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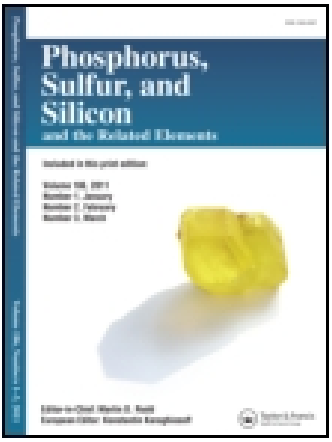

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Synthesis and Characterization of Cu(II), Ni(II), Co(II), Mn(II), and Cd(II) Transition Metal Complexes of Tridentate Schiff Base Derived from O-Vanillin and N-Aminopyrimidine-2-Thione

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SYNTHESIS AND CHARACTERIZATION OF Cu(II), Ni(II), Co(II), Mn(II), AND Cd(II) TRANSITION METAL COMPLEXES OF TRIDENTATE SCHIFF BASE DERIVED FROM *O*-VANILLIN AND *N*-AMINOPYRIMIDINE-2-THIONE

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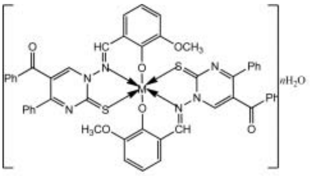
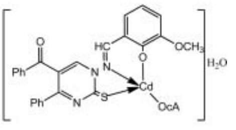
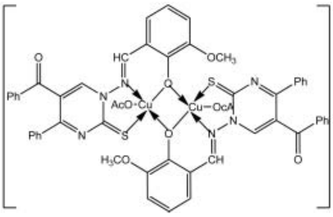
GRAPHICAL ABSTRACT







Abstract *Monobasic tridentate Schiff base ligand having ONS donor sequence was prepared by condensing N-aminopyrimidine-2-thione with o-vanillin. The complexes were formed by reacting ligand and the metal acetates of Cu(II), Ni(II), Co(II), Mn(II), and Cd(II) in methanol to get a series of mononuclear and dinuclear complexes. The characterization of ligand and metal complexes were carried out by elemental analyses, conductivity measurements, magnetic susceptibility data, FTIR, UV-vis, NMR, and API-ES mass spectral data. The structure of the complexes was confirmed on the basis of elemental analyses, magnetic susceptibility, API-ES mass spectral data and thermal gravitational analysis (TGA).*

Keywords Schiff base metal complex; *N*-aminopyrimidine-2-thione; *o*-vanillin

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INTRODUCTION

Schiff base complexes have been among the most widely studied coordination compounds for many years, since they have attracting interest as biochemical, analytical, and antimicrobial reagents.[1] Schiff base complexes containing different central metal atoms have been studied in great detail for their various crystallographic features, enzymatic reactions, steric effects, structure-redox relationships, mesogenic characteristics, catalysis, magnetic properties, and their important role in the understanding of the coordination chemistry of transition metal ions.[2] Compounds containing pyrimidine rings play a significant role in many biological systems. The pyrimidine ring system; present in nucleic acids, several vitamins, coenzymes, and antibiotics; provides potential binding sites for metal ions, and their coordination nature is important in the understanding role of the metal ions in biological systems.[3] A number of previous studies proposed that pyrimidines and their complexes can display effective and selective antimicrobial activity against bacteria, fungi, and virus.[4–6] Vanillin is the most prominent principal flavor and aroma compound in vanilla, and its synthetic one used as a flavoring agent in foods, beverages, and pharmaceuticals.[7] Redox property and antibacterial activity have been reported for the Ru (II) complex of the Schiff base of vanillin and 2-aminopyridine.[8] Electronic absorption and emission properties of o-vanillin Schiff base derivatives and their complexes with Cu(II) were studied.[9] The Schiff bases derived from *o*-vanillin and 2,3-diaminopyridine have been used as ionophores in a Cu(II) selective electrochemical sensors.[10]

