

Research Article

Synthesis and Antibacterial Activities of Sulfur-Containing Bissalicylaldehyde Schiff Base and Binuclear Nickel(II) Nanorod Complex

Xiao-Lan Yang, Guo-Qing Zhong, and Li Wu

State Key Laboratory Cultivation Base for Nonmetal Composite and Functional Materials, School of Material Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, China

Correspondence should be addressed to Guo-Qing Zhong; zgq316@163.com

Received 29 May 2013; Revised 31 July 2013; Accepted 3 August 2013

Academic Editor: Charles A. Mebi

Copyright © 2013 Xiao-Lan Yang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Nickel(II) acetate tetrahydrate was treated with the ligand $\text{CH}_2(\text{H}_2\text{sal-sbdt})_2$ in methanol heated at reflux to yield a novel binuclear Ni(II) nanorod complex of the formula $\text{CH}_2\{\text{Ni}(\text{II})(\text{sal-sbdt})(\text{H}_2\text{O})\}_2$. The ligand of $\text{CH}_2(\text{H}_2\text{sal-sbdt})_2$ was derived from 5,5'-methylene-bissalicylaldehyde and *S*-benzylthiocarbazate. The complex was characterized by elemental analysis, UV-Vis, FT-IR spectra, thermal analysis (TG-DSC), and scanning electron microscopy (SEM). The nickel(II) was coordinated by imino nitrogen, thiolato sulfur, and phenolic oxygen from the Schiff base ligand, and oxygen from the coordinated water, respectively. The pyrolysis reactions in the thermal decomposition process of the complex, the experimental, and calculated percentage mass loss were also given. The Ni(II) complex belonged to nanocrystalline metal complex, and the average size of the nanorod complex was about 30 nm × 150 nm. The antibacterial activities were screened for the Schiff base ligand and the Ni(II) nanorod complex against four bacteria: *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*, and *Staphylococcus epidermidis*. Both the ligand of $\text{CH}_2(\text{H}_2\text{sal-sbdt})_2$ and the Ni(II) complex had the most intense antibacterial activities against *Escherichia coli*.

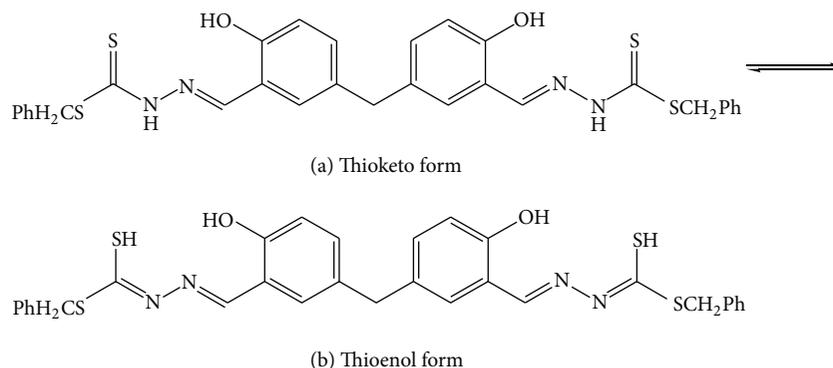
1. Introduction

The sulfur-containing bissalicylaldehyde Schiff base ligands and the corresponding complexes of Schiff bases are becoming rather important for their various structures and extensive applications. Those Schiff bases derived from the condensation of *S*-benzylthiocarbazate with dialdehyde [1, 2]. Although synthesis of sulfur-containing bissalicylaldehyde Schiff base and its complexation products containing molybdenum and vanadium ion were reported in recent years [3, 4], the synthesis of its nickel complex has not been reported. Because of the special biological [5, 6] and catalytic [7, 8] properties, chemists have great interest in the coordination chemistry of nickel. The sulfur-containing bissalicylaldehyde Schiff base derived nickel ion complexes have been extensively studied some time ago owing to their great variety of biological activity ranging from antibacterial, antitumoral, and antiviral activities, and so forth [9–11]. In this research we used a bistridentate ONS Schiff base, derived

from the condensation of 5,5'-methylene-bissalicylaldehyde with *S*-benzylthiocarbazate, as ligand and nickel(II) acetate tetrahydrate to synthesize one new nanorod complex, the average size of the complex was about 30 nm × 150 nm. In order to evaluate its novel coordination chemistry and biological properties, we described the new complex potential as antibacterial agents.

