J Therm Anal Calorim (2012) 109:991–998
DOI 10.1007/s10973-011-1808-y

Synthesis, spectroscopic, and thermal properties of some azomethine complexes of Cu(II), Ni(II), and Pt(II)

Murat Turkyilmaz · Alper Onder · Yakup Baran

Received: 24 May 2011 / Accepted: 18 July 2011 / Published online: 3 August 2011

Abstract Four polydentate azomehines and their mono- and binuclear Pt(II), Cu(II), and Ni(II) complexes were synthesized and characterized. The resulting complexes were characterized by FTIR, magnetic measurements, elemental analysis, conductivity measurements, and thermal analysis. Electronic spectra and magnetic susceptibility measurements sustain the proposed distorted square-planar structures for the copper complexes. The electronic spectra display the characteristic pattern of square-planar stereochemistry for the other complexes. The thermal analyses have evidenced the thermal intervals of stability and also the thermodynamic effects that accompany them. Azomethine complexes have a similar thermal behavior for the selected metal ions. The decomposition processes as water elimination, chloride anion removal as well as degradation of the organic ligands were observed.

Keywords Azomethine · Polydentate · TG · Stability · Complexes · Spectroscopy

Introduction

Azomethine metal complexes attract considerable interest and occupy an important role in the development of the chemistry of chelate systems because of the presence of hard nitrogen, oxygen, and soft sulfur donor atoms in backbones of these ligands. Tridentate and tetradentate azomethines and their complexes are of particular interest not only for their ability to form complexes with unusual coordination numbers, high thermodynamic stability, and kinetic inertness but also for their ability to exhibit catalytic [1], magnetic [2], biological properties such as antimicrobial [3–6], antitumor [7–9], antiviral [10], fungicidal [11] mimic biological sites upon complexation with metal ions [12–16] and nonlinear optical (NLO) [17], and materials chemistry by coordination chemists at all times [18–22].

Due to such a wide range of applications, new series of polydentate complexes of Pt(II), Cu(II), and Ni(II) are of particular interest. In our present struggle, we have chosen four azomethines, teradentate, (3-morpholin-4-ylpropyl)[(1*Z*)-pyridin-2-ylmethylene]amine (L^1); pentadentate, *N*,*N*′-(bis(pyridine-2-yl) formylidene)diethylenetriamine (L^2); tetradentate, 2-piperazin-1-yl-*N*-[(1*Z*)-pyridin-2-yl methylene]ethanamine (L^3); and a tridentate, 1-pyridin-2-yl-*N*-[(1*E*)-pyridin-2-yl methylene] methanamine (L^4) to prepare Cu(II), Ni(II), and Pt(II) complexes with different molecular properties. Polyamines, heterocycles, and azomethines are important chelating ligands [23–25] in this regard. The thermal behavior of the complexes with azomethines have attracted attention in the last years [26, 27], this attention being focused on the species that could have some practical applications [28, 29].The details of synthetic, spectral, magnetic, and thermal behaviors of these compounds are described.

Electronic supplementary material The online version of this article (doi:10.1007/s10973-011-1808-y) contains supplementary material, which is available to authorized users.

M. Turkyilmaz
Department of Chemistry, Science Faculty, Trakya University,
Edirne, Turkey

A. Onder · Y. Baran (✉)
Department of Chemistry, Art and Science Faculty,
Onsekiz Mart University, Canakkale, Turkey
e-mail: yakupbaran@yahoo.com

Experimental

Materials

The high purity reagents were obtained commercially and used as received without further purification. Spectroscopic grade and argon saturated methanol was used for the azomethine syntheses to prevent the hydration.

Physical measurements

Elemental analyses (carbon, hydrogen, and nitrogen) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra (KBr discs, 4000–400 cm^{-1}) were recorded using a Perkin Elmer BXII spectrometer. ^{1}H and ^{13}C NMR spectra of the ligands were measured with a Varian 300 MHz spectrometer in $CDCl_3$ and CD_3OH and chemical shifts were indicated in ppm relative to the solvent peak. Mass spectra were measured with GC–MS, Thermo Finnigan Trace DSQ. Molar conductance was measured using a WTW inolab cond 720 conductivity meter, where the cell constant was calibrated with 0.001 M KCl solution, and methanol was used as solvent. Thermal studies were made with a Seiko SII TG–DTA 6300 TG/DT analyzer heated from 20 to 1200 °C under dry air. The end products in TG–DTA study were analyzed by a Bruker D2 Phaser XRD. Electronic spectra were measured with an Agilent diode array HP 8453 UV–VIS spectrophotometer. The molar magnetic susceptibilities of the complexes were measured on powdered sample at room temperature using a Sherwood Scientific Magnetic Susceptibility Balance.