In this study, we report synthesis, characterization, and biological activity of a novel pyrimidine Schiff base ligand [(E)-(1-((2-hydroxy-3-methoxybenzylidene)amino)-4-phenyl-2-thioxo-1,2-dihydropyrimidin-5-yl)phenyl)methanone) obtained by condensation of]*o*-vanillin with *N*-aminopyrimidine-2-thione and its metal complexes. The compounds were characterized by elemental analysis, FTIR, NMR, API-ES mass, and UV-vis spectral techniques. The thermal stabilities of the complexes were also investigated using thermal gravimetric analysis (TGA).

RESULTS AND DISCUSSION

Spectral Characterization

Electronic Spectra and Magnetic Measurements. The electronic absorption spectra were recorded in DMF. UV-vis, molar conductivity, and magnetic susceptibility data of the Schiff base and its complexes are presented in Table 1. In the UV-vis region,

Table 1 UV-vis, molar conductivity and magnetic susceptibility data of the Schiff base and its transition metal complexes

Compound	UV-vis λ (nm), ε (M^{-1} cm^{-1})	λ_M (DMF, S cm^2 mol^{-1})	μ_{eff} (BM)
$C_{25}H_{19}N_3O_3S$(HL)	424 (97), 409 (395), 359 (2920), 280 (3800)	—	—
$[Cu_2(L)_2(AcO)_2]$	494 (55), 483 (202), 455 (1240), 276 (3932)	22.1	4.32
$[Ni(L)_2]\cdot 2.5H_2O$	552 (27), 529 (38), 507 (135), 394 (1480), 278 (3725)	2.45	3.29
$[Co(L)_2]\cdot 2H_2O$	629 (15), 597 (88), 449 (912), 299 (3945)	4.90	2.48
$[Mn(L)_2]\cdot H_2O$	527 (?), 481 (76), 452 (498), 310 (3589)	1.83	5.80
$[Cd(L)(AcO)]\cdot H_2O$	451 (110), 410 (310), 362 (2650), 289 (3290)	21.7	D

the compounds show bands at approximately 280 nm and in the range 359–424 nm as the weaker bands. The weak bands were attributed to intramolecular charge transfer (CT) transition[11] from the π orbital on the phenolate oxygen to the empty d orbitals of the metal.

On the basis of the magnetic data, the Cu(II) complex probably has a binuclear structure with phenolic oxygen bridges. The Cu(II) complex with HL, a tridentate, has been found to have an acetate group in the coordination sphere. Magnetic moment value for the Cu(II) complex is greater than the spin only value for a dimeric system. High magnetic moment for the complex may be caused by the admixture of copper diacetate. The complex exhibits a weak transition at 494 nm assigned to $^{2}B_{1g}\rightarrow{}^{2}B_{2g}$ which indicates the presence of a five-coordinate geometry.[12]

The electronic spectrum of the Ni(II) complex showed two d–d transitions at 552 and 507 nm assignable to the $^{3}A_{2g}\rightarrow{}^{3}T_{1g}$(F) ($\nu_2$) and $^{3}A_{2g}\rightarrow{}^{3}T_{1g}$(P) ($\nu_2$) transitions, respectively, which indicative of an octahedral environment around the metal ion.[13,14] The observed magnetic moment of the Ni(II) complex was 3.29 b.m.

The measured magnetic moment value (2.48 b.m.) of the Co(II) complex was lower than spin-only value (3.87 b.m.) and also lower than the values reported for octahedral complexes.[15] The electronic spectrum of $(CoL_2)\cdot 4H_2O$ in DMF solution shows two broad bands at 629 and 597 nm for the $^{4}T_{1g}\rightarrow{}^{4}A_{2g}$ and $^{4}T_{1g}\rightarrow{}^{4}T_{1g}$ (P) transitions, respectively, in around the Co (II) ion.[16,17]

The electronic spectra of the Mn(II) complexes exhibit four intensity absorption bands. The CT bands have covered the entire visible region, the d-d electronic transition bands submerged under the CT bands, have not been identified. In the present investigation, the observed magnetic moment value for Mn(II) complex is 5.80 BM, which is in the expected range of octahedral geometry around the central metal ion.[16,19]

Cd(II) complex is a diamagnetic due to its d^{10} configuration and this complex doesn't show any d-d transition but displays CT bands at 451, 410 and 362 nm respectively.[1]

FTIR Spectra. Characteristic FTIR bands of the ligand and its transition metal complexes are presented in Table 2 with their assignment. The FTIR spectrum of the ligand showed a ν(C=N) peak at 1608 cm^{-1} and the absence of ν(C=O) at 1643 cm^{-1} and $\nu(NH_2)$ peaks around 3250–3300 cm^{-1} is because of Schiff base condensation. The absorption band at 1659 cm^{-1} is assigned to benzoyl ν(C=O) moiety.

The FTIR spectrum of Schiff base ligand showed a broad band at near ~3200–3500 cm^{-1} due to ν(OH) (see Figure 1). The free ν(OH) was generally observed between 3500–3650 cm^{-1}.[20,21] The intense band at 1291 cm^{-1} in the FTIR spectrum of the Schiff base ligand might be assigned to phenolic (C-O) stretching mode, according to the previous

Table 2 Infrared data of Schiff base and its transition metal complexes (in cm^{-1})

Compound	(C=S)	Phenolic (C-O)	Azomethine (C=N)	(OH/H_2O)	Benzoyl (C=O)	Pyrimidine (C-H)	M-N	M-O
$C_{25}H_{19}N_3O_3S$(HL)	726, 1251	1291	1608	~3200–3500	165 9	3059	—	—
$[Cu_2(L)_2(AcO)_2]$	758, 1245	1283	1596	—	1657	3058	426	468
$[Ni(L)_2]\cdot 2.5H_2O$	737, 1241	1287	1575	~3350–3400	1657	3058	440	470
$[Co(L)_2]\cdot 2H_2O$	737, 1244	1288	1584	~3350–3400	1661	3057	430	480
$[Mn(L)_2]\cdot H_2O$	735, 1240	1287	1592	~3350–3400	1658	3056	425	475
$[Cd(L)(AcO)]\cdot H_2O$	739, 1241	1288	1591	3465	1660	3057	435	~450–470

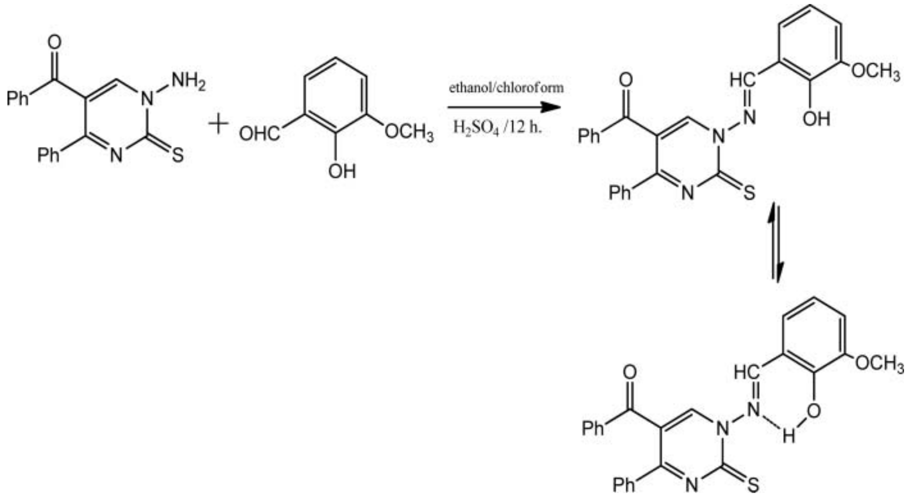

Figure 1 Synthesis protocol of the Schiff base ligand (HL).