2. Experimental

2.1. Materials and Physical Measurements. All materials were commercial products of analytical-grade purity and used without further purification. *S*-benzylthiocarbazate [12] and 5,5'-methylene-bissalicylaldehyde [13] were prepared by the literature methods. Salicylaldehyde and nickel(II) acetate tetrahydrate were received from Chengdu Kelong Chemical Reagent Company. *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*, and *Staphylococcus epidermidis* were provided by the 404 hospital of Sichuan Mianyang.



SCHEME 1: Tautomeric forms of the Schiff base ligand.

The nickel content was determined by EDTA complexometric titration with murexide as the indicator and the sample was heated in the muffle furnace at 500°C for 2 h and dissolved by a small quantity of diluted sulphuric acid. The carbon, hydrogen, nitrogen, and sulphur analyses in the complex were obtained using a Vario EL CUBE elemental analyzer. The IR spectra were recorded on an FT-IR spectrophotometer (Nicolet-5700) in the region from 4000 to 225 cm^{-1} using KBr pellets. UV-Vis spectra in DMSO solvent were recorded on a Unico (UV-2102) spectrophotometer over the ranges of 200–600 nm. The thermogravimetric analysis of the metal complex was measured by a SDT Q600 thermogravimetric analyzer under air. The measurement was recorded from 30 to 800°C at the heating rate of 10°C min^{-1} . The morphology of the metal complex was obtained by a Ultra-55 scanning electron microscopy.

2.2. Synthesis of the Schiff Base of $\text{CH}_2(\text{H}_2\text{sal-sbdt})_2$. The Schiff base of $\text{CH}_2(\text{H}_2\text{sal-sbdt})_2$ was prepared by adapting methods reported in the literatures [3, 4]. A solution of 5,5'-methylbis(salicylaldehyde) (4.48 g, 17.5 mmol) was prepared in hot methanol (70 mL), and a solution of S-benzylthiocarbamide (6.93 g, 35.0 mmol) in methanol (40 mL) was added to the above. The reaction mixture was heated at reflux for 5 h on a water bath and was put in a refrigerator for 10 h. The deposited yellow solid was filtered, washed with methanol, and dried at 50°C. Finally, it was recrystallized from hot methanol to give a slight yellow solid. The yield was about 75%.

2.3. Synthesis of the Nickel(II) Complex $\text{CH}_2\{\text{Ni(II)}(\text{sal-sbdt})(\text{H}_2\text{O})\}_2$. The Schiff base $\text{CH}_2(\text{H}_2\text{sal-sbdt})_2$ (1.85 g, 3 mmol) was dissolved in the hot mixed solvent of methanol (60 mL) and DMF (10 mL), and nickel(II) acetate tetrahydrate (1.51 g, 6 mmol) dissolved in methanol (50 mL) was added to the above solution with vigorous stirring. The reaction mixture was refluxed on a water bath for 4 h. The deposited slight yellow solid was filtered, washed with methanol and tetrahydrofuran, and dried at 70°C. Some brown powder was obtained. The yield of the complex was about 90%.

2.4. Qualitative Antimicrobial Assay. Four pathogenic bacteria were used to test the biological potential of the Schiff base

ligand and its nickel(II) complex. They were *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*, and *Staphylococcus epidermidis*. The culture maintenance and preparation of inoculum were referenced by the literature method [14]. The antimicrobial activity of these compounds was determined qualitatively by Oxford cup diffusion method [14, 15]. A lawn of microorganisms was prepared by pipetting and evenly spreading inoculums (10^6 – 10^7 CFU cm^{-3}) (CFU = colony forming units) on to agar set in petri dishes, using nutrient agar (NA) for the bacteria. The Oxford cups were stuck on the previously inoculated agar surface and injected solution of the complex (0.15 mL) under sterile conditions. The plates were incubated for 24 h at 37°C. The antimicrobial activity was indicated by the presence of clear inhibition zones around the discs.

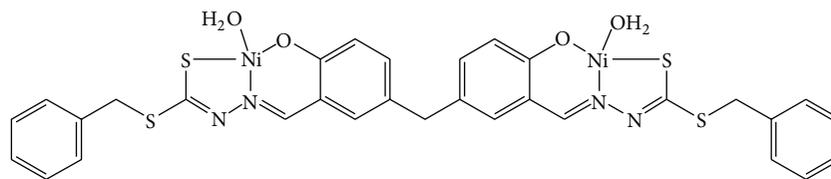
3. Results and Discussion

The Schiff base ligand of $\text{CH}_2(\text{H}_2\text{sal-sbdt})_2$ was soluble in coordinating solvents such as DMSO, DMF, THF, and Py, and it had high decomposition temperature. It existed in tautomeric forms (Scheme 1), and in the presence of alkali, the thiol proton undergoes deprotonation. The ligand thereby coordinated through the thiolate sulfur, the azomethine nitrogen, and the hydroxyl oxygen atoms.

The Ni(II) complex was soluble in DMSO, DMF, THF, Py, and slight soluble in MeCN. Proposed structure of the complex (Scheme 2) was based on its elemental analysis, UV-Vis, FT-IR spectra, and TG-DSC. The ligand coordinates through its dianionic $(\text{ONS})^{2-}$ thioenolate tautomeric form.

3.1. Elemental Analysis. Table 1 showed that the results of elemental analysis were agreed well with the calculated data. The composition of the ligand and the complex was $\text{C}_{31}\text{H}_{28}\text{O}_2\text{N}_4\text{S}_4$ ($M_r = 616.81$) and $\text{Ni}_2\text{C}_{31}\text{H}_{28}\text{O}_4\text{N}_4\text{S}_4$ ($M_r = 766.19$), respectively. And as suggested by the thermogravimetric analysis and the chemical assay of nickel, the stoichiometry of the Ni(II) complex indicated that the possible formula was $\text{CH}_2\{\text{Ni(II)}(\text{sal-sbdt})(\text{H}_2\text{O})\}_2$ ($\text{Ni}_2\text{C}_{31}\text{H}_{28}\text{O}_4\text{N}_4\text{S}_4$).

3.2. IR and Electronic Spectra. A listing of the IR spectral data of the Schiff base $\text{CH}_2(\text{H}_2\text{sal-sbdt})_2$ and the Ni(II) complex



SCHEME 2: Structure of the title complex.

TABLE 1: Analytical and physicochemical data of the ligand and title complex.

Compound stoichiometry	Color	m.p./°C	Found (calcd.)/%				
			C	H	N	S	Ni
CH ₂ (H ₂ sal-sbdt) ₂	Yellow	217-218	60.02 (60.36)	4.80 (4.58)	9.20 (9.09)	20.65 (20.79)	—
CH ₂ {Ni(II)(sal-sbdt)(H ₂ O)} ₂	Brown	>300	48.91 (48.59)	3.78 (3.68)	6.97 (7.31)	16.56 (16.74)	15.60 (15.32)

TABLE 2: IR and electronic spectral data of the ligand and title complex.

Compound	IR (cm ⁻¹)							Uv-Vis spectra (λ _{max} , nm)			
	ν(C=S)	ν(C-S)	ν(C=N)	ν(N-N)	ν(Ni-N)	ν(Ni-O)	ν(Ni-S)				
CH ₂ (H ₂ sal-sbdt) ₂	1036	—	1624	952	—	—	—	213	267	326	379
CH ₂ {Ni(II)(sal-sbdt)(H ₂ O)} ₂	—	766	1617	998	524	470, 387	241	—	273	—	388

was given in Table 2 and Figure 1. The IR spectra were investigated by using KBr pellets between 4000 and 225 cm⁻¹. There was no characteristic peak of the Schiff base ligand in the ranges of 2650 to 2450 cm⁻¹. This indicated that it remained in the thione form in the solid state, while presented different absorption bands at around 3197, 3118, 1303, and 1036 cm⁻¹, which were assigned to one broad weak band in the region 3197 cm⁻¹ due to ν(O-H), another at 3118 cm⁻¹ belonged to ν(N-H), one sharp band in the region 1303 cm⁻¹ due to ν(C=N) and δ(N-H), and another at 1036 cm⁻¹ due to ν(C=S), respectively. The disappearance of these bands in the spectra of the complex indicated coordination of the phenolic oxygen to nickel(II) and coordination of the thioenolization sulfur to nickel(II). The azomethine ν(C=N) band of the ligand appeared at 1624 cm⁻¹. The band showed up at 1617 cm⁻¹ in the metal complex, thereby suggesting the coordination of the azomethine nitrogen atom. A broad absorption peak at 3433 cm⁻¹ was assigned to stretching vibration of hydroxyl from water molecule, and the frequency of the peak was higher than 3400 cm⁻¹ showing that the O atoms of the water molecules were coordinated to the nickel ion. The absorption peaks at 1578, 1350, and 1466 cm⁻¹ were the frame vibration absorption peaks of benzene ring. A new band showed up at 766 cm⁻¹ in the nickel(II) complex due to ν(C-S). There was peak at 952 cm⁻¹ in IR spectra of the Schiff base; a shift to higher wavenumber of the ν(N-N) band was expected because of the complex formation and the diminished repulsion between the lone pairs of adjacent nitrogen atoms [16], and we assigned this band to a peak that appeared at 998 cm⁻¹. For the title complex, further evidence

in support of the coordination sites employed was provided by the ν(Ni-N), ν(Ni-O), and ν(Ni-S) vibrations at 524, 470–387, and 241 cm⁻¹, respectively. Therefore, the nickel(II) was coordinated by imino nitrogen, thiolato sulfur, and phenolic oxygen from the Schiff base ligand and oxygen from the coordinated water, respectively.

The UV-Vis spectra in DMSO solvent were recorded and the Schiff base exhibited absorption bands at around 213, 267, 326, and 379 nm, which were assigned to φ-φ*, π-π*, π-π*, and n-π* transitions, respectively. These bands disappeared in the spectra of the nickel(II) complex, but two new bands of medium intensity appeared at approximately 273 and 388 nm, which were assigned to a ligand-to-metal charge transfer bands.

3.3. Thermal Decomposition Reaction. To study the thermal decomposition process of complexes is helpful to the understanding of the coordination structure of complexes. The thermal stability and decomposition patterns of the nickel(II) complex of CH₂{Ni(II)(sal-sbdt)(H₂O)}₂ were investigated in air at the heating rate of 10°C min⁻¹. The TG-DSC curves of the complex were shown in Figure 2. There were one endothermic peak at 145°C and three exothermic peaks at 329°C, 373°C, and 424°C in the DSC curve. The complex continued to lose weight for two steps from 125 to 677°C, and became to constant weight at 677°C, at last only inorganic compound NiO was obtained. In the first step the TG curve showed an obvious weight loss of 5.48% between 125 and 170°C, corresponding to the simultaneous loss of two molecules of H₂O (calcd. 4.70%), and then the complex became to be CH₂{Ni(II)(sal-sbdt)}₂. As well as

TABLE 3: Antibacterial activity of the Schiff base and the complex.

Compound	Concentration (mg/mL)	Inhibition zone (mm)			
		<i>S. aureus</i>	<i>E. coli</i>	<i>B. subtilis</i>	<i>S. epidermidis</i>
$\text{CH}_2(\text{H}_2\text{sal-sbdt})_2$	1.5	14.0	18.0	15.0	13.0
$\text{CH}_2\{\text{Ni(II)(sal-sbdt)}_2(\text{H}_2\text{O})\}_2$	1.5	9.0	16.0	13.0	11.0
Moxifloxacin	1.5	22.0	25.0	35.0	30.0

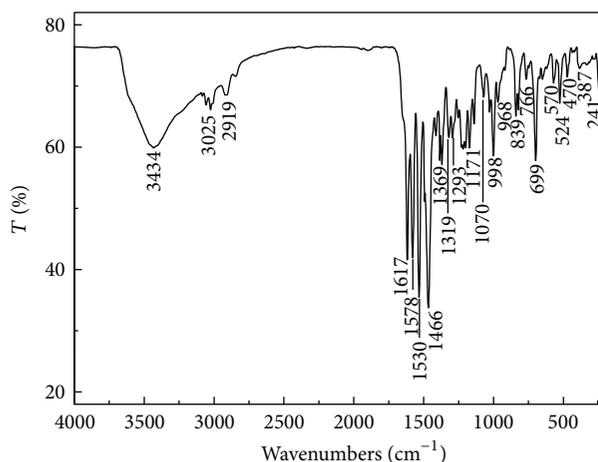


FIGURE 1: FT-IR spectra of the title complex.

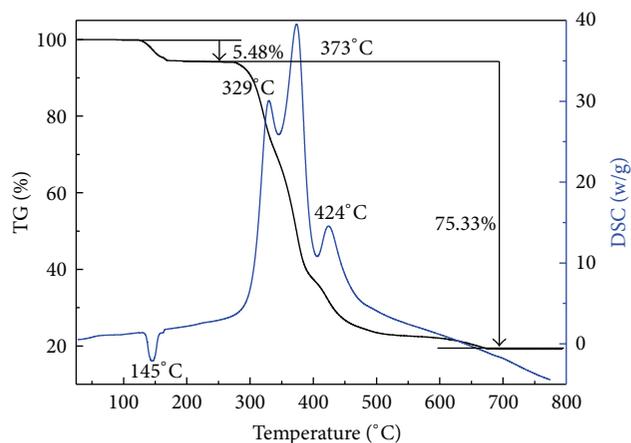


FIGURE 2: TG and DSC curves of the title complex.

$\text{CH}_2\{\text{Ni(II)(sal-sbdt)}_2$ was successively oxidated and decomposed from 170 to 677°C in the second step. The TG curve displayed an obvious weight loss in this step that agreed with the evolution of $\text{CH}_2(\text{sal-sbdt})_2$ (calcd. 75.80%, found 75.33%), among which the ligands were burnt completely; only two molecules of NiO were obtained and its weight content was 19.19% (calcd. 19.50%). Because of the high dehydration temperature, it could be coordinated water. The analysis result further ascertained that the molecule composition of the complex was $\text{CH}_2\{\text{Ni(II)(sal-sbdt)(H}_2\text{O)}\}_2$.

3.4. Scanning Electron Microscopy. The complex was dispersed in methanol, scattered in the surface of glass slide, and dried in air. The morphology of the sample was observed by scanning electron microscopy. The typical SEM images of the nickel(II) complex were depicted in Figure 3. These showed that the length of nanorod arrays of the complex was about 150 nm and the average diameter was about 30 nm.

3.5. Qualitative Antimicrobial Activity. Preliminary screening for antimicrobial activities of the stock solutions of the Schiff base and the nickel(II) complex was performed qualitatively using the disc diffusion assay in Table 3. Moxifloxacin was used as a standard drug. The Schiff base and the complex yielded clear inhibition zones around the discs. Each of the compounds was tested three times and recorded the average data. The results showed that the Schiff base and the nickel(II) complex had significant antibacterial activities against four bacteria; the antibacterial activities of the sequence were

Escherichia coli, *Bacillus subtilis*, *Staphylococcus aureus*, and *Staphylococcus epidermidis*, respectively. Both the Schiff base and its Ni(II) complex had the most effective antibacterial activity against *Escherichia coli*, and the diameter of inhibition zone of the Schiff base was 18.0 mm with the concentration of 1.5 mg mL⁻¹ while the diameter of the Ni(II) complex was 16.0 mm.

