# Mononuclear Complexes Based on Pyrimidine Ring Azo Schiff-Base Ligand: Synthesis, Characterization, Antioxidant, Antibacterial, and Thermal Investigations

Mehmet Gulcan,\*<sup>[a]</sup> Sadin Özdemir,<sup>[b]</sup> Abdurrahman Dündar,<sup>[c]</sup> Esin İspir,<sup>[d]</sup> and Mükerrem Kurtoğlu<sup>[d]</sup>

Keywords: Azo Schiff base complexes; Pyrimidine; Thermal behavior; Antioxidant activity; Antibacterial activity

**Abstract.** Six transition metal(II) complexes with the heterocyclic ligand HL (1),  $[CuL_2]\cdotH_2O$  (2),  $[NiL_2]\cdot3H_2O$  (3),  $[CoL_2]\cdot3H_2O$  (4),  $[MnL_2]\cdot3H_2O$  (5),  $[ZnL_2]\cdot2H_2O$  (6),  $[PdLOAc]\cdotH_2O$  (7) [HL = 5-benzoyl-1-((*E*)-(2-hydroxy-5-((*E*)-phenyldiazenyl)benzylidene)amino)-4phenylpyrimidin-2(1H)-one] were synthesized. The features of the azoSchiff bases were assigned from microanalytical, spectroscopic (IR,UV/Vis., <sup>1</sup>H- and <sup>13</sup>C NMR, API-ES mass), magnetic, and molar conductivity measurements at room temperature as well as thermal analysis. The electronic absorption spectroscopy and magnetic susceptibilitymeasurements of the complexes indicate square pyramidal arrangement for Pd<sup>II</sup> and octahedral environment for all the other complexes.The azo Schiff base HL acts as a monobasic tridentate ligand, which

### Introduction

The electrophilic carbon atoms of aldehydes and ketones can be targets of nucleophilic attack by primary amines. The result of this reaction is a compound in which the C=O double bond is replaced by a C=N double bond. This type of compound is known as an imine, or Schiff base, which was first reported by *Schiff* in 1864.<sup>[1]</sup>

Schiff bases and their metal complexes have expanded enormously and include a vast area of organometallic compounds and various aspects of bioinorganic chemistry.<sup>[1-3]</sup> Similarly, azo compounds are important molecules, which have attracted much attention in both academic and applied research.<sup>[4]</sup> Azo compounds, with two phenyl rings separated by an azo (–N=N–) bond, are versatile molecules and have received

*	Assist. Prof. Dr. M. Gulcan
	Fax: +90-4322251806
	E-Mail: mehmetgulcan65@gmail.com
[a]	Department of Chemistry, Faculty of Science
	Yuzuncu Yil University
	Van, 65080, Turkey
[h]	Department of Biology Faculty of Science and

- [b] Department of Biology, Faculty of Science and Arts Siirt University Siirt, 56100, Turkey
- [c] Health Services Vocational High School Medical Marketing and Promotion Programme Mardin Artuklu University Mardin, 47200, Turkey
- [d] Department of Chemistry Kahramanmaraş Sütçü İmam University Kahramanmaraş, 46050, Turkey

commonly coordinates through the oxygen atoms of the phenol OH and the pyrimidine one group, and the nitrogen atom of the azomethine group. The thermal behaviors of the ligand and its metal complexes were studied using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The metal complexes proved to be more thermally stable than the ligand; they decomposed at 10–30 °C higher temperatures. Antioxidant properties of the ligand and its metal complexes (DPPH free radical scavenging, ferrous chelating and reducing power activities) were tested. Antimicrobial activities were studied with gram-positive bacteria, which included *Bacillus subtilis* and *Staphylococcus aureus*, whereas *Escherichia coli* and *Pseudomonas aeruginosa* represented gram negative bacteria.

much attention in research areas both fundamental and application. The strong electronic absorption maximum can be tailored by ring substitution to fall anywhere from the ultraviolet to red-visible regions, allowing chemical fine- tuning of color.<sup>[5,6]</sup> This, combined with the fact that these azo groups are relatively robust and chemically stable, has prompted extensive study of azobenzene-based structures as dyes and colorants. Furthermore, the light-induced interconversion allows systems incorporating azo group to be used as photoswitches, effecting rapid and reversible control over a variety of chemical, mechanical, electronic, and optical properties.<sup>[7,8]</sup> Because of the good thermal stability of azo compounds, one of the most important applications of azo compounds is in the optical data storage. In general, cyanine dyes, phthalocyanine dyes, and metalazo complex dyes are used for DVD-R (digital versatile disc-recordable) as recording layer.<sup>[9]</sup> Azo dyes are a wellknown class of organic photoactive materials due to their excellent optical switching properties, good chemical stabilities and high solution process abilities.<sup>[10,11]</sup> These materials are widely used in heat transfer printing and textile industries,<sup>[12,13]</sup> optical data storage,<sup>[14]</sup> switching technologies,<sup>[15]</sup> and photo-refractive polymer industries.<sup>[16]</sup> Additionally, azo dyes are used as sensitizers in dye-sensitized solar cells (DSSCs) based on photosensitization of nanocrystalline titanium dioxide (nc-TiO<sub>2</sub>). Azo and azomethine dyes are organic dyes that contain the characteristic -N=N- and -CH=N- chromophores. Metal complexes of these dyes are considered to be

Pages: 10



Scheme 1. Preparation of the azo-Schiff base ligand (HL).

important stereochemical models in transition metal coordination chemistry due to their preparative accessibility and structural variety.<sup>[17]</sup> In addition to these properties, azo group-containing Schiff bases and their metal complexes were found to be biologically important compounds.<sup>[18]</sup>

In this work, the novel azo Schiff base, 5-benzoyl-1-((*E*)-(2-hydroxy-5-((*E*)-phenyldiazenyl)benzylidene)amino)-4-phenyl-pyrimidin-2(1H)-one (HL) was prepared and its behavior towards some transition metal ions were studied using different techniques such as elemental analyses, IR, <sup>1</sup>H-, <sup>13</sup>C NMR, and UV/Vis spectroscopy, mass spectrometry, thermal analysis, molar conductivity, and magnetic property measurements. The synthesis route for the title azo Schiff base is shown in Scheme 1. Additionally, the antioxidant and antimicrobial activities of the synthesized compounds were examined.

### **Results and Discussion**

### Synthesis and Solubility

The condensation reaction of pyrimidin-one with the azoaldehyde in EtOH results in the formation of the azo chromophore group containing tridentate Schiff base (HL). The reaction of HL and appropriate metal salts in 2:1 molar ratio in EtOH/CHCl<sub>3</sub> gives mononuclear coordination compounds of the types:  $ML_2$  ( $M = Cu^{II}$ , Co<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>, and Mn<sup>II</sup>) and [PdL(CH<sub>3</sub>COO)].

The formation of coordination compounds may be represented by taking the representative case of HL by the following Equation (1) and Equation (2):

$$2\text{HL} + M(\text{CH}_3\text{COO})_2 \cdot m\text{H}_2\text{O} \xrightarrow[\text{Reflux}]{\text{Reflux}} [M\text{L}_2] \cdot n\text{H}_2\text{O} + 2\text{CH}_3\text{COOH}$$
(1)

$$HL + Pd(CH_{3}COO)_{2} \xrightarrow{EtOH/CHCl_{3}} [PdL(CH_{3}COO)] \cdot nH_{2}O + CH_{3}COOH$$
(2)

The color of the Schiff base-linked phenylazo group is yellow, whereas those of the metal complexes are dark yellow, red, and claret red. All prepared compounds are air stable and soluble in DMSO and DMF. The analytical data and physical properties of novel azo Schiff base and metal(II) complexes are in good agreement with calculated values. The molar conductance of the complexes implies that the complexes are non-electrolytes.<sup>[19]</sup> Single crystals of the new azo-Schiff base ligand and its transition metal chelates could not be isolated from any organic solution, thus, no definite structures could be described. However, the analytical and spectroscopic data enables prediction of the possible structures of the complexes as shown in the Experimental Section.

#### Infrared Spectroscopy

The infrared spectra of the free azo Schiff base ligand and its complexes exhibit several bands in the region of 400– 4000 cm<sup>-1</sup>. To study the binding of tridentate ligand to the metal ion in the complexes, the infrared spectra of the metal complexes were compared with that of the free azo Schiff base ligand. Selected IR bands are listed in the Experimental Section.

The fundamental stretching mode of the azomethine moiety v(C=N) appear at 1617 cm<sup>-1</sup> in the spectrum of azo Schiff base ligand. All complexes spectra display also a very strong band about 1605-1610 cm<sup>-1</sup>, shifted to lower wavenumbers in comparison with free ligand. Such shift supports the participation of the azomethine nitrogen in coordination.<sup>[20-25]</sup> The stretching vibration v(C-O) of the phenol group of the free ligand is shifted from 1272 cm<sup>-1</sup> to lower wavenumbers (1259-1266 cm<sup>-1</sup>) in the complexes spectra suggesting coordination of this group.<sup>[26]</sup> Moreover, the strong band at 3446 cm<sup>-1</sup> in the Schiff base spectrum disappears in the spectra showing deprotonation of phenol group. Instead, a broad band about 3400-3500 cm<sup>-1</sup> that appears in the spectra of the complexes can be assigned to the v(OH) stretching vibration of water molecules (the presence was confirmed by elemental and thermal analyses as well). In the ranges of 416-442 and 510-528 cm<sup>-1</sup> two supplementary bands, tentatively assigned to stretching vibrations v(M-N) and v(M-O), can be observed in the spectra of the complexes.<sup>[27]</sup> The spectra of all complexes showed a band in the region 3051–3072 cm<sup>-1</sup> corresponding



to pyrimidine ring characteristic stretching absorption band. The other characteristic IR absorption band of the ligand is the stretching frequency v(N=N) at 1472 cm<sup>-1</sup>.<sup>[28]</sup> These data are well in accordance with those of reported complexes.

### *Electronic Absorption Spectroscopy and Magnetic Measurements*

The electronic spectra of the ligand and its complexes were recorded in DMF at room temperature. Electronic absorption spectroscopic data, molar conductivity, and magnetic susceptibility values of azo-linked Schiff base ligand (HL) and its transition metal complexes are given in the Experimental Section.

The chemical shift values ( $\lambda_{max}$ ) were determined by taking the difference between the absorption maxima of the metal complexes and the ligand. The bands at 226-368 nm were assigned to the imine  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  transition.<sup>[29,30]</sup> In the complexes,  $\pi \rightarrow \pi^*$  transitions shifted to longer wavelengths as a consequence of coordination when binding with a metal, confirming the imine nitrogen was coordinated to the metal atom.<sup>[31]</sup> In the spectra of the complexes, the absorption bands in the visible region shifted to higher wavelengths relative to their corresponding metal free ligand. These strong absorptions of the complexes in the near ultraviolet region can be assigned as ligand-to-metal charge transition (LMCT). As the -N=Nbands of the free ligand (478 nm) did not show important shift in the metal complexes, this was considered as evidence that the diazo group did not participate in complex formation. Therefore, it was assumed that the azo-linked Schiff base ligands coordinated to the metal atom through the salicylaldehyde oxygen, the pyrimidine-2-one, and imine nitrogen atoms. The electronic spectra of all the complexes were characterized by low-intensity absorptions with shoulders at approx. 492-642 nm, which can be associated with d-d transitions.<sup>[32]</sup> The Ni<sup>II</sup> complexes reveal two bands at 522 and 492 nm, which can be assigned to  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$ ,  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$  transitions, respectively. This is in accordance with the earlier reported values for the octahedral Ni<sup>II</sup> complexes.<sup>[33,34]</sup> The Cu<sup>II</sup> complexes reveal one broad band at 642 nm, which can be assigned to  $^2E_g{\rightarrow}^2T_{2g}$  transition in a distorted octahedral arrangement.<sup>[35]</sup> The electronic spectrum of the Mn<sup>II</sup> complex showed bands in the region 440–552 nm due to  ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$  (4G) (v<sub>1</sub>),  ${}^{6}A_{1g} \rightarrow {}^{4}Eg$  (4G) (v<sub>2</sub>),  ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$  (4D) (v<sub>3</sub>),  ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$ (4P) (v<sub>4</sub>) transitions, respectively, indicating an octahedral environment.<sup>[36]</sup> The electronic spectrum of the Co<sup>II</sup> complex shows two d-d bands at 507 and 466 nm, which are assigned<sup>[37]</sup> to the  ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}$  and  ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$  transitions for an octahedral arrangement. The Zn<sup>II</sup> complex does not show any d-d transition but the electronic spectra display supplementary intense bands at 444 and 392 nm, that may be assigned to metal-to-ligand charge transfer transitions.<sup>[38]</sup> The electronic spectra of the palladium(II) complex contain intense bands at 438 and 388 nm, assigned to charge transfer and spin allowed transition  ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$  for Pd<sup>II</sup> with a square planar stereochemistry.<sup>[26]</sup> The general structural formula of the complexes is shown in Figure 1. It was determined that Cu<sup>II</sup>, Ni<sup>II</sup>,

 $Co^{II}$ , and  $Mn^{II}$  complexes are paramagnetic. The magnetic moment values ( $\mu_{eff}$ ) are in the 1.84–5.73 B.M. range for metal complexes at room temperature. As it was expected zinc(II) and palladium(II) complexes did not show any magnetism.



Figure 1. Absorption spectra of the azo-Schiff base in various solvents.

In this study, UV/Vis absorption spectra in the range of 200 to 800 nm wavelength of the azo-pyrimidine Schiff base ligand in five organic solvents having different polarities were taken and given in Figure 1. In absorption spectra of the ligand in solution prepared in CH<sub>3</sub>CN, a maximum absorption band of around 390 nm was observed. This absorption is related to transmission of the electrons in non-bonding orbitals of the ligand to antibonding molecular orbitals  $(n \rightarrow \pi^*)$ .

In the absorption spectra of the ligand in the THF,  $CH_2Cl_2$ ,  $CHCl_3$ , and DMF solutions, the maximum absorption bands concerning transmitting  $n \rightarrow \pi^*$  were emerged in the range of the 410–418 nm. Besides, in THF and DMF solutions, a maximum absorption at 450 and 500 nm was formed, respectively. This maximum absorption in THF, which is shoulder-shaped, is significantly emerged in DMF. In particular this situation occurred in these two solutions was interpreted as the presence of a tautomeric structure.

On the other hand, the absorption of azo Schiff base ligands prepared in 1:1 ratio of (1) CH<sub>3</sub>CN-THF, (2) THF-CH<sub>2</sub>Cl<sub>2</sub>, (3) CH<sub>2</sub>Cl<sub>2</sub>-CHCl<sub>3</sub>, (4) CH<sub>3</sub>CN-DMF, and (5) CHCl<sub>3</sub>-DMF solutions was examined and the spectra are shown in Figure 2. The UV/Vis absorption spectra of the solutions numbered as (1), (2), and (3) are very similar to each other. Absorption curves of the solutions numbered as (4) and (5) are similar to each other. Absorption band around 500 nm obtained in pure DMF



Figure 2. Absorption spectra of the azo-Schiff base in various solvent mixtures.

Date: 08-05-14 17:28:14

# ARTICLE

solution was lost in mixtures of DMF. This may have occurred due to the decrease in polarity of the prepared solution.

# <sup>1</sup>H and <sup>13</sup>C NMR Spectroscopy

The <sup>1</sup>H- and <sup>13</sup>C NMR spectra of the azo Schiff base ligand were measured at room temperature in  $[D_6]DMSO$  and the <sup>1</sup>Hand <sup>13</sup>C NMR spectroscopic data are listed in the Experimental Section. The spectra of the ligand are shown in Figure 3 and Figure 4, respectively. The <sup>1</sup>H NMR spectrum of the azo Schiff base ligand exhibits a singlet signal in the 8.78 ppm, which is attributed to the azomethine group (-CH=N-) proton.<sup>[39]</sup> The singlet at 9.56 ppm (d) was due to pyrimidine ring (C-H) proton in the spectrum of the ligand.<sup>[42]</sup> The spectrum of the ligand showed other signals at 8.45 (d, 1 H, Ar-H, *J* = 2.4 Hz), 8.07 (dd, 1 H, Ar-H, *J* = 2.4 Hz and 8.8 Hz), 7.87 ppm (t, 4 H, Ar-H, *J* = 6.4 Hz), 7.62–7.31 ppm (m, 11 H, Ar-H), and 7.22 ppm (d, 1 H, Ar-H, *J* = 8.8 Hz) for aromatic protons. OH was not observed.<sup>[40]</sup>



Figure 3. <sup>1</sup>H-NMR spectrum of the azo-Schiff base ligand.



The <sup>13</sup>C NMR spectrum of the ligand displayed characteristic signals at 192.1, 171.2, and 162.1 ppm due to (OC–Ar), (C=O, pyrimidine), and (–C<sub>6</sub>, pyrimidine ring) of the azo Schiff base ligand, respectively. The peak at  $\delta$  = 161.9 ppm was due to azomethine carbon of the ligand.<sup>[37,41]</sup> Moreover, the spectrum of the ligand showed peaks in the region of 152.4–116.1 ppm (152.4, 151.7, 149.4, 145.4, 137.4, 137.3, 133.9, 131.6, 131.2, 130.2, 129.9, 129.2, 129.1, 128.7, 122.8, 119.2, 118.2 and 116.1 ppm) due to aromatic carbon atoms.

Since the solubilities of the diamagnetic Zn<sup>II</sup> and Pd<sup>II</sup> complexes in deuterated solvents are not at the desired level, NMR spectroscopic data and the spectra of these complexes are not included in the study.

#### Mass Spectroscopy

The mass spectrum of the azo Schiff base ligand showed a molecular ion peak at m/z: 501 [M + 2H]<sup>+</sup> corresponding to its proposed molecular formula. The mass spectrum of the azo Schiff base ligand is presented in Figure 5.



Figure 5. Mass spectrum of the ligand (HL).

#### Thermal Analyses

Thermal behaviors of the azo-azomethine ligand and its metal complexes were studied with TG and DTA. The analyses were carried out in order to investigate the content and nature of the water molecules in the complexes, as well as their thermal stabilities. Thermogravimetry (TG) is a powerful method to determine stoichiometry of metal complexes. The data of thermal analyses of the compounds are listed in Table 1.

The thermograms of the azo azomethine ligand, HL, and its  $Mn^{II}$  complex are taken as representative examples and are shown in Figure 6 and Figure 7. It can clearly be seen that the TGA curve of the ligand does not show any mass losses up to 200 °C, which indicates that no water molecule was incorporated in the ligand. The main weight loss began at 220 °C for the ligand. The endothermic effect with a maximum at 244 °C corresponded to degradation combined with the melting of the ligand. The data from the thermogravimetric analysis clearly indicated that the decomposition of the -N=N- and -CH=N- containing tridentate ligand proceeds in three steps at 221–392 °C, 392–477 °C, and 477–600 °C temperature ranges.

Thermal curves obtained for the synthesized metal complexes are very similar. The TG curves of  $[ML_2]\cdot nH_2O$  complexes consist mainly of three steps in the range of 20–150, 150–600 and >600 °C. The first estimated mass losses (%) for  $[ML_2]\cdot nH_2O$  complexes are of 4.46, 1.7, 4.2, 4.9, 3.3, and 4.7 within the temperature range of 20–150 °C and may be attributed to the losses of hydrated water molecules.<sup>[42]</sup> The second weight loss begin nearly at 240 °C for the metal complexes.



<b>Tuble If</b> Include decomposition of the neuro metal complete	Table 1.	Thermal	decom	position	of the	ligand	and	its	metal	compl	exe
---	----------	---------	-------	----------	--------	--------	-----	-----	-------	-------	-----

Compound	TG range /°C	Mass loss /%	Assignment
Ligand (HL) (1)	20-200	0	_
<b>-</b>	200-700	100	Decomposition of ligand
$[MnL_2] \cdot 3H_2O(2)$	20-150	4.2	Water evolution
	150-700	95.8	Decomposition of ligand and formation metal oxide
[NiL <sub>2</sub> ]·3H <sub>2</sub> O ( <b>3</b> )	20-150	4.7	Water evolution
2 23 2 ()	150-700	95.3	Decomposition of ligand and formation metal oxide
$[CoL_2]$ ·3H <sub>2</sub> O (4)	20-150	4.7	Water evolution
2 23 2 ,	150-700	95.3	Decomposition of ligand and formation metal oxide
$[CuL_2] \cdot H_2O(5)$	20-150	1.7	Water evolution
2 23 2 ( )	150-700	98.3	Decomposition of ligand and formation metal oxide
$[ZnL_2]$ ·2H <sub>2</sub> O (6)	20-150	3.3	Water evolution
2 23 2 ()	150-700	96.7	Decomposition of ligand and formation metal oxide
$[PdLOAc] \cdot H_2O(7)$	20-150	4.7	Water evolution
	150-700	95.3	Decomposition of ligand and formation metal oxide



Figure 6. Thermogram of the ligand (HL).



Figure 7. Thermogram of the [MnL<sub>2</sub>]·3H<sub>2</sub>O complex.

Except the first decomposition, the other decompositions could be correlated with the ligand decomposition products. The decomposition of the metal complexes in air ended at >600 °C with metal oxide formation. Comparison of the ligand and its metal complexes showed that the metal complexes are more thermally stable than the ligand with decomposing at temperatures that were 10-30 °C higher. The results are in accordance with the composition of the complexes as determined by elemental analyses.

#### **Biochemical Activity**

#### **DPPH Scavenging Activity**

The DPPH radical scavenging activity is the most commonly used method to determine antioxidant activities in a relatively short time compared with other methods. The DPPH

Z. Anorg. Allg. Chem. 0000, 0-0

radical scavenging activity of the compounds is shown in Figure 8. The DPPH scavenging activity range of the compounds was changed from 5 to  $100 \text{ mg} \cdot \text{L}^{-1}$  concentration. The experimental results showed that the scavenging effect of the compound and its metal complexes tested was concentration-dependent and the radical scavenging ratio increased with increasing concentrations in the tested range. The activities were: 1.01-30.83 % for HL (1), 1.14-17.51 % for [CoL<sub>2</sub>]·3H<sub>2</sub>O (2), for  $[NiL_2]$ ·3H<sub>2</sub>O (**3**), 02.-22.08% 2.28-23.47 % for  $[ZnL_2]$ ·2H<sub>2</sub>O (4), 0.5–23.98% for [PdLOAc]·H<sub>2</sub>O (5), 0.88-25.76% for [CuL2]·H2O (6), and 3.42-56.47% for [MnL<sub>2</sub>]·3H<sub>2</sub>O (7), The highest and the lowest free radical scavenging activity was obtained with 7 (56.47%) and 2 (17.51%) at concentration of 100 mg·L<sup>-1</sup>, respectively. In this study, ascorbic acid and trolox are used as standard antioxidants and they showed higher activities than the compounds at all concentration. The experimental results are also in agreement with the previous report by Prakash and Agirtas.[43-45]



Figure 8. DPPH scavenging activity of different concentrations of azo linked Schiff base ligand and its metal complexes and standards (Trolox and ascorbic acid).

#### Ferrous Ions Chelating Activity

In the presence of chelating agents, the complex formation is disrupted with the result that the red color of the complex is decreased. Measurement of color reduction therefore allows estimation of the chelating activity of the coexisting chelator.<sup>[46]</sup> The chelating activities of the synthesized azo-Schiff bases 1-7 and EDTA are shown in Figure 9. Ferrous ions chelating effect of the DMF solution of ligand and metal com-

# ARTICLE

plexes EDTA was increased with increasing concentration. Compounds 1, 3, and 6 revealed good chelating abilities at a concentration of 100 mg·L<sup>-1</sup>. Compound 5 showed the most active chelating activity among the tridentate ligand and its metal complexes. EDTA showed the highest activity (91.37– 99.01%).



Figure 9. Metal chelating activity of different concentrations of compounds and EDTA.

#### Determination of Reducing Power

The reducing power of the compounds is shown in Figure 10. To determine the reducing activity, it was experimented with the Fe<sup>III</sup> to Fe<sup>II</sup> transformations in presence of the compounds. The reducing ability of the compounds may be accepted as an important indicator for its potential antioxidant activity.<sup>[47]</sup> The superior activity was exhibited by  $\alpha$ -tocopherol at reducing power assay. The compounds did not show significantly reducing power abilities activity. The reducing power ability of [CoL<sub>2</sub>]·3H<sub>2</sub>O (4) chelate showed maximum reducing activity. Compounds 1–7 showed higher reducing activities than the compounds of tridentate Schiff base ligand containing azo chromophore.<sup>[47]</sup>



Figure 10. Reducing power of different concentrations of azo-Schiff base and its metal complexes  $\alpha$ -tocopherol.

#### Antimicrobial Activity

The antimicrobial effect of the azo Schiff base and its transition metal complexes were evaluated against *Bacillus subtilis* (ATCC 6051), *Escherichia coli* (ATCC 10536), *Pseudomonas aeruginosa* (ATCC 9027), and *Staphylococcus aureus* (ATCC 6538). The obtained data of antibacterial activity of the tested compounds is shown in Figure 11. All of the synthesized compounds examined exhibited antibacterial activity against *P. aeriginosa*, which increased in the following order: 1 < 2= 3 = 4 = 5 < 7 < 6. Schiff base demonstrated the weakest antibacterial activity against the tested bacteria among the tested compounds. The palladium(II) chelate of the azo Schiff base ligand [PdLOAc]·H<sub>2</sub>O (7) exhibited antibacterial activity against all the tested four bacteria. [CoL<sub>2</sub>]·3H<sub>2</sub>O (4) chelate showed antibacterial activity against E. coli, P. aerinogosa, and S. aureus, whereas the copper(II) (2) chelate showed antibacterial activity against B. subtilis, P. aerinogosa, and S. aureus. Schiff base derived from furylglyyoxal and *p*-toluidene and its metal complexes showed antibacterial activity against E.coli, S. aureus, and B. subtilis.<sup>[48]</sup> The compounds described herein showed similar antibacterial activity with this results. The results compared with standard antibiotic disc have indicated that some of studied compounds have antibacterial activity but the activity was lower than the standard antibiotic disc.



**Figure 11.** Antimicrobial activity of synthesized compounds (1–7) and standard antibiotics. AK30 = Amikacin (30  $\mu$ g), TE30 = Tetracycline (30  $\mu$ g), E15 = Erythromycin (15  $\mu$ g).

## Conclusions

The azo-linked Schiff base complexes of Cu<sup>II</sup>, Ni<sup>II</sup>, Co<sup>II</sup>, Mn<sup>II</sup>, Zn<sup>II</sup>, and Pd<sup>II</sup>, derived from 5-benzoyl-1-((*E*)-(2-hydroxy-5-((*E*) phenyldiazenyl)benzylidene)amino)-4-phenylpyrimidin 2(1H)-one (HL), were synthesized. On the basis of various physico-chemical and spectroscopic data presented and discussed above, the complexes may tentatively suggested to have octahedral arrangement around the central metal atom except Pd<sup>II</sup> complex, which was proposed to have squareplanar environment. According to these investigations, the ligand acts as tridentate compound coordinating through the nitrogen atom of the azomethine group and both the oxygen atoms of the phenol –OH and the pyrimidin-2(1H)-one part. All the synthesized metal complexes are found to be mononuclear.

The magnetic studies of the metal complexes account for their high spin nature due to the presence of five, three, two, and one unpaired electrons in  $Mn^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ , and  $Cu^{II}$  complexes, respectively. The antioxidant and antibacterial activities of the ligand and metal complexes were studied in vitro. [Pd(L)OAc]·H<sub>2</sub>O (**5**) complex showed the maximum ferrous chelating activity (90.92%) and from that point of view it might be used as a standard. Reducing power and DPPH free radical activities of the compounds showed lower activities



than the standard. Metal complexes of **6** and **7** showed high antibacterial effect against *E. coli* and *P. aeruginosa*, respectively. On the other hand, comparison of the ligand and its metal complexes showed that the metal complexes are more thermally stable than the ligand, decomposing at temperatures that were 10-30 °C higher. The results are in accordance with the composition of the metal complexes as determined by elemental analyses.

# **Experimental Section**

**Materials:** All of the reagents and solvents involved in synthesis were of analytical grade and obtained commercially. 1,1-Diphenyl-2-picryl-hydrazyl (DPPH), ferrous chloride, 3-(2-pyridyl)-5,6-bis(4-phenyl-sulfonic acid)-1,2,4-triazine (Ferrozine), trichloracetic acid (TCA), ascorbic acid, trolox, and dimethylformamide (DMF) were purchased from Sigma (Sigma-Aldrich GmbH, Sternheim, Germany). Blank anti-microbial susceptibity test discs were obtained from Oxoid. 1-Amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one (*N*-aminopyrimidine-2-one)<sup>[49]</sup> and 2-hydroxy-5-(phenyldiazenyl)benzaldehyde<sup>[50]</sup> were synthesized according to the method described in literature.

**Instruments:** The chemical analyses (C, H, N) were performed with a Leco CHNS model 932 elemental analyzer. FT-IR spectra were recorded using KBr pellets (4000–400 cm<sup>-1</sup>) with a Bio-Rad-Win-IR spectrophotometer. The electronic spectra in the range of 200–900 nm were recorded in DMF with a Unicam UV2–100 UV/Vis spectrophotometer. Magnetic measurements were carried out by Gouy method using Hg[Co(SCN)<sub>4</sub>] as a calibrant. Molar conductance of the azo Schiff base ligand and its transition metal complexes were determined in DMF at room temperature with a IQ Scientific Instruments Multimeter. The <sup>1</sup>H- and <sup>13</sup>C NMR spectra of the azo Schiff base were obtained with a Bruker 300 MHz Ultrashield TM NMR instrument. LC/MS-API-ES mass spectrum of the ligand was recorded with an Agilent model 1100 MSD mass spectrophotometer. The heating curves (TG and DTA) were recorded with a Shimadzu-50 thermobalance over the temperature range 20–700 °C at a heating rate of 10 °C·min<sup>-1</sup>.

Preparation of 5-Benzoyl-1-((E)-(2-hydroxy-5-((E)-phenyldiazenyl)benzylidene)amino)-4-phenylpyrimidin-2(1H)-one (HL) (1): The azo-aldehyde used for the synthesis of HL ligand was prepared by the diazo-coupling reaction (Scheme 1) between aniline and salicylaldehyde in alkaline medium under cold conditions by the method described in an earlier report.<sup>[50]</sup> A hot EtOH solution (30 mL) of the azo-aldehyde (0.226 g, 1 mmol) was added dropwise to a hot EtOH solution (30 mL) of N-aminopyrimidine-2-one (0.291 g, 1 mmol) whilst stirring. Afterwards the mixture was heated to reflux for 4 h. A yellow precipitate formed. The isolated solid precipitate was filtered off, washed with hot EtOH and Et<sub>2</sub>O and dried in vacuo over P<sub>2</sub>O<sub>5</sub>. The yellow product was soluble in chloroform, dimethylsolfoxide, and N,N'-dimethylformamide. Yield 340 mg (68%); Mp: 244 °C. C<sub>30</sub>H<sub>21</sub>N<sub>5</sub>O<sub>3</sub> (499,52 g·mol<sup>-1</sup>): calcd. C 72.13; H 4.24; N 14.02%; found: C, 72.02; H, 4.21; N, 13.94%. IR (KBr, selected data):  $\tilde{v} = 3346 v(OH/H_2O)$ , 3051 (C–H<sub>pyrimidine</sub>), 1672 v(C=O), 1617 (C=N<sub>azomethine</sub>), 1472 v(N=N) 1272 v(C-O<sub>phenol</sub>) cm<sup>-1</sup>. UV/Vis  $[\lambda \text{ (nm)}]: 478, 368, 348, 300 226.$  <sup>1</sup>**H NMR** (300 MHz, [D<sub>6</sub>]DMSO):  $\delta$ = 8.45 (d, 1 H, Ar-H, J = 2.4 Hz), 8.07 (dd, 1 H, Ar-H, J = 2.4 Hz and 8.8 Hz), 7.87 ppm (t, 4 H, Ar-H, J = 6.4 Hz), 7.62-7.31 ppm (m, 11 H, Ar–H), and 7.22 ppm (d, 1 H, Ar–H, J = 8.8 Hz) for aromatic protons. <sup>13</sup>C NMR (75 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 116.1–152.4 (aromatic C), 161.9 (-HC=N-), 162.1 (OC-Ar), 171.2 (C=Opyrimidine), 192.1 (-CO-Ph) ppm. API-ES: m/z 501.0 [M + 2H]+.

General Procedure for the Preparation of Metal Complexes 2-7: A solution of the metal salt M(CH<sub>3</sub>COO)<sub>2</sub>·xH<sub>2</sub>O (0.25 mmol) [50 mg  $Cu(CH_3COO)_2 \cdot H_2O;$ 62.5 mg Ni(CH<sub>3</sub>COO)<sub>2</sub>•4H<sub>2</sub>O; 62.5 mg  $Co(CH_3COO)_2 \cdot 4H_2O;$ 61.5 mg  $Mn(CH_3COO)_2 \cdot 4H_2O;$ 55 mg Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O; 56.5 mg Pd(CH<sub>3</sub>COO)<sub>2</sub>] in MeOH (25 mL) was added dropwise to a stirred solution of 5-benzoyl-1-((E)-(2-hydroxy-5-((E)-phenyldiazenyl)benzylidene)amino)-4-phenyl pyrimidin-2(1H)one (HL) (0.5 mmol, 250 mg) in a mixture of MeOH/CHCl<sub>3</sub> 1:1 (30 mL, V:V) as solvent at room temperature. The solution mixture was stirred and heated to reflux for 1 h at 80 °C. The solution was concentrated in a rotary evaporator to a volume of approx. 15 mL. The precipitate was filtered and washed with hot methanol and ethyl ether. The obtained solid was dried under vacuum at 80 °C overnight (Figure 12).



M=[Cu(II), n=1; Ni(II), n=3; Co(II), n=3; Mn(II), n=3; Zn(II), n=2]

Figure 12. Proposed feasible structures of the Schiff base transition metal complexes.

[**CuL**<sub>2</sub>]·**H**<sub>2</sub>**O** (2): The dark yellow product is soluble in dimethylsulfoxide, *N*,*N*'-dimethylformamide. Yield 140 mg (52%); Mp: 244 °C. C<sub>60</sub>H<sub>42</sub>CuN<sub>10</sub>O<sub>7</sub> (1078,58 g·mol<sup>-1</sup>): calcd. C 66.81; H 3.92; N 12.99%; found: C 66.49; H 3.90; N 12.79%. **IR** (KBr, selected data):  $\tilde{v} = 3500$ v(OH/H<sub>2</sub>O), 3072 (C–H<sub>pyrimidine</sub>), 1652 v(C=O), 1609 (C=N<sub>azomethine</sub>), 1471 v(N=N) 1259 v(C–O<sub>phenol</sub>); 528 (M–O), 417 (M–N) cm<sup>-1</sup>. **UV**/ **Vis** [ $\lambda$  (nm)]: 642, 472, 374, 236.  $\mu_{eff}$ , 1.84 BM,  $\Lambda_o$  (S·cm<sup>2</sup>·mol<sup>-1</sup>) 7.12.

[NiL<sub>2</sub>]·3H<sub>2</sub>O (3): The claret red product is soluble in dimethylsulfoxide, *N*,*N*'-dimethylformamide. Yield 110 mg (40%); Mp: 252 °C. C<sub>60</sub>H<sub>46</sub>NiN<sub>10</sub>O<sub>9</sub> (1109,76 g·mol<sup>-1</sup>): calcd. C 64.94; H 4.18; N 12.62%; found: C 64.56; H 4.15; N 12.58%. **IR** (KBr, selected data):  $\tilde{v} = 3546$ v(OH/H<sub>2</sub>O), 3064 (C–H<sub>pyrimidine</sub>), 1654 v(C=O), 1607 (C=N<sub>azomethine</sub>), 1471 v(N=N) 1261 v(C–O<sub>phenol</sub>); 515 (M–O), 420 (M–N) cm<sup>-1</sup>. **UV/Vis** [ $\lambda$  (nm)]: 522, 492, 476, 348, 228;  $\mu_{eff}$ , 2.91 BM,  $\Lambda_o$ (S·cm<sup>2</sup>·mol<sup>-1</sup>) 6.54.

**[CoL<sub>2</sub>]·3H<sub>2</sub>O** (4): The claret red product is soluble in dimethylsulfoxide, *N*,*N*′-dimethylformamide. Yield 125 mg (45%); Mp: 248 °C. C<sub>60</sub>H<sub>46</sub>CoN<sub>10</sub>O<sub>9</sub> (1110,00 g·mol<sup>-1</sup>): calcd. C 64.92; H 4.18; N 12.62%; found: C 64.58; H 4.03; N 12.34%. **IR** (KBr, selected data):  $\tilde{v} = 3521$  v(OH/H<sub>2</sub>O), 3056 (C–H<sub>pyrimidine</sub>), 1658 v(C=O), 1606 (C=N<sub>azomethine</sub>), 1473 v(N=N) 1261 v(C–O<sub>phenol</sub>); 513 (M–O), 416 (M–N) cm<sup>-1</sup>. **UV/Vis** [ $\lambda$  (nm)]: 507, 476, 466, 372, 234.  $\mu_{eff}$ , 3.96 BM,  $\Lambda_{o}$ (S·cm<sup>2</sup>·mol<sup>-1</sup>) 11.73.

$$\begin{split} & [\text{MnL}_2] \cdot 3H_2O \ (5): \text{The claret red product is soluble in dimethylsulfox-} \\ & \text{ide, $N,N'$-dimethylformamide. Yield 165 mg (60\%); Mp: 280 °C. \\ & C_{60}H_{46}\text{MnN}_{10}O_9 \ (1106,01 \text{ g}\cdot\text{mol}^{-1}): \text{ calcd. C } 65.16; \text{ H } 4.19; \text{ N} \\ & 12.66\%; \text{ found: C } 65.85; \text{ H } 3.86; \text{ N } 12.69\%. \text{ IR (KBr, selected data):} \\ & \tilde{v} = 3530 \ v(\text{OH/H}_2\text{O}), \ 3068 \ (\text{C-H}_{\text{pyrimidine}}), \ 1654 \ v(\text{C=O}), \ 1605 \end{split}$$

Pages: 10

# **ARTICLE**

(C=N<sub>azomethine</sub>), 1472 v(N=N) 1263 v(C–O<sub>phenol</sub>); 512 (M–O), 420 (M–N) cm<sup>-1</sup>. **UV/Vis** [ $\lambda$  (nm)]: 552, 484, 477 464, 440, 398, 234.  $\mu_{eff}$ , 5.73 BM,  $\Lambda_o$  (S·cm<sup>2</sup>·mol<sup>-1</sup>) 9.83.

[ZnL<sub>2</sub>]·2H<sub>2</sub>O (6): The red product is soluble in dimethylsulfoxide, *N*,*N*'-dimethylformamide. Yield 110 mg (40%). Mp: 285 °C. C<sub>60</sub>H<sub>44</sub>ZnN<sub>10</sub>O<sub>8</sub> (1098,43 g·mol<sup>-1</sup>): calcd. C 65.61; H 4.04; N 12.75%; found: C 65.98; H 3.88; N 12.73%. **IR** (KBr, selected data):  $\tilde{v} = 3441$ v(OH/H<sub>2</sub>O), 3051 (C–H<sub>pyrimidine</sub>), 1646 v(C=O), 1607 (C=N<sub>azomethine</sub>), 1472 v(N=N) 1264 v(C–O<sub>phenol</sub>); 512 (M–O), 416 (M–N) cm<sup>-1</sup>. **UV**/ **Vis** [ $\lambda$  (nm)]: 475, 444, 392, 306, 238.  $\mu_{eff}$ , D,  $\Lambda_o$  (S·cm<sup>2</sup>·mol<sup>-1</sup>) 17.83.

#### Antioxidant Activity

Scavenging Ability on DPPH Radicals: The hydrogen atoms or electrons donation ability of the tridentate ligand and its metal complexes and standards were determined by observing the bleaching of purple colored MeOH solution of 1,1-diphenyl-2-picrylhydrazyl (DPPH). The effect of the compounds on DPPH radical was estimated according to *Hatano* et al.<sup>[51]</sup> with some modification. 1 mL of different concentrations (5–100 mg·L<sup>-1</sup>) of the compounds was added into 2 mL of DPPH radical solutions. After shaking the mixture vigorously, the mixture allowed to standing for 30 min. The absorbance of the final solutions was measured at 517 nm with a spectrophotometer (Shimadzu, UV mini-1240 model). Inhibition of DPPH in percent (I%) was calculated in given formula:

$$\% = (A_{\text{control}} - A_{\text{compound}}/A_{\text{control}}) \times 100$$

where  $A_{\text{compound}}$  is the absorbance in the presence of compound and  $A_{\text{control}}$  is the absorbance in the absence of compound, respectively. Trolox and ascorbic acid were used as standards.

**Ferrous Ions Chelating Ability:** The method of *Dinis* et al.<sup>[52]</sup> was used for determining the chelating ability of compounds. The ligand (1 mL) and its metal chelates solutions (DMF) were prepared at 5–100 mg·L<sup>-1</sup> concentration range and were 0.1 mL of 2 mmol·L<sup>-1</sup> ferrous chloride. By adding of 0.2 mL of 5 mmol·L<sup>-1</sup> ferrozine, 1.85 mL of DMF solution was added. The mixture was incubated 10 min at room temperature and the absorbance was measured at 562 nm against blank. The results were shown as percentage of inhibition of the ferrozine-Fe<sup>2+</sup> compound formation. EDTA was used as a positive control to compare with the samples. By using the formula given

Chelating ability (%) =  $(A_{\text{control}} - A_{\text{compound}}/A_{\text{control}}) \times 100$ 

where  $A_{\text{control}}$  is the absorbance of the control reaction (containing only FeCl<sub>2</sub> and ferrozine), and  $A_{\text{compound}}$  is the absorbance of the compounds/reference. EDTA was used as a positive control.

**Reducing Power:** With using of the method of  $Oyaizu^{[53]}$  the reducing power of the compounds was determined. 1.25 mL of various concentrations of compounds (5–100 mg·L<sup>-1</sup>) were mixed with sodium phosphate buffer (1.25 mL, 200 mM, pH 6.6) and potassium ferricyanide (1.25 mL, 1%). The mixture was incubated at 50 °C for 20 min. After

incubation trichloroacetic acid (1.25 mL, 10%, w/v) were added and the mixture was centrifuged at 10000 rpm for 10 min. The supernatant fluid of the solution (1.25 mL) was mixed with deionized water (1.25 mL) and ferric chloride (0.25 mL, 0.1%). The absorbance of the final solution was measured spectrophotometrically at 700 nm.  $\alpha$ -Toc-opherol was used as standard.

**Antimicrobial Activity:** The synthesized ligand and its metal chelates were tested against gram-positive and gram-negative bacteria. Grampositive included *Bacillus subtilis* (ATCC 6051) and *Staphylococcus aureus* (ATCC 6538), and *Escherichia coli* (ATCC 10536) and *Pseudomonas aeruginosa* (ATCC 9027) represented gram-negative bacteria. Disc diffusion method was used for determination of antibacterial activity of the synthesized compounds on test bacteria.<sup>[54]</sup>

# Acknowledgements

*M.G.* thanks the Presidency of Scientific Research Projects of University of Yüzüncü Yıl (2011-FED-B009) for the financial support.

#### References

- [1] T. T. Tidwell, Angew. Chem. Int. Ed. 2008, 47, 1016–1020.
- [2] N. E. Borisova, M. D. Reshetova, Y. A. Ustynyuk, *Chem. Rev.* 2007, 107, 46–79.
- [3] A. A. Jarrahpour, M. Motamedifar, K. Pakshir, N. Hadi, M. Zarei, *Molecules* 2004, 9, 815–824.
- [4] A. Kakanejadifard, F. Esna-ashari, P. Hashemi, A. Zabardasti, Spectrochim. Acta Part A 2013, 106, 80–85.
- [5] H. Zollinger, Azo and Diazo Chemistry, Interscience, New York, 1961.
- [6] H. Zollinger, Colour Chemistry: Syntheses, Properties, and Applications of Organic Dyes, Wiley-VCH, Weinheim, 1987.
- [7] R. H. El Halabieh, O. Mermut, C. J. Barret, Pure Appl. Chem. 2004, 76, 1445–1465.
- [8] H. Nishihara, Bull. Chem. Soc. Jpn. 2004, 77, 407–428.
- [9] K. Nejati, Z. Rezvani, B. Massoumi, Dyes Pigm. 2007, 75, 653– 657.
- [10] A. Vig, K. Sirbiladze, H. J. Nagy, P. Aranyosi, I. Rusznak, P. Sallay, *Dyes Pigm.* **2006**, *71*, 199–205.
- [11] M. M. M. Raposo, A. M. R. C. Sousa, A. M. C. Fonseca, G. Kirsch, *Tetrahedron* 2005, 61, 8249–8256.
- [12] A. T. Slark, P. M. Hadgett, Polymer 1999, 40, 4001-4011.
- [13] G. Hallas, J. H. Choi, Dyes Pigm. 1999, 40, 119-129.
- [14] M. S. Ho, A. Natansohn, P. Rochon, *Macromolecules* **1995**, *28*, 6124–6127.
- [15] Y. Nabeshima, A. Shishido, A. Kanazawa, T. Shiono, T. Ikeda, T. Hiyama, *Chem. Mater.* **1997**, *9*, 1480–1487.
- [16] G. Iftime, F. L. Labarthet, A. Natansohn, P. Rochon, K. Murti, *Chem. Mater.* 2002, 14, 168–174.
- [17] R. J. Cassella, V. A. Salima, L. S. Jesuino, R. E. Santelli, *Talanta* 2001, 54, 61–67.
- [18] A. S. El-Tabl, M. M. E. Shakdofa, A. M. E. Shakdofa, J. Serb. Chem. Soc. 2013, 78, 39–55.
- [19] W. L. Geary, Coord. Chem. Rev. 1971, 7, 81-122.
- [20] F. Dogan, M. Ulusoy, O. F. Ozturk, I. Kaya, B. Salih, J. Therm. Anal. Calorim. 2009, 961, 267–276.
- [21] G. Avsar, H. Altinel, M. K. Yilmaz, B. Guzel, J. Therm. Anal. Calorim. 2010, 101, 199–203.
- [22] A. D. Khalaji, S. M. Rad, G. Grivani, J. Therm. Anal. Calorim. 2011, 103, 747–751.
- [23] G. Pethe, A. Yaul, A. Aswar, J. Therm. Anal. Calorim. 2012, 107, 97–103.
- [24] S. Shukla, A. P. Mishra, J. Therm. Anal. Calorim. 2012, 107, 111– 117.
- [25] N. Nishat, S. Hasnain, T. Ahmad, A. Parveen, J. Therm. Anal. Calorim. 2011, 105, 969–979.

8



- [26] E. Tas, A. Kilic, M. Durgun, L. Kupecik, I. Yilmaz, S. Arslan, Spectrochim. Acta Part A 2010, 75, 811–818.
- [27] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1997.
- [28] Z. Rezvani, M. A. Ghanea, K. Nejati, S. A. Baghaei, *Polyhedron* **2009**, *28*, 2913–2918.
  [29] H. Colchoubian, W. L. Waltz, J. W. Quail, *Can. J. Chem.* **1999**,
- 77, 37–56.
- [30] S. F. Dyke, A. J. Floyd, M. Sainsbury, R. S. Theobald, Organic Spectroscopy – An Introduction, Longman, New York, 1978.
   [21] W. Crambin, S. Letter, 1999, 322 (70) (22)
- [31] W. Guangbin, Spectrosc. Lett. 1999, 32, 679-688.
- [32] K. Saridha, R. Karvembu, P. Viwanathamurthi, S. Yasodhai, Synth. React. Inorg. Met-Org. Nano-Chem. 2005, 35, 707–711.
- [33] A. B. P. Lever, Inorganic Electronic Spectroscopy, 2nd ed., Elsevier, Amsterdam, 1984.
- [34] M. Sönmez, M. Çelebi, A. Levent, İ. Berber, Z. Şentürk, J. Coord. Chem. 2010, 63, 1986–2001.
- [35] H. Liu, H. Wang, F. Gao, D. Niu, Z. Lu, J. Coord. Chem. 2007, 60, 2671–2678.
- [36] K. B. Gudasi, S. A. Patil, R. S. Vadavi, R. V. Shenoy, M. S. Patil, J. Serb. Chem. Soc. 2006, 71, 529–542.
- [37] M. Sönmez, M. Çelebi, İ. Berber, Eur. J. Med. Chem. 2010, 45, 1935–1940.
- [38] M. Kalanithi, M. Rajarajan, P. Tharmaraj, J. Coord. Chem. 2011, 64, 842–850.
- [39] C. Anitha, C. D. Sheela, P. Tharmaraj, S. Sumathi, Spectrochim. Acta Part A 2012, 96, 493–500.
- [40] A. D. Khalaji, D. Das, J. Therm. Anal. Calorim, DOI 10.1007/ s10973-013-2974-x.

- [41] A. M. A. Alaghaz, H. A. Bayoumi, Y. A. Ammar, S. A. Aldhlmani, J. Mol. Struct. 2013, 1035, 383–99.
- [42] E. Ispir, S. Serin, J. Therm. Anal. Calorim. 2008, 94, 281-288.
- [43] C. R. Prakash, S. Rajal, G. Saravanan, P. D. Kumar, T. P. Selvam, *Asian J. Res. Pharm. Sci.* 2011, *1*, 140–143.
- [44] M. S. Agirtas, I. Gümüş, V. Okumus, A. Dundar, Z. Anorg. Allg. Chem. 2012, 638, 1868–1872.
- [45] M. S. Agirtas, B. Cabir, S. Ozdemir, *Dyes Pigm.* 2013, 96, 152– 157.
- [46] F. Yamaguchi, T. Ariga, Y. Yoshimira, H. Nakazawa, J. Agric. Food Chem. 2000, 48, 180–185.
- [47] G. Ceyhan, C. Çelik, S. Urus, İ. Demirtas, M. Elmastas, M. Tumer, Spectrochim. Acta Part A 2011, 81, 184–198.
- [48] C. G. Saxena, S. V. Shrivastava, J. Indian Chem. Soc. 1987, 64, 685–686.
- [49] B. Altural, Y. Akçamur, E. Sarıpınar, I. Yıldırım, G. Kollenz, *Monatsh. Chem.* **1989**, *120*, 1015–1020.
- [50] K. Sarma, T. S. Basu Baul, W. L. Basaiawmoit, R. Saran, Spectrochim. Acta Part A 1993, 49, 1027.
- [51] T. Hatano, R. Edamatsu, A. Mori, Y. Fujita, E. Yasuhara, *Chem. Pharm. Bull.* **1989**, *37*, 2016–2021.
- [52] T. C. P. Dinis, V. M. C. Madeira, L. M. Almeida, Arch. Biochem. Biophys. 1994, 315, 161–169.
- [53] M. Oyaizu, Jpn. J. Nutr. 1986, 44, 307-315.
- [54] D. Kalemba, A. Kunicka, Curr. Med. Chem. 2003, 10, 813-829.

Received: February 20, 2014 Published Online: ...

Date:

.

# ARTICLE \_

М.	Gulcan,*	S. Ozdemir, A. Dündar, E. Ispir,	
М.	Kurtoğlu		1–10

Mononuclear Complexes Based on Pyrimidine Ring Azo Schiff-Base Ligand: Synthesis, Characterization, Antioxidant, Antibacterial, and Thermal Investigations



M=[Cu(II), n= 1; Ni(II), n=3; Co(II), n= 3; Mn(II), n=3; Zn(II), n=2]