assignments. The pyrimidine ring shows characteristic stretching absorption bands at the 3059 cm^{-1}. The strong bands at 1291 and 1608 cm^{-1} in the IR spectra of the free ligand assigned to ν(C-O) and ν(C=N)[20] that changes in the FTIR of complexes, indicating coordination through azomethine nitrogen and phenolic oxygen of Schiff base (see Figure 1). The ν(C=S) at 1251 and 726 cm^{-1} [22,23] in the free ligand shifts to higher frequency upon complexation, due to coordination with nitrogen of azomethine, oxygen of hydroxyl, and sulfur of thione group for complexes. In the spectra of the complexes, the bands observed in the ~425–440 cm^{-1} and ~450–480 cm^{-1} region might be due to ν(M-N) and ν(M-O), respectively.[21,22] The IR spectra of the Co(II), Ni(II), Mn(II), and Cd(II) complexes were characterized by the appearance of a broad band in the region ~3350 and 3465 cm^{-1} due to the ν(O-H) frequency of water of crystallization, existence of it was also proved by elemental analyses. Broad bands of all the complexes in the 3400–3500 cm^{-1} region were assigned to the ν(OH) vibration of the water molecules.[24,25]

NMR Spectra. $CDCl_3$ was used as a solvent to measure the ^{1}H NMR and ^{13}C NMR spectra of the ligand and DMSO-d_6 was also used to measure the ^{1}H NMR and ^{13}C NMR spectra of the Cd(II) complex. ^{1}H NMR bands of the ligand and its Cd(II) complex with their assignment are presented in Table 3.

The ^{1}H NMR spectrum of the ligand (see Figure S1 in the Supplemental Materials) showed signal at δ 9.01 ppm corresponding to the signals of azomethine. The sharp singlet observed at about δ 10.06 ppm due to phenolic proton of the ligand. The singlets at δ 8.35 and δ 8.72 ppm are coming from pyrimidine ring (C-H) proton in the spectrum of the ligand and Cd(II) complex, respectively. The multiplets corresponding aromatic protons appeared between δ 6.99–7.70 ppm and δ 6.96–7.90 ppm are assigned to aromatic protons, respectively.[26,27] The hydroxyl proton (phenolic OH) disappears in the Cd(II) complex, indicating that the OH group have been deprotonated and bonded to metal ion.

^{13}C NMR spectra displayed characteristic signals at 191.54 and 150 ppm due to the (OC-Ar) and (C=S, pyrimidine) of the Schiff base ligand, respectively (see Figure S2 in the Supplemental Materials). Given ^{13}C NMR bands of the ligand and its Cd(II) complex with their assignment are in Table 3.

Table 3 ^{1}H and ^{13}C NMR data of Schiff base and its Cd(II) complex (in ppm)

Compound	(C=S)	Phenolic (OH)	Azomethine (HC=N)	Benzoyl (C=O)	Pyrimidine (C-H)	Aromatic	Phenyl	OCH_3	Acetate (CH_3COO)
HL[a]	—	10.06 (s, 1H)	9.01 (s, 1H)	—	8.35 (s, 1H)	7.70 (d, 1H, Ha, $J =$ 7.5 Hz) 7.54–7.45 (dd, 1H, Hb, $J = 7.4$ Hz) 7.58 (d, 1H, Hc, $J =$ 7.2 Hz)	6.99–7.33 (m, 10H)	3.95 (s, 3H)	—
$[Cd(L)(AcO)]\cdot H_2O$[a]	—	—	9.25 (s, 1H)	—	8.72 (s, 1H)	7.90 (d, 1H, Ha, $J =$ 6Hz) 7, 63–7.56 (dd, 1H, Hb, $J = 7.2$ Hz) 7.80 (d, 1H, Hc, $J =$ 6.9 Hz)	6.96–7.52 (m, 10H)	3.81 (s,3H)	2.51 (s, 3H)
HL[b]	150		148.49	191.54	—	—	115.92–144.58	56.79	—
$[Cd(L)(AcO)]\cdot H_2O$[b]	161		145.03	192.41	—	—	120.60–136.52	56.40	22.21

[a] ^{1}H NMR.

[b] ^{13}C NMR.

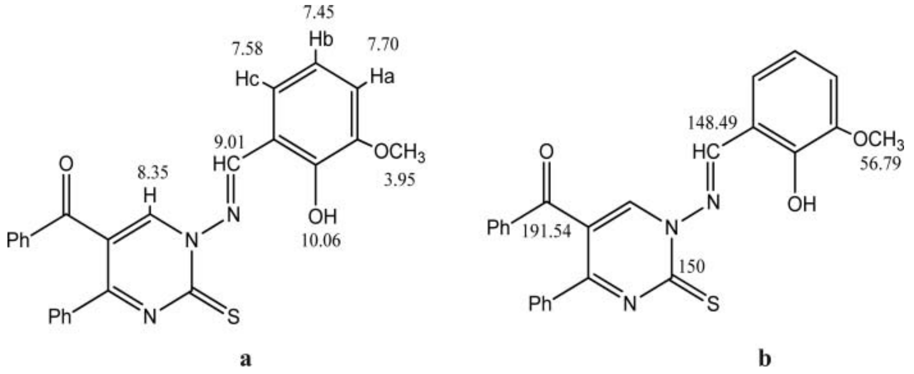

Figure 2 ^1H and ^{13}C NMR bands of the ligand depiction on the structure.

The singlet peak at 148.49 ppm is due to azomethine carbon of the ligand. On the other hand, the spectrum of the ligand showed peaks in the region δ 115.92–144.58 ppm, due to aromatic carbons. Otherwise, The ^{13}C NMR spectrum of the Cd(II) complex showed signal at 22.21 ppm of acetate carbon. ^1H and ^{13}C NMR bands of the ligand are depicted in Figure 2.

Mass Spectra. In the mass spectra of the ligand and Cu(II), Ni(II), Co(II), Mn(II), and Cd(II) metal complexes, peaks were attributable to the molecular ions; *m/z*: 442 [M+1], *m/z*: 1016 [M–2(CH_3COO)+4], *m/z*: 973 [M+2H_2O]$^+$, *m/z*: 972 [M+2H_2O-3H], *m/z*: 958 [M+4H], and *m/z*: 611 [M]$^+$ respectively.

Thermal Gravimetric Analysis (TGA). The TGA data agree with the formula suggested from elemental analyses. The thermal stabilities are investigated by TGA with 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 Ni(II), Co(II), Mn(II), and Cd(II) complexes suffer from the loss of H_2O in the first stage, 65–130 °C, and the ligands gradually decompose 220–580 °C. The complexes contain 2.5, 2, 1, and 1 moles of water of crystallization per complex molecule, respectively. The complexes decomposed to metal oxides at higher temperatures.[16,28–31]

CONCLUSIONS

We report the synthesis and spectroscopic study of the new HL heterocyclic Schiff base ligand and its metal complexes of the types [$M_2L_2(AcO)_2$], [M(L)AcO], and [ML_2]·nH_2O. However, single crystals of the complexes could not be isolated from any solutions, thus no definitive structure can be described. But, the analytical, spectroscopic and magnetic data enable us to predict the possible structures as shown in Figure 3.