4. Conclusion

In conclusion, a new complex $\text{CH}_2\{\text{Ni(II)(sal-sbdt)(H}_2\text{O)}\}_2$ was synthesized. The structure and molecular formula of the complex was determined by elemental analysis, FTIR, UV-Vis, TG-DSC, and SEM. The nickel ion was coordinated by imino nitrogen, thiolato sulfur, and phenolic oxygen from the Schiff base ligand, and oxygen from water, respectively. The thermal decomposition processes of the complex include dehydration, oxidation, and pyrolysis of the ligand and the last residue was NiO at the temperature of 677°C. The complex belonged to nanocrystalline metal complex and also displayed strongly active against *Escherichia coli*.

Acknowledgments

This work is supported by Postgraduates Innovation Fund of Southwest University of Science and Technology (no. 12ycj12). The authors are very grateful to State Key Laboratory Cultivation Base for Nonmetal Composite and Functional Materials, and Engineering Research Center of

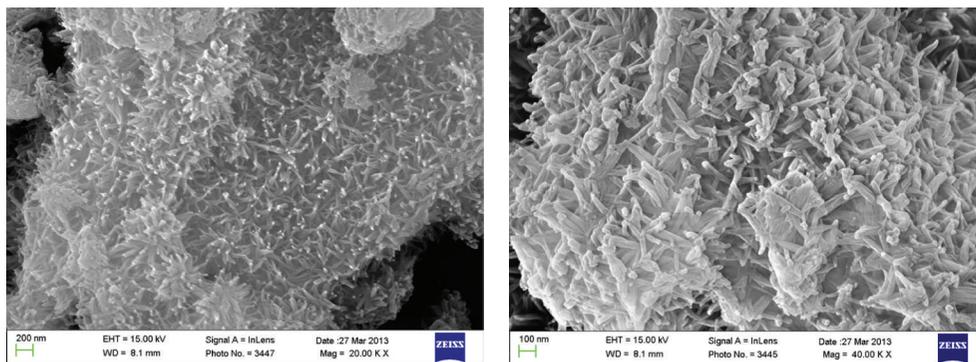


FIGURE 3: SEM images of the title complex with different amplifying times.

Biomass Materials of Education Ministry for the analysis testing.