Synthesis of (3-morpholin-4-ylpropyl)[(1*Z*)-pyridin-2-ylmethylene]amine, L^{1}

(3-Morpholine-4-ylpropyl)amine (2.88 g, 20 mmol) and pyridine-2-carboxaldehyde (2.14 g, 20 mmol) were mixed together in 50 mL dry argon saturated methanol and refluxed for 9 h. The yellowish solution was concentrated on a rotary evaporator and left for crystallization. A yellowish oily product was obtained. The purity of the substance was checked by thin layer and one component was observed. Yield: % 71, 3.31 g. Anal. calcd. for $C_{13}H_{19}N_3O$, (233.31 g/mol): C 66.9; H 8.2; N 18.1%. Found: C 66.7; H 8.4; N 18.3%. FTIR (KBr, cm^{-1}): 3057 *v*(Ar–CH), 2949–2812 *v*(R–CH), 1648 *v*(CH=N). ^{1}H NMR (δ, ppm, $CDCl_3$): 13.15 (OH, s), 8.65 (CH=N, s), 8.56–7.32 (Ar–H), 3.72 (t, CH_2–O,), 2.71 (t, CH_2–N), 2.44 (t, CH_2–), 1.93 (t, CH_2–N), 1.74 (m, –CH_2–) ^{13}C NMR (δ, ppm, $CDCl_3$): 178.79 (CH=N), 162.33, 154.52, 149.55, 136.80, 121.41 (aromatics) 67.11, 59.52, 56.76, 53.83, 27.66 (aliphatics and morpholine –CH_2–). MS (Eİ): *m/z* 234.15 [M]$^{+}$.

Synthesis of *N*,*N*′-(bis(pyridine-2-yl)formylidene)diethylenetriamine, L^{2}

This ligand was prepared by the same procedure with L^{1}. Yield: (76%) 4.71 g. Anal. calcd. for $C_{16}H_{19}N_5$ (281.36): C 68.3; H 6.8; N 24.9%. Found: C 68.5; H 6.9; N 25.1%. IR (KBr, cm^{-1}): 3304 (NH), 3012 (Ar–CH), 2933–2835 (R-CH), 1653 (C=N), 1595(C=C). ^{1}H NMR (δ, ppm, $CDCl_3$): 8.53 (s, CH=N), 7.67–7.11 (Ar–H), 3.90 (t, –CH_2), 2.72 (t, –CH_2). ^{13}C NMR (δ, ppm, $CDCl_3$): 178.79 (CH=N), 159.74, 149.23, 136.67, 122.47, 122.07 (aromatics), 55.07, 48.95 (aliphatics). MS (Eİ): 282.17: *m/z*: 281.33.

Synthesis of 2-piperazin-1-yl-*N*-[(1*Z*)-pyridin-2-ylmethylene]ethanamine, L^{3}

This ligand was prepared by the same procedure with L^{1}. Yield: % 81, 3.72 g. Anal. calcd. for $C_{12}H_{18}N_4$ (218.30): C 66.0; H 8.3; N 25.7%. Found: C 66.1; H 8.2; N 25.6%. FTIR (KBr, cm^{-1}): 3360–3291 *v*(NH), 3080 *v*(Ar–CH), 2940–2815 *v*(R–CH), 1649 *v*(CH=N. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.58 (CH=N, s), 8.35–7.26 (Ar–H), 3.78 (t, CH_2–N=), 2.85 (t, CH_2–N,), 2.67 (t, CH_2–), 2.47 (t, CH_2). ^{13}C NMR (δ, ppm, $CDCl_3$): 178.79 (CH=N), 154.48, 149.62, 137.30, 125.01, 121.60 (aromatics), 58.78, 54.87, 53.94, 46.11 (aliphatics and piperazine). MS (Eİ): *m/z* 219.19 [M]$^{+}$.

Synthesis of 1-pyridin-2-yl-*N*-[(1*E*)-pyridin-2-ylmethylene]methanamine, L^{4}

This ligand was prepared by the same procedure with L^{1}. Yield: % 81, 3.72 g. Anal. calcd. for $C_{12}H_{11}N_3$ (197.24): C 73.1; H 5.6; N 21.3%. Found: C 73.0; H 5.7; N 21.1%. FTIR (KBr, cm^{-1}): 3062-3012 *v*(Ar–CH), 2916–2860 *v*(R–CH), 1648 *v*(CH=N, ^{1}H NMR (δ, ppm, $CDCl_3$): 8.30 (CH=N, s), 8.33–7.16 (Ar–H), 3.73 (s, CH_2–N=). ^{13}C NMR (δ, ppm, $CDCl_3$): 160.94 (CH=N), 158.25, 157.20, 149.52, 148.31, 136.74, 135.70, 124.16, 123.58, 122.17, 121.69 (aromatics), 73.87 (N–CH_2). MS (Eİ): *m/z* 197.24 [M]$^{+}$.

Synthesis of the complexes

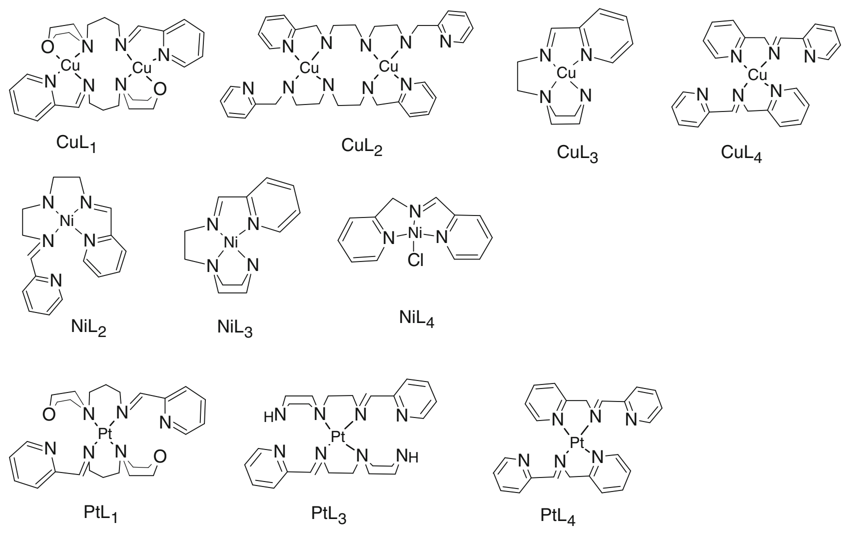
All the complexes of azomthines with Pt(II), Ni(II), and Cu(II) were prepared by following general method. The metal salt (10 mmol) was dissolved in 40 mL argon saturated methanol and the solution was added to a stirred solution of azomethine (12 mmol) in 30 mL argon saturated methanol solution at room temperature. On addition of metal to ligand solution immediate color change was observed according to the metal ions. Then the solution was warmed up to 50 °C and stirred for 10 h and then solution was concentrated on rotary evaporator. Solutions were left for crystallization but amorphous powders were obtained. The resulting precipitates were filtered by suction and then dried at vacuum oven at room temperature for 24 h. The elemental analysis data are summarized in Table 1. The proposed structures of the complexes and ligands are given in Schemes 1 and 2.

FTIR study

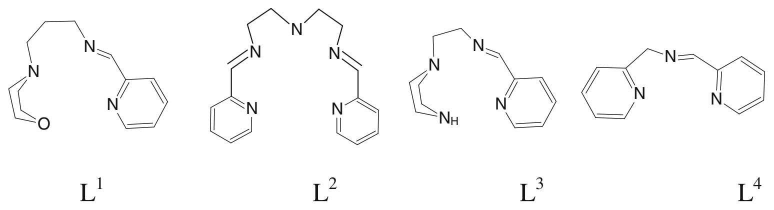
The FTIR spectra of the azomethines show N–H stretching vibration around 3200 cm^{-1} in L^2 and L^3 along with the several weak bands in the region 2940–2840 cm^{-1} for aliphatic C–H stretching. The moderately intense bands are

Table 1 Analytical data of the azomethines and their complexes

Compounds	Analysis found %/calc.				μ_{eff}/B.M.
	C	H	N	M	
L^1	66.83/66.72	8.41/8.27	18.31/18.01	–	–
$[\mathrm{PtL}^1_2]\ \mathrm{Cl}_2\cdot\mathrm{H}_2\mathrm{O}$	40.73/40.63	5.39/5.51	10.85/10.93	25.19/25.38	Diamagnetic
$[\mathrm{CuL}^1]_2\mathrm{Cl}_4\cdot 3\mathrm{H}_2\mathrm{O}$	39.42/39.55	5.53/5.62	10.52/10.64	15.92/16.10	1.34
L^2	68.51/68.34	6.92/6.81	25.11/24.89	–	–
$[\mathrm{NiL}^2]\mathrm{Cl}_2\cdot 2\mathrm{H}_2\mathrm{O}$	42.81/42.99	5.26/5.19	15.86/15.67	13.08/13.13	Diamagnetic
$[\mathrm{CuL}^2]_2\mathrm{Cl}_4\cdot 3\mathrm{H}_2\mathrm{O}$	43.27/43.40	5.21/5.02	15.93/15.82	14.21/14.35	1.39
L^3	66.13/66.02	8.24/8.31	25.61/25.67	–	–
$[\mathrm{NiL}^3]\ \mathrm{Cl}_2\cdot 3\mathrm{H}_2\mathrm{O}$	35.86/35.99	5.83/5.78	14.52/14.64	14.57/14.65	Diamagnetic
$[\mathrm{PtL}^3_2]\mathrm{Cl}_2\cdot\mathrm{H}_2\mathrm{O}$	40.17/40.00	5.44/5.32	15.41/15.55	27.13/27.07	Diamagnetic
$[\mathrm{CuL}^3]\mathrm{Cl}_2\cdot\mathrm{H}_2\mathrm{O}$	38.85/38.98	5.32/5.18	14.21/15.15	17.13/17.19	1.81
L^4	73.18/73.07	5.71/5.62	21.14/21.30	–	–
$[\mathrm{NiL}^4\mathrm{Cl}]\mathrm{Cl}\cdot 2\mathrm{H}_2\mathrm{O}$	39.73/39.61	4.48/4.33	6.03/6.14	16.07/16.14	Diamagnetic
$[\mathrm{PtL}^4_2]\ \mathrm{Cl}_2\cdot\mathrm{H}_2\mathrm{O}$	42.61/42.49	3.78/3.57	12.27/12.39	28.68/28.75	Diamagnetic
$[\mathrm{CuL}^4_2]\mathrm{Cl}_2$	50.37/54.50	4.38/4.19	15.66/15.89	11.89/12.01	1.88



Scheme 1 Proposed structures of the complexes. Counter ions and water are omitted



Scheme 2 Structure of the ligands

Table 2 Selected FTIR/cm^{-1} and electronic/nm spectral data of the ligands and complexes

Compounds	ν/H_2O	ν/NH	ν/C=N	ν/C=N(cyc)	ν/C–O	ν/M–O	ν/M–N	C.T. bands
L^1	–	–	1648	1589	1437	–	–	–
$[PtL^1_2]\ Cl_2 \cdot H_2O$	3431	–	1616	1581	1447	483	431	266
$[CuL^1]_2Cl_4 \cdot 3H_2O$	3432	–	1635	1600	1446	491	419	390, 510
L^2	–	3308	1653	1593	–	–	–	–
$[NiL^2]Cl_2 \cdot 2H_2O$	3466	3214	1642	1606	–	–	422	283, 390
$[CuL^2]_2Cl_4 \cdot 3H_2O$	3446	3025	1635	1607	–	–	421	295, 612
L^3	–	3291	1649	1588	–	–	–	–
$[NiL^3]\ Cl_2 \cdot 3H_2O$	3438	3218	1632	1599	–	–	420	277, 376
$[PtL^3_2]Cl_2 \cdot H_2O$	3427	3286	1629	1544	–	–	432	261
$[CuL^3]Cl_2 \cdot H_2O$	3431	3204	1646	1598	–	–	419	334, 663
L^4	–	–	1658	1592	–	–	–	–
$[NiL^4Cl]Cl \cdot 2H_2O$	3450	–	1647	1604	–	–	425	274, 393
$[PtL^4_2]\ Cl_2 \cdot H_2O$	3440	–	1631	1605	–	–	433	280
$[CuL^4_2]Cl_2$	–	–	1644	1606	–	–	418	390, 660

observed in between 3030 and 3100 cm^{-1} due to aromatic symmetric asymmetric C–H stretchings. The bands between 1648 and 1658 cm^{-1} in the free ligands are assigned to ν/C=N. These bands are shifted to lower wave numbers 1616–1647 cm^{-1} in the complexes due to the coordination of the nitrogen atom of the azomethine group to the metal ion [30, 31]. The band assignable to ν/C–O at 1437 cm^{-1} is shifted to higher wave number 1447 cm^{-1} in complexes. This shift is the indication of involvement of morpholine oxygen in complex formation. The ν/C=N (cyclic) IR bands in the ligands are also shifted higher frequencies in the complexes, indicating that pyridine nitrogen is coordinated to the metal ions. The bands observed for the complexes between 483–491 and 418–433 cm^{-1} were metal sensitive and are assigned to ν/M–O and ν/M–N [32], respectively. The appearance of the strong bands at 3400–3450 cm^{-1} suggests the presence of water in the complexes. The selected and most important IR absorption bands of the ligands and complexes are listed in Table 2.

Electronic spectra

Electronic spectra of metal complexes were recorded in argon saturated ultrapure water. Electronic spectra of the complexes show d–π* Metal–Ligand Charge Transfer (MLCT) transitions in the region 350–400 nm which can be assigned to the combination of $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions [33] in a distorted square-planar environment [34] and another high intensity intra-ligand (π–π*) transitions in between at 290 and 319 [35, 36]. The second expected low-energy ligand field bands, observed in between 480 and 650 nm range and are assigned as *d–d* transitions. The Ni(II) complexes are diamagnetic and the bands around 390–427 nm could be assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition [37] consistent with low spin square-planar geometry. Pt(II) complexes are all four coordinated; therefore square-planar geometry around the metal is expected. The appearance of two/three bands in the present complexes suggests them to possess square-planar structures.

^1H and ^{13}C NMR spectra

The ^1H and ^{13}C NMR spectra of the azomethines were carried out at room temperature in $CDCl_3$. The data are summarized in the synthesis of ligands. All the ligands show characteristic singlets at 8.65(L^1), 8.53(L^2), 8.58(L^3), and 8.30(L^4) ppm for –CH=N– protons and ^{13}C peaks at 162.33, 178.79, 178.79, and 160.94 ppm are observed for –CH=N–, respectively. Aromatic protons appear in between 8.56 and 711 ppm and ^{13}C peaks are observed in between 162.33 and 121.66 ppm.

Molar conductance

The observed molar conductances of the Cu(II), Ni(II), and Pt(II) complexes in 1 × 10^{-3} molar methanol solution are in the range 107–178 S cm^2 mol^{-1} for all complexes except for NiL^4 which is found to be 71 S cm^2 mol^{-1}. The molar conductivity measurements show that all the complexes are electrolytes in methanol. $[NiL^4]Cl$ complex has monovalent cation and counter ion, chloride for the electrical neutrality. The molar conductance values are consistent with the divalent cation and monovalent anions for $[CuL^3]Cl_2$, $[CuL^4]Cl_2$, $[NiL^2]Cl_2$, $[NiL^3]Cl_2$, $[PtL^1]Cl_2$, $[PtL^2]Cl_2$, $[PtL^4]Cl_2$ and tetravalent cations with monovalent anions for $[Cu_2L^1_2]Cl_4$ and $[Cu_2L^2_2]Cl_4$.

Table 3 Thermoanalytical results for the complexes

Complex	Step	Onset/°C	Endset/°C	Leaving group	Mass loss/%		Residue Expt./Calc.
					Exp	Calc.	
$[CuL^1]_2Cl_4{\cdot}3H_2O$	1	25	198	H_2O	6.1	6.8	CuO 6.1/9.9
	2	198	417	$L^1 + Cl_2$	87.6	80.7	
	3	417	620				
$[CuL^2]_2Cl_4{\cdot}3H_2O$	1	25	198	H_2O	6.1	6.1	CuO 7.6/8.9
	2	198	356	$L^2 + Cl_2$	86.9	79.6	
	3	356	644				
$[CuL^3]\ Cl_2{\cdot}2H_2O$	1	25	190	H_2O	4.5	4.8	CuO 14.3/17.1
	2	190	354	$L^3 + Cl_2$	82.1	78.2	
	3	354	614				
$[CuL^4_2]Cl_2$	1	25	390	$L^4 + Cl_2$	92.1	88.4	CuO 7.5/12.0
	2	390	629				
$[PtL^1_2]\ Cl_2{\cdot}2H_2O$	1	25	223	H_2O	5.6	4.7	PtO 19.8/25.4
	2	223	339	$L^1 + Cl_2$	74.1	70.0	
	3	339	579				
	4	579	975				
$[PtL^3_2]Cl_2{\cdot}H_2O$	1	25	198	H_2O	3.2	2.5	PtO 24.1/29.3
	2	198	361	$L^3 + Cl_2$	71.5	70.5	
	3	361	581				
	4	581	917				
$[PtL^4_2]\ Cl_2\ H_2O$	1	25	196	H_2O	2.6	2.6	PtO 29.0/31.1
	2	196	391	$L^4 + Cl_2$	68.5	68.6	
	3	391	598				
	4	598	988				
$[NiL^2]\ Cl_2\ 2H_2O$	1	25	204	H_2O	8.0	6.5	NiO 20.0/17.3
	2	204	376	$L^2 + Cl_2$	78.8	76.1	
	3	376	649				
$[NiL^3]Cl_2\ 3H_2O$	1	25	178	H_2O	14.5	13.5	
	2	178	368	$L^3 + Cl_2$	72.1	69.2	NiO 18.6/18.6
	3	368	638				
$[NiL^4Cl]Cl{\cdot}2H_2O$	1	25	188	H_2O	10.0	10.9	NiO 22.9/21.0
	2	188	668	$L^4 + Cl_2$	73.9	67.5	

Thermal analysis

TG–DTA analyses were performed in the temperature range of 25 and 1200 °C in the static dry air atmosphere to examine thermal stabilities of complexes. The TG curves of the Ni(II), Cu(II), and Pt(II) complexes with the same ligands are very similar and that of complex NiL^3 is discussed as an example. Thermal analysis data of the complexes are summarized in Table 3. The TG curves show mainly three stages in the decomposition process. The first stage decomposition temperature is in the range of 25–162 °C, with a mass loss of 14.5%, which corresponds to the loss of 3 mole of water calculated (13.5%). In the second to third stage of decomposition in the 162–638 °C temperature range, the remaining organic ligand molecule and two chloride ions are lost, with a mass loss of 69.2% (calcd. 72.1%). The final product is the NiO (18.6%, calcd. 18.6%). These results are in good accordance with the composition of the complexes. The thermogravimetric analyses reveal greater thermal stability of the Pt(II) complexes over the Ni(II) and Cu(II) azomethine complexes. It is confirmed that most of the complexes contain water in the structure. As a result of the thermal study, qualitative conclusion can be done for the stability of the complexes. PtL^1 complex is the most stable one and Pt(II) complexes are much more stable than the other complexes. The TG curves of the complexes are given in Figs. 1, 2, 3, 4, and 5.

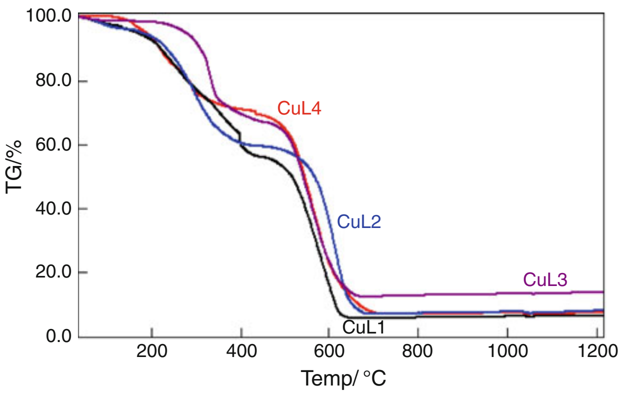


Fig. 1 TG curves of the Cu(II) complexes in dry air with heating rate 15 °C $\min^{-1}$. Sample holder: silica, sample mass: 8–10 mg

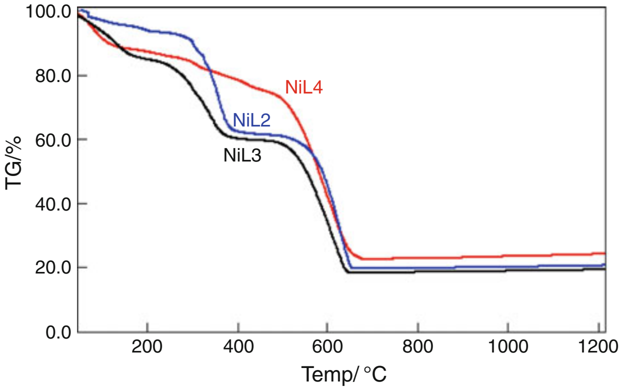


Fig. 2 TG curves of the Ni(II) complexes in dry air with heating rate 15 °C $\min^{-1}$. Sample holder: silica, sample mass: 8–10 mg

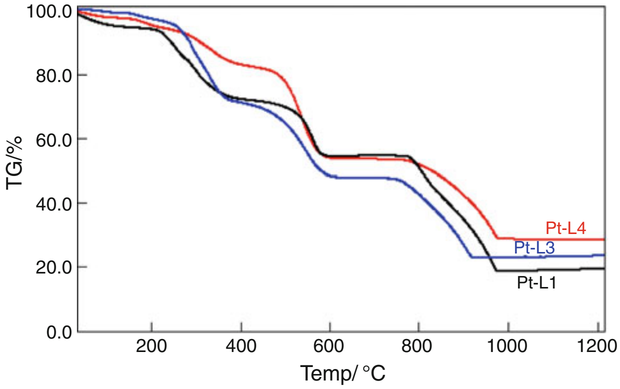


Fig. 3 TG curves of the Pt(II) complexes in dry air with heating rate 15 °C $\min^{-1}$. Sample holder: silica, sample mass: 8–10 mg

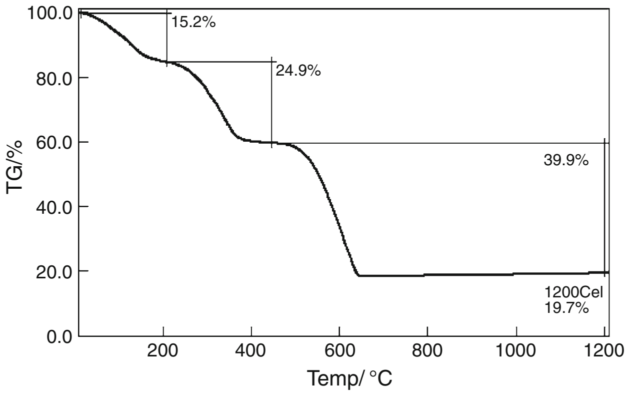


Fig. 4 The thermal decomposition of the NiL^3 complex

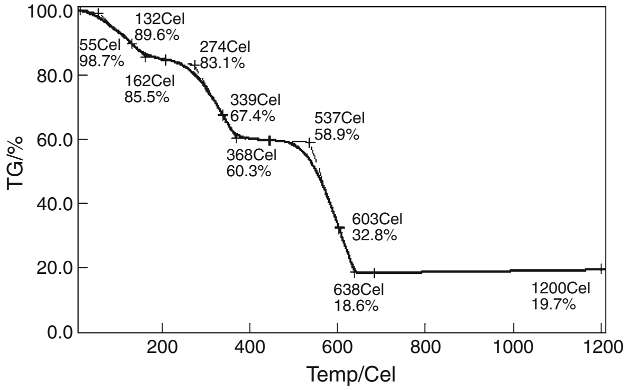


Fig. 5 The labeled TG decomposition curve of the NiL^3 complex

Magnetic moments of the complexes

The magnetic susceptibilities of the solid-state complexes under discussion were measured by the Gouy balance method. It was found that the effective magnetic moments of some of the complexes at room temperature are substantially lower (1.34 and 1.39 for CuL^1 and Cu L^2, respectively) than the pure spin value. The reduced magnetic moments of the dimeric copper complexes (L^1 and L^2) are consistent with the proposed dimeric planar structures with some tetrahedral distortion. The lowered magnetic moments are entirely due to exchange couplings since the magnetic moments of complexes with L^3 and L^4 which are found as monomeric complexes have magnetic moments 1.81–1.88. These data suggest that the L^1 and L^2 copper complexes have dimeric structures. The absorption spectra of the dimeric and monomeric structures show a broad absorption in the region 480–660 nm. The positions of absorption bands are consistent with square planar structures. Ni and Pt complexes are monomeric square planar diamagnetic complexes.

Conclusions

In this article, we presented copper(II), nickel(II), and platinum(II) complexes of four polydentate azomethine ligands. The metal centers in all complexes are four coordinated with square-planar geometry for Pt(II) and

Ni(II). The copper center is four coordinated with distorted square-planar geometry, which was also confirmed through UV–Vis spectral studies in solution. Cu2L$_2^1$ and Cu2L$_2^2$ are bimetallics while CuL^3 and CuL^4 are monometallic complexes. The structure of the complex is well sustained by the other spectral, room temperature magnetic moment, thermal, and conductometric studies. Since the similar configurations of the three Pt(II) complexes, their three-step thermal decomposition processes are also very similar. Ni(II) and Cu(II) complexes have two or three steps decomposition according to the structure of the ligands. The lattice water in the structures leads to remarkable increase inner and inter hydrogen bonds, so complexes are more tightly combined with each other. As a result azomethines in the complex structure posses less flexibility and lead to high thermal stability. The higher decomposition temperature under the linear heating rate indicates that Pt(II) complexes are much more stable than the other metal complexes. Cu(II) complexes are the least stable in the series studied.

Acknowledgements We thank the Trakya University TBAP 2101-113 for the financial support.

References

1. Pouralimardan O, Chamayou AC, Janiak C, Monfared HH. Hydrazone Schiff base-manganese(II) complexes: synthesis, crystal structure and catalytic reactivity. Inorg Chim Acta. 2007; 360:1599–608.
2. Sen S, Talukder P, Dey SK, Mitra S, Rosair GM, Hughes DL, Yap GPA, Pilet G, Gramlich V, Matsushita T. Ligating properties of a potentially tetradentate Schiff base [(CH$_3$)$_2$NCH$_2$CH$_2$N=CHC$_6$H$_3$(OH)(OMe)] with zinc(II),cadmium(II), cobalt(II), cobalt (III) and manganese(III) ions: synthesis and structural studies. J Chem Soc Dalton Trans. 2006; 1758–1767.
3. Mastrolorenzo A, Scozzafava A, Supuran CT. Arylsulfonyl-N,N-dialkyl-dithio carbamates as tumor cell growth inhibitors: novel agents targeting-tubulin. J Enzyme Inhib. 2001;16:54–65.
4. Chohan ZH, Pervez H, Rauf A, Scozzafava A, Supuran CT. Antibacterial Co(II), Cu(II), Ni(II) and Zn(II) complexes of thiadiazole derived furanyl, thiophenyl and pyrrolyl Schiff bases. J Enzyme Inhib. 2002;17:117–22.
5. Chohan ZH, Pervez H, Rauf A, Supuran CT. Antibacterial role of SO$_4^{2-}$, NO^{3-}, C$_2$O$_4^{2-}$ and CH$_3$COO$^-$ anions on Cu(II) and Zn(II) complexes of thiadiazole-derived pyrrplyl Schiff bases. Met Based Drugs. 2002;8:263–7.
6. Costes JP, Dahan F, Dupius A. Influence of anionic ligands (X) on the nature and magnetic properties of dinuclear LCuGdX3 center dot nH(2)O complexes (LH2 standing for tetradentate Schiff base ligands deriving from 2-hydroxy-3-methoxybenzaldehyde and X being Cl, N$_3$C$_2$, and CF$_3$COO). Inorg Chem. 2000;39:165–8.
7. West DX, Swearingen JK, Valde′s-Martinez J, Hernandez-Ortega S, El-Sawaf AK, Van Meurs F, Castineiras A, Garcia I, Bermejo E. Spectral and structural studies of iron(III), cobalt(II, III) and nickel(II) complexes of 2-pyridineformamide N(4)-methyl thio semicarbazone. Polyhedron. 1999;18:2919–29.
8. Tarasconi P, Capacchi S, Pelosi G, Cornia M, Albertini R, Bonati A, Dall' Aglio PP, Lunghi P, Pinelli S. Synthesis, spectroscopic characterization and biological properties of new natural aldehydes thiosemicarbazones. Bioorg Med Chem. 2000;8:157–62.
9. Ackerman LJ, Fanwick PE, Green MA, John E, Running WE, Swearingen JK, Webb JW, West DX. Structural and spectral studies of copper(II) and nickel(II) complexes of pyruvaldehyde mixed bis{N(4)-substituted thiosemicarbazones}. Polyhedron. 1999;18:2759–67.
10. Sartorelli AC, Agarwal KC, Tsiftsoglou AS, Moore EC. Characterization of the biochemical mechanism of action of α-(N)-heterocyclic carboxaldehyde thiosemi carbazones. Adv Enzyme Regul. 1977;15:117–39.
11. Teoh SG, Ang SH, Fun HK, Ong CW. Synthesis, crystal structure and biological activity of thiophene-2-carboxaldehyde thiosemicarbazone and its tin complexes. J Organomet Chem. 1999;580: 17–23.
12. Chohan ZH, Scozzafava A, Supuran CT. Unsymmetrical 1,1′-disubstituted ferrocenes: synthesis of Co(II), Cu(II), Ni(II) and Zn(II) chelates of ferrocenyl-1-thiadiazolo-1′-tetrazole, -1-thiadiazolo-1′-triazole and -1-tetrazolo-1′-triazole with antimicrobial properties. J Enzyme Inhib Med Chem. 2002;17:261–6.
13. Singh HL, Sharma M, Varshney AK. Studies on coordination compounds of organotin(IV) with schiff bases of amino acids. Synth React Inorg Met-Org Chem. 2000;30(3):445–56.
14. Nath M, Pokharia S, Yadav R. Organotin(IV) complexes of amino acids and peptides. Coord Chem Rev. 2001;215:99–149.
15. Chohan ZH, Praveen M, Ghaffer A. Structural and biological behaviour of Co(II), Cu(II) and Ni(II) metal complexes of some amino acid derived schiff-bases. Met-Based Drugs. 1997;4:267–72.
16. Lv J, Liu T, Cai S, Wang X, Liu L, Wang Y. Synthesis, structure and biological activity of cobalt(II) and copper(II) complexes of valine-derived schiff bases. J Inorg Biochem. 2006;100:1888–96.
17. Coghi L, Lanferdi AMM, Tiripicchio A. Crystal and molecular structure of thiosemicarbazide hydrochloride. J Chem Soc Perkin II. 1976; 1808–10.
18. Kasai K, Aoyagi M, Fujita M. Flexible coordination networks with fluorinated backbones. remarkable ability for ınduced-fit enclathration of organic molecules. J Am Chem Soc. 2000; 122(9):2140–1.
19. Kitagawa S, Kitaura R, Noro SI. Functional porous coordination polymers. Angew Chem Int Ed. 2004;43(18):2334–75.
20. Hoshino N, Ito T, Nihei M, Oshio H. Syntheses, structures and magnetic properties of multinuculear manganese complexes with Schiff base ligands. Inorg Chem Commun. 2003;6(4):377–80.
21. Khandar AA, Nejati K. Synthesis and characterization of a series of copper(II) complexes with azo-linked salicylaldimine Schiff base ligands. Polyhedron. 2000;19(6):607–13.
22. Zhou HP, Li DM, Wang P, Cheng LH, Gao YH, Zhu YM, Wu JY, Tian YP, Tao XT, Jiang MH, Fun HK. Synthesis, crystal structures, and two-photon absorption properties of dithiocarbazate Zn(II) and Pd(II) complexes. J Mol Struct. 2007;826(3): 205–10.
23. Chan WK. Metal containing polymers with heterocyclic rigid main chains. Coord Chem Rev. 2007;251:2104–18.
24. Vigato PA, Tamburini S. Advances in acyclic compartmental ligands and related complexes. Coord Chem Rev. 2008;252: 1871–995.
25. Lodeiro C, Pina F. Luminescent and chromogenic chemosensors based on polyamine and related compounds. Coord Chem Rev. 2009;253:1353–83.
26. Basak S, Sen S, Mitra S, Marschner C, Sheldrick WS. Square planar complexes of Cu(II) and Ni(II) with N$_2$O donor set of two Schiff base ligands: synthesis and structural aspects. Struct Chem. 2008;19:115–21.

27. Fan YH, Gao ZX, Bi CF, Xie ST, Zhang X. Synthesis and thermal decomposition kinetics of La(III) complexwith unsymmetrical Schiff base ligand. J Therm Anal Calorim. 2008;91: 919–23.
28. Patel SH, Pansuriya PB, Chhasatia MR, Parekh HM, Patel MN. Coordination chain polymeric assemblies of trivalent lanthanides with multidentate Schiff base synthetic, spectral investigation and thermal aspects. J Therm Anal Calorim. 2008;91:413–8.
29. Lalia-Kantouri M, Tzavellas L, Paschalidis D. Novel lanthanide complexeswith di-2-pyridyl ketone-p-chloro-benzoylhydrazone. J Therm Anal Calorim. 2008;91:937–42.
30. Nakamoto K. Infrared and Raman spectra of inorganic and coordination compounds, vol. 242. 3rd ed. New York: Wiley; 1978.
31. Surati KR, Thaker BT. Synthesis, spectroscopic and thermal investigation of Schiff-base complexes of Cu(II) derived from heterocyclic β-diketone with various primary amines. J Coord Chem. 2006;59:1191–202.
32. Ferraro JR. Low frequency vibrations of inorganic and coordination compounds. New York: Plenum Press; 1971.
33. Natarajan C, Tharmaraj P, Murugesan R. In situ synthesis and spectroscopic studies of copper(II) and nickel(II) complexes of 1-hydroxy-2-naphthylstyrylketoneimines. J Coord Chem. 1992;26: 205–13.
34. Dehghanpour S, Bouslimani N, Welter R, Mojahed F. Synthesis, spectral charac terization, properties and structures of copper(I) complexes containing novel bidentate iminopyridine ligands. Polyhedron. 2007;26:154–62.
35. Samanta B, Chakraborty J, Shit S, Batten SR, Jensen P, Masuda JD, Mitra S. Synthesis, characterisation and crystal structures of a few coordination complexes of nickel(II), cobalt(III) and zinc(II) with *N*′-[(2-pyridyl)methylene]salicyloylhydrazone Schiff base. Inorg Chim Acta. 2007;360:2471–81.
36. Ray A, Banerjee S, Butcher RJ, Desplanches C, Mitra S. Two new end-on azido bridged dinuclear copper and cobalt(II) complexes derived from the (*E*)-N′-((pyridine-2-yl)methylene acetohydrazide Schiff base ligand: characterisation, crystal structure and magnetic study. Polyhedron. 2008;27:2409–15.
37. Del Paggio AA, McMillin DR. Substituent effects and the photoluminescence of Cu(PPh3)2(NN)+ systems. Inorg Chem. 1983; 22:691–2.