EXPERIMENTAL MEASUREMENTS

All chemicals are commercially available and were used without further purification. 1-Amino-5-benzoyl-4-phenyl-1*H*-pyrimidine-2-thione (*N*-aminopyrimidine-2-thione) was synthesized as described elsewhere.[32]

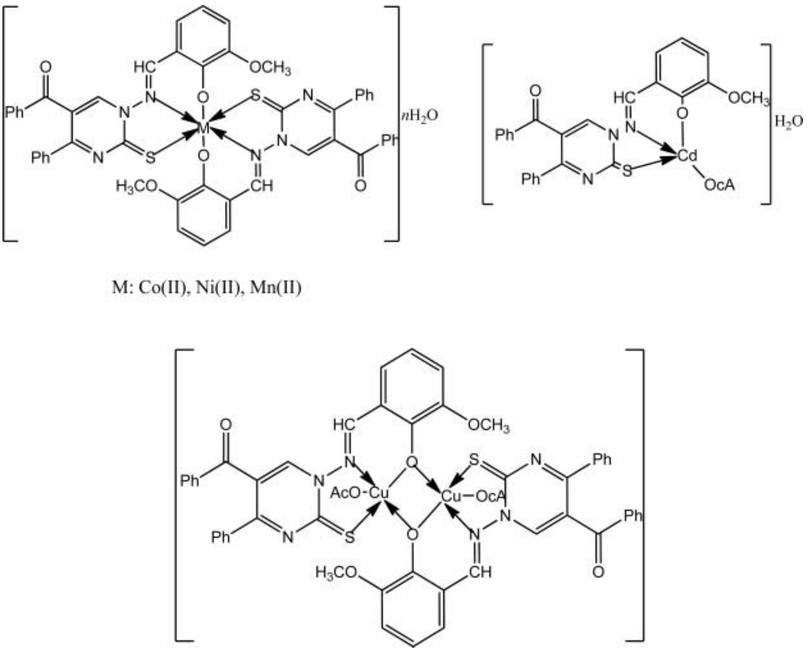

Figure 3 Suggested possible structures of the Schiff base transition metal complexes.

Physical Measurements

The elemental analyses (C, H, N, S) were performed by using Leco CHNS model 932 elemental analyzer. FTIR spectra were obtained using KBr pellets (4000–400 cm^{-1}) on Bio-Rad-Win-IR Spectrophotometer. The electronic spectra in the 200–900 nm range were recorded in DMF on Unicam UV2-100 UV-vis spectrophotometer. Magnetic measurements were carried out by Gouy method using $Hg[Co(SCN)_4]$ as a calibrant. Molar conductance of the Schiff base ligand and its transition metal complexes were determined in DMF at room temperature (r.t.) by using IQ Scientific Instruments Multimeter. The ^{1}H NMR and ^{13}C NMR spectra of the Schiff base were taken on Bruker 300 MHz Ultrashield TM NMR instrument. LC/MS-API-ES mass spectra were recorded with Agilent model 1100 MSD mass spectrophotometer. TGA measurements were performed by a Shimadzu-50 thermal analyzer.

The synthesized novel mononuclear and binuclear Schiff base complexes are stable at r.t. in the solid state. The metal complexes are generally soluble in DMF and DMSO. The analytical data of the ligand and their complexes together with physical properties are summarized in Table 4.

The metal-to-ligand ratio of pentacoordinated Cu(II) and tetracoordinated Cd(II) complexes was found to be 1:1. On the other hand, the metal-to-ligand ratio of Ni(II), Co(II), and Mn(II) complexes was found to be 2:1. All complexes had additional water of crystallization except for Cu(II) complex. This Schiff base have donor sites with the ONS sequence and varied coordination abilities. This nature of the Schiff base attracted our attention and aroused our interest in elucidating the structure of Co(II), Ni(II), and Cu(II) complexes.