References

- [1] T. B. S. A. Ravooof, K. A. Crouse, M. I. M. Tahir, A. R. Cowley, and M. A. Ali, "Synthesis, characterization and bioactivity of mixed-ligand Cu(II) complexes containing Schiff bases derived from *S*-benzylthiocarbamate and saccharinate ligand and the X-ray crystal structure of the copper-saccharinate complex containing *S*-benzyl- β -*N*-(acetylpyrid-2-yl)methylenedithiocarbamate," *Polyhedron*, vol. 26, no. 6, pp. 1159–1165, 2007.
- [2] A. L. Smith, C. S. Day, L. Que Jr., Y. M. Zhou, and U. Bierbach, "Unexpected assembly of a novel triply bridged diiron(II) core by a bidentate Schiff base ligand," *Inorganica Chimica Acta*, vol. 360, no. 8, pp. 2824–2828, 2007.
- [3] M. R. Maurya, D. C. Antony, S. Gopinathan, and C. Gopinathan, "Binuclear dioxomolybdenum(VI) complexes of flexibly-bridged hexadentate tetraanionic Schiff's bases derived from methylene- or dithio-bis(salicylaldehyde) and *S*-methylthiocarbamate or *S*-benzylthiocarbamate," *Bulletin of the Chemical Society of Japan*, vol. 68, no. 2, pp. 554–565, 1995.
- [4] M. R. Maurya, C. Haldar, A. A. Khan et al., "Synthesis, characterization, catalytic and antimicrobial activity of vanadium complexes of binucleating bis(dibasic tridentate ONS donor) ligand systems," *European Journal of Inorganic Chemistry*, vol. 2012, no. 15, pp. 2560–2577, 2012.
- [5] M. T. H. Tarafder, M. A. Ali, D. J. Wee, K. Azahari, S. Silong, and K. A. Crouse, "Complexes of a tridentate ONS Schiff base: synthesis and biological properties," *Transition Metal Chemistry*, vol. 25, no. 4, pp. 456–460, 2000.
- [6] X. S. Zhou, X. S. Cheng, Y. N. Li, F. Y. Tian, F. Y. Xu, and Z. L. You, "Synthesis, structures and antimicrobial activity of trinuclear cobalt(II) and nickel(II) complexes derived from *N*, *N'*-bis(4-methoxysalicylidene)propane-1, 3-diamine," *Chinese Journal of Inorganic Chemistry*, vol. 29, no. 2, pp. 397–402, 2013.
- [7] S. Matsui and T. Fujita, "FI catalysts: super active new ethylene polymerization catalysts," *Catalysis Today*, vol. 66, no. 1, pp. 63–73, 2001.
- [8] L. K. Johnson, C. M. Killian, and M. Brookhart, "New Pd(II)- and Ni(II)-based catalysts for polymerization of ethylene and α -olefins," *Journal of America Chemistry Society*, vol. 117, no. 23, pp. 6414–6415, 1995.
- [9] T. Rosu, E. Pahontu, C. Maxim, R. Georgescu, N. Stanica, and A. Gulea, "Some new Cu(II) complexes containing an ON donor Schiff base: synthesis, characterization and antibacterial activity," *Polyhedron*, vol. 30, no. 1, pp. 154–162, 2011.
- [10] G. B. Bagihalli, P. G. Avaji, S. A. Patil, and P. S. Badami, "Synthesis, spectral characterization, in vitro antibacterial, antifungal and cytotoxic activities of Co(II), Ni(II) and Cu(II) complexes with 1,2,4-triazole Schiff bases," *European Journal of Medicinal Chemistry*, vol. 43, no. 12, pp. 2639–2649, 2008.
- [11] X. Y. Qiu, Q. F. Liu, P. Zhang, and L. Q. Sheng, "Synthesis, crystal structure and antitumor activities of zinc(II) complex with bidentate Schiff base derived from *S*-*p*-chlorobenzylthiocarbamate," *Chinese Journal of Inorganic Chemistry*, vol. 28, no. 2, pp. 362–366, 2012.
- [12] M. A. Ali and M. T. H. Tarafdar, "Metal complexes of sulphur and nitrogen-containing ligands: complexes of *S*-benzylthiocarbamate and a Schiff base formed by its condensation with pyridine-2-carboxaldehyde," *Journal of Inorganic and Nuclear Chemistry*, vol. 39, no. 10, pp. 1785–1791, 1977.
- [13] C. S. Marvel and N. Tarköy, "Heat stability studies on chelates from Schiff bases of salicylaldehyde derivatives," *Journal of the American Chemical Society*, vol. 79, no. 22, pp. 6000–6002, 1957.
- [14] S. M. Zhao, L. J. Zheng, and B. Du, "Measurement of antimicrobial activity of ketone in pocynum with agar diffusion method," *Science & Technology Review*, vol. 27, no. 7, pp. 37–40, 2009.
- [15] A. M. Ali, M. M. Mackeen, I. Intan-Safinar et al., "Antitumor-promoting and antitumour activities of the crude extract from the leaves of *Juniperus chinensis*," *The Journal of Ethnopharmacology*, vol. 53, no. 3, pp. 165–169, 1996.
- [16] S. P. Perlepes, D. Nicholls, and M. R. Harrison, "Coordination compounds of benzildihydrazone," *Inorganica Chimica Acta*, vol. 102, no. 2, pp. 137–143, 1985.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

