Asian Journal of Chemistry Vol. 21, No. 7 (2009), 5749-5756

Synthesis, Characterization and Antimicrobial Activity of Cu(II), Ni(II), Co(II), Zn(II) Complexes with Isonicotinoylhydrazone-4-benzyloxybenzaldehyde

LIVIU MITU*, NATARAJAN RAMAN†, ANGELA KRIZA‡,
NICOLAE STANICA§ and MARIANA DIANU‡
Department of Physics and Chemistry, Faculty of Science, University of Pitesti,
Targul din Vale Street, No. 1, 110040, Pitesti, Romania
E - mail : ktm7ro@yahoo.com

The complexes of Co(II), Ni(II), Cu(II) and Zn(II) with isonicotinoylhydrazone-4-benzyloxybenzaldehyde (INHBBA) are reported. The complexes have been characterized by analytical data, IR, UV-Vis, NMR spectra, magnetic susceptibility, thermal analysis and for the Cu(II) complex the ESR spectrum has been registered. The biological activity of these complexes were investigated against *Staphylococcus aureus, Escherichia coli* and *Klebssiella pneumoniae* bacteria. The experimental data suggest a stoichiometry of 1:2 (metal:ligand) for all these complexes. The INHBBA ligand is coordinated bidentate by the C=O amide oxygen and the azomethine nitrogen in the complexes of Cu(II), Ni(II), Co(II) and monodentate by the nitrogen of the pyridinic ring in the complex of Zn(II).

Key Words: Template synthesis, Isonicotinoylhydrazone, Complexes, Azomethine group, Antimicrobial activity.

INTRODUCTION

The coordination chemistry of the acyl, aroyl and heteroaroylhydrazones has been published by Dutta and Hossain[1]. A number of complexes of the transitional metals with the aroylhydrazone ligands have a large spectrum of biological and pharmaceutical activities[2-4]. The Cu(II) complex with benzoylhydrazonesalicylaldehyde presents antitumoural activity[5] and the Ni(II) and Mn(II) complexes with the isonicotinoylhydrazone-α-pyridinaldehyde show the antituberculosis activity[6]. In continuation of our studies on the complexes with the ligands from the aroylhydrazone class[7,8], in this paper the synthesis and characterization of the complexes of Cu(II), Ni(II), Co(II), Zn(II) with the isonicotinoylhydrazone-4-benzyloxybenzaldehyde ligand have been reported.

---

† Department of Chemistry, VHNSN College, Virudhunagar-626 001, India.
‡ Department of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest, Bucharest-020461, Romania.
§Romanian Academy, Physical-Chemistry Institute, I.G. Murgulescu, Bucharest-060021, Romania.

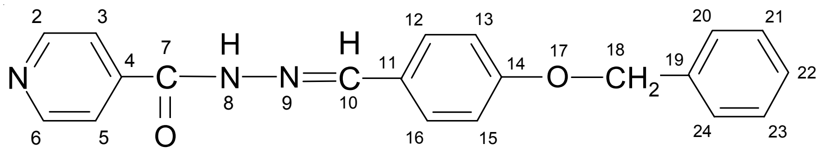


Fig. 1. Isonicotinoylhydrazone-4-benzyloxybenzaldehyde ($C_{20}H_{17}N_3O_2$) (INHBBA = HL)

EXPERIMENTAL

All reagents and solvents used are of the AR grade and were used without further purification. The metal content and chlorine was obtained by the literature methods[9] and carbon, hydrogen and nitrogen were determined with an analyzer CHN-Hewlett Packard185. The IR spectra were recorded between 4000-400 cm^{-1} on a BIORAD-FT-IR135FTS spectrophotometer in a disc of anhydrous KBr. The electronic spectra in reflection (300-1100 nm) were obtained on a VSU-2P Zeiss-Jena spectrophotometer using MgO as a standard. The ESR spectrum for the Cu(II) complex was obtained at room temperature (293 K) on a microcrystalline powder with an ART 5 spectrophotometer. The magnetic moments were determined by the Faraday method at the room temperature. The ^1H NMR and ^{13}C NMR spectra were recorded on a device Varian Gemini 300BB in DMSO-d_6. The molar electric conductivity for the complexes of Cu(II), Co(II), Zn(II) were measured with a HACH-sens ion 5-conductivitymeter to the solutions in DMF 10^{-3} M. The thermic analysis was realized with an MOM-Q-1500D derivatograph in air with a heating rate of 5 ºC/min. The biological activity of the complexes was studied by the diffusion technic in agar plates using DMF as solvent at the concentration of 200 µg/mL.

The ligand isonicotinoylhydrazone-4-benzyloxybenzaldehyde is formed by the condensation of the isonicotinoylhydrazine with 4-benzyloxybenzaldehyde. Isonicotinoylhydrazone-4-benzyloxybenzaldehyde (INHBBA): Calculated for $C_{20}H_{17}N_3O_2$: C, 72.50; H, 5.13; N, 12.68. Found: C, 72.31; H, 4.95; N, 12.49. The colour of the ligand is white; m.p. 187-189 ºC.