Table 4 Analytical and physical data of the Schiff base and its transition metal complexes

Compound	Formula weight	Yield (%) (mg)	Color	m.p. m.p. (°C)	Anal. found (calc.)(%)			
					C	H	N	S
$C_{25}H_{19}N_3O_3S$(HL)	441	70 (310)	Orange	187	67.76 (68.01)	4.40 (4.34)	8.86 (9.52)	7.39 (7.26)
$[Cu_2(L)_2(AcO)_2]$	1128.2	56 (315)	Purple	149 (d)	57.29 (57.59)	3.62 (3.76)	7.75 (7.46)	6.01 (5.69)
$[Ni(L)_2]\cdot 2.5H_2O$	984.72	64 (315)	burgundy	224	60.83 (60.99)	3.93 (4.20)	8.79 (8.53)	6.51 (7.12)
$[Co(L)_2]\cdot 2H_2O$	975.95	66 (322)	dark blue	208	61.09 (61.53)	3.99 (4.13)	9.00 (8.61)	7.05 (6.57)
$[Mn(L)_2]\cdot H_2O$	953.94	59 (281)	Red	226	62.82 (62.95)	3.92 (4.02)	8.86 (8.81)	7.11 (6.72)
$[Cd(L)(AcO)]\cdot H_2O$	629.96	49 (308)	Red	156 (d)	51.83 (51.48)	3.71 (3.68)	6.79 (6.67)	5.54 (5.09)

Synthesis of the Ligand (HL)

The ligand (HL) was prepared by condensation between N-aminopyrimidine-2-thione and 3-methoxy-2-hydroxybenzaldehyde (o-vanillin). The hot ethanol solution (30 mL) of 3-methoxy-2-hydroxybenzaldehyde (0.152 g, 1 mmol) and hot solution mixture of ethanol-chloroform (7:3) (30 mL) of N-aminopyrimidine-2-thione (0.307 g, 1 mmol) were mixed slowly with a constant stirring (see Figure 1). Then the mixture was refluxed for 12 h. An orange precipitate was formed. The isolated solid precipitate was filtered off, washed with hot ethanol and methanol and then dried in vacuum over P_2O_5.

Synthesis of the Complexes

The ligand (HL) of 1 mmol (0.441 g) was dissolved in chloroform and methanol mixture (50 mL; 1:1, v/v) and a solution of 0.5 mmol of $M(AcO)_2 \cdot nH_2O$ in 15 mL of methanol was added drop-wise with continuous stirring. The mixture was stirred at 60 °C. The precipitated compound was removed by filtration, washed with hot methanol, and dried in vacuum desiccator. The complexes $[Cu_2(L)_2(CH_3COO)_2]$, $[Ni(L)_2] \cdot 2.5H_2O$, $[Co(L)_2] \cdot 2H_2O$, $[Mn(L)_2] \cdot H_2O$, and $[Cd(L)(CH_3COO)] \cdot H_2O$ were synthesized by following the above procedure using $Cu(CH_3COO)_2 \cdot H_2O$ (0.5 mmol, 0.100 g), $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol, 0.125 g), $Co(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol, 0.125 g), $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol, 0.123 g), and $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.5 mmol, 0.133 g).

REFERENCES

1. A. Golcu, M. Tumer, H. Demirelli, and R. A. Wheatley, *Inorganica Chimica Acta*, **358,** 1785–1797 (2005).
2. M. Asadi, S. Esmaielzadeh, and K. Mohammadi, *Phosphorus, Sulfur and Silicon*, **185,** 1445–1454 (2010).
3. B. Simo, L. Perello, R. Ortiz, A. Castineiras, J. Latorre, and E. Canton, *J. Inorg. Biochem.*, **81,** 275–283 (2000).
4. H. Francisco, A. Nuria, N. Miguel, M. Jose, and J. Maria, *J. Inorg. Biochem.*, **94,** 326 (2003).
5. R. Hilal, Z. M. Zaky, and S. A. K. Elroby, *Spectrochim. Acta Part A*, **63,** 740 (2006).
6. M. Gülcan and M. Sönmez, *J. Chem. Res.*, 274–277 (2010).
7. M. S. Nair and R. S. Joseyphus, *Spectrochim. Acta A*, **70,** 749–753 (2008).
8. K. N. Kumar and R. Ramesh, *Spectrochim. Acta A*, **60,** 2913–2918 (2004).
9. N. Galic, Z. Cimerman, V. Tomisic, *Spectrochim. Acta A*, **71,** 1274–1280 (2008).
10. L. P. Singh and J. M. Bhatnagar, *Talanta.*, **64,** 313 (2004).
11. G. Ferguson, J. N. Low, M. Quirós-Olozábal, J. M. Salas-Peregrin, F. Hueso-Urena, and M. N. Moreno-Carretero, *Polyhedron.*, **15,** 3233–3239 (1996).
12. S.-L. Ma, X.-X. Sun, S. Gao, C.-M. Qi, H.-B. Huang, and W.-X. Zhu, *Eur. J. Inorg. Chem.*, 846–851 (2007).
13. K. Siddappa, K. Mallikarjun, T. Reddy, M. Mallikarjun, C. V. Reddy, and M. Tambe, *E. J. Chemistry*, **6**(3), 615–624 (2009).
14. M. M. Bekhet and K. M. İbrahim, *Synth. React. Inorg. Met-Org. Chem.*, **16,** 1135 (1986).
15. A. A. A. Emara and O. M. I. Adly, *Trans. Met. Chem.*, **32,** 889–901 (2007).
16. N. Patel, H. Parekh, and M. Patel, *Trans. Met. Chem.*, **30,** 13–17 (2005).
17. A. B. P. Lever, *Inorganic Electronic Spectroscopy* (Elsevier, Amsterdam, 1984), 2nd ed.
18. J. R. Anacona, T. Martell, and I. Sanchez, *J. Chil. Chem. Soc.*, N 1 (2005).
19. S. Roy, T. N. Mandal, A. K. Barik, S. Gupta, R. J. Butcher, M. Nethaji, and S. K. Kar, *Polyhedron*, **27,** 593–601 (2008).

20. K. Nakamoto, *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds* (John Wiley & Sons, New York, 1997).
21. M. Sönmez and M. Şekerci, *Synth. React. Inorg. Met. Org. Chem.*, **34,** 485–498 (2004).
22. Z. Önal and B. Altural, *Turk. J. Chem.*, **23,** 401 (1999).
23. P. Maravali, K. Gudasi, and R. Goudar, *Trans. Met. Chem.*, **25,** 411 (2000).
24. S. S. Kandil, G. B. El-Hefnawy, E. A. Bakr, and A. Z. Abou El-Ezz, *Trans. Met. Chem.*, **28,** 168 (2003).
25. S. S. Kandil, S. M. A. Katib, and N. H. M. Yarkandi, *Trans. Met. Chem.*, **32,** 791 (2007).
26. J. Costamagna, J. Vargas, R. Latorre, A. Alvarado, and G. Mena, *Coord. Chem. Rev.*, **119,** 67–88 (1992).
27. M. Sönmez, *Polish J. Chem.*, **77,** 397–402 (2003).
28. P. Aranz-Mascaros, L. Godino-Salido, R. Lopez-Garzon, and P. Aranz-Mascaros, *Trans. Met. Chem.*, **26,** 581 (2001).
29. K. Aravindakshan and C. Nair, *J. Chem. Sci.*, **93,** 111 (1984).
30. N. Raman, V. Muthuraj, S. Ravichandran, and A. Kulandaisamy, *Proc. Indian Acad. Sci. (Chem. Sci.).*, **115,** 161 (2003).
31. N. Özpozan, H. Arslan, T. Özpozan, N. Özdes, and N. Külcü, *Thermochim. Acta*, **343,** 127 (2000).
32. Y. Akçamur, B. Altural, E. Sarıpınar, G. Kollenz, O. Kappe, K. Peters, E. Peters, and H. J. Schering, *Heterocycl. Chem.*, **25,** 1419 (1988).