetic moment of 1.66 B.M. in good agreement with spin only value [26]. Electronic spectral data showing absorption at 610 nm corresponding to $^1A_{1g} \rightarrow {}^1B_{1g}$ also supports square planar geometry [27].

3.4. *Thermal study*

The TGA data agree with the formula suggested from elemental analyses. The thermal stabilities were investigated using TGA at a heating rate of 10°C min^{-1} in N_2 from 20 to 850°C. Mass losses correspond to H_2O, Ph–CO– and the other organic moieties in the first, second, third, fourth, and fifth stages of decomposition. The Cu(II), Ni(II), Zn(II), Co(II), and Cd(II) complexes suffered loss of H_2O in the first stage, 38–130°C, and the ligands gradually decomposed from 220 to 580°C. The complexes contain 1, 2, 3, 3, and 4 moles of water of crystallization per complex molecule, respectively. The complexes decomposed to CuS, CoS, NiS, CdS, and ZnO at higher temperatures [16, 28]; the Co(II) complex is most thermally stable.

4. Conclusion

We have described the synthesis and structure of new heterocyclic Schiff base and its metal complexes in 1 : 2 metal : ligand ratio. The ligand is a bidentate or tridentate chelating agent coordinating through a deprotonated phenolic group, azomethine nitrogen, and sulphur of pyrimidine thione group. The analytical data, electronic spectra, magnetic susceptibility, IR, NMR, and API-ES mass spectral data reveal mononuclear octahedral configuration of Zn(II) and Cd(II) complexes, mononuclear square-planar configuration for Co(II) and Ni(II) while the Cu(II) complex is binuclear square-planar.

Acknowledgment

We are grateful to the Yuzuncu Yil University Research Foundation (YUAP-2006-FBE-086) for their support in this research.

References

[1] P.G. Baraldi, M.G. Pavani, N. Nunes, P. Brigidi, B. Vitali, R. Gambari, R. Romagnoli. *Arch. Pharm.*, **10**, 449 (2002).
[2] M.N. Nasr, M.M. Gineinah. *Arch. Pharm.*, **335**, 289 (2002).
[3] S. Leistner, G. Wagner, M. Guetscharo, E. Glusa. *Pharmazie*, **41**, 54 (1989).
[4] E. Bousquet, G. Romero, F. Guerrera, A. Caruso, M.A. Roxas. *Farmaco Ed. Sci.*, **40**, 869 (1985).
[5] N. Kumar, G. Singh, A.K. Yadav. *Heteroat. Chem.*, **12**, 52 (2001).
[6] G. Mangalagiu, M. Ungureanu, G. Grosu, I. Mangalagiu, M. Petrovanu. *Ann. Pharm. Fr.*, **59**, 139 (2001).
[7] P.D. Akrivos. *Coord. Chem. Rev.*, **213**, 181 (2001).
[8] J. Becher, H. Toftlund, P.H. Olesen, H. Nissen. *Inorg. Chim. Acta*, **103**, 167 (1985).
[9] Y. Akçamur, B. Altural, E. Sarıpınar, G. Kollenz, O. Kappe, K. Peters, E. Peters, H.J. Schering. *Heterocycl. Chem.*, **25**, 1419 (1988).
[10] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[11] K. Nakamato. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, J. Wiley, New York (1978).
[12] M. Sönmez, M. Şekerci. *Synth. React. Inorg. Met.-Org. Chem.*, **34**, 485 (2004).
[13] Z.H. Abd El-Wahab. *J. Coord. Chem.*, **61**, 1696 (2008).
[14] Z. Önal, B. Altural. *Turk. J. Chem.*, **23**, 401 (1999).
[15] P. Maravali, K. Gudasi, R. Goudar. *Trans. Met. Chem.*, **25**, 411 (2000).
[16] M. Sönmez, M. Şekerci. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 1689 (2003).
[17] H.C. Aspinall, J. Black, I. Dood, M.M. Harding, S.J. Winkly. *J. Chem. Soc., Dalton Trans.*, 709 (1993).
[18] S.S. Kandil, G.B. El-Hefnawy, E.A. Bakr, A.Z. Abou El-Ezz. *Trans. Met. Chem.*, **28**, 168 (2003).
[19] M. Sönmez. *Polish J. Chem.*, **77**, 397 (2003).
[20] J. Matijevic, M. Vinkoviç, D. Vikiç. *Crotica Chem. Acta*, **79**, 489 (2006).
[21] A. Sousa-Pedrares, N. Camina, J. Romero, M.L. Duran, J.A. Garcia-Vazquez. *Polyhedron*, **27**, 3391 (2008).
[22] A.I. El-Said. *Trans. Met. Chem.*, **28**, 749 (2003).

[23] A.A.A. Emara, O.M.I. Adly. *Trans. Met. Chem.*, **32**, 889 (2007).

[24] P. Aranz-Mascaros, L. Godino-Salido, R. Lopez-Garzon, P. Aranz-Mascaros. *Trans. Met. Chem.*, **26**, 581 (2001).

[25] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam (1984).

[26] K. Aravindakshan, C. Nair. *J. Chem. Sci.*, **93**, 111 (1984).

[27] N. Raman, V. Muthuraj, S. Ravichandran, A. Kulandaisamy. *Proc. Indian Acad. Sci. (Chem. Sci.)*, **115**, 161 (2003).

[28] N. Özpozan, H. Arslan, T. Özpozan, N. Özdeş, N. Külcü. *Thermochim. Acta*, **343**, 127 (2000).