Synthesis of the complexes: A methanolic solution of respective metal chloride (0.002 mol/25 mL MeOH) was added to a mixture of isonicotinoylhydrazine (0.004 mol/40 mL MeOH)and 4-benzyloxybenzaldehyde (0.004 mol/40 mL MeOH). The reaction mixture was refluxed on a water-bath for 4 h, after which part of the solvent was removed by distillation. The precipitated complexes were filtered, washed with methyl alcohol and then with ether and finally dried in vacuum on anhydrous $CaCl_2$. Analysis, calculated % for $[Cu(HL)_2Cl_2]$: Cu, 7.97; C, 60.26; H, 4.26; N, 10.54; Cl, 8.91; Found: Cu, 7.78; C, 60.05; H, 4.04; N, 10.33; Cl, 8.69. Calculated for % $[Ni(HL)_2Cl_2]\cdot 2H_2O$: Ni, 7.09; C, 57.99; H, 4.59; N, 10.14; Cl, 8.57; Found: Ni, 6.88; C, 57.78; H, 4.38; N, 9.95; Cl, 8.36. Calculated for % $[Co(HL)_2Cl_2]$: Co, 7.44; C, 60.61; H, 4.29; N, 10.60; Cl, 8.96; Found: Co, 7.23; C, 60.39; H, 4.07; N, 10.37; Cl, 8.75. Calculated for % $[Zn(HL)_2Cl_2]$: Zn, 8.18; C, 60.12; H, 4.25; N, 10.52; Cl, 8.89; Found: Zn, 7.96; C, 59.93; H, 4.03; N, 10.34; Cl, 8.67.

RESULTS AND DISCUSSION

The metal complexes are presented in the way of coloured powders, insoluble in methyl alcohol, ethyl alcohol, chloroform, acetone while Cu(II), Co(II), Zn(II) complexes are soluble in DMF and the Ni(II) complex is partly soluble in DMF.

From the analytical data of the complexes result a stoichiometry 1:2 (metal: ligand) for all the complex combinations (Table-1) The values of the molar conductivity for the Cu(II), Co(II), Zn(II) complexes sustain a non-electrolyte structure of these. The bands of the IR spectra are presented in the Table-2.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES

Compounds	m.p. (ºC)	Colour	μ_{eff} (BM)	Λ_m (Ω^{-1} cm^2 mol^{-1})*
$[Cu(HL)_2Cl_2]$	276	Green	1.81	12.37
$[Ni(HL)_2Cl_2]\cdot 2H_2O$	268	Yellow-green	3.16	–
$[Co(HL)_2Cl_2]$	247	Light grey	4.96	15.28
$[Zn(HL)_2Cl_2]$	254	Yellow	–	14.19

*10^{-3} M solution in DMF.

TABLE-2
KEY IR (cm^{-1}) BANDS FOR LIGAND AND ITS METAL COMPLEXES

Compounds	ν(OH) water	ν(NH)	ν(C=O) Amide I	ν(C=N)	δ(NH) Amide II	β ring pyridine in plane	ν(M-N) Azomethine
INHBBA(HL)	–	3040	1650	1604	1548	595	–
$[Cu(HL)_2Cl_2]$	–	3050	1595	1571	1503	590	446
$[Ni(HL)_2Cl_2]\cdot 2H_2O$	3409	3060	1600	1567	1505	592	450
$[Co(HL)_2Cl_2]$	–	3045	1605	1550	1511	588	473
$[Zn(HL)_2Cl_2]$	–	3040	1667	1604	1569	647	–

The INHBBA (HL) ligand presents bands of absorption at 3185 cm^{-1}, 3040 cm^{-1} assigned to the asymmetrical and symmetrical stretching vibrations, respectively for the NH groups from the amide group[10]. The ν(C=O) amide I vibration is observed at 1650 cm^{-1} and the band at 1604 cm^{-1} corresponds to the ν(C=N) vibration from the azomethine group. The amide II δ(NH) and amide III γ(NH) bands observed at 1548 and 1366 cm^{-1}, respectively. In the INHBBA ligand, a spectrum is observed a band with medium intensity at 1067 cm^{-1} as well as a weak band at 595 cm^{-1}, both of them are associated to the vibrational modes from the pyridinic ring. The band at 1067 cm^{-1} put in evidence the symmetrical valency vibration of the ring (ν_{sim}^{ring} Py-A_1)[11] and the band at 595 cm^{-1} represent the bending, β″ vibration in plane for the pyridinic ring.

The Cu(II), Co(II), Zn(II) complexes don't show the IR spectra bands of intense absorption between 3500-3350 cm^{-1}, but Ni(II) complex put in evidence a large band at 3409 cm^{-1}; this band is assigned to the lattice water from the composition of the complex[12]. The ν(NH)-asymmetrical and ν(NH)-symmetrical vibrations are found to the closed values from those of the ligand and as consequence the imido functional group does not show any change in its structure after the complexes were obtained. The amide I valency vibration and the band of the azomethine group shift towards the lower wave numbers ($\Delta\nu$ = 55-45 cm^{-1}, respectively $\Delta\nu$ = 54-33 cm^{-1}) to the Cu(II), Ni(II), Co(II) complexes. For the Zn(II) complex, the amide I band presents a positive variation and there is no changes in the vibration of the azomethine group. These results demonstrate that the INHBBA ligand is coordinated to the Cu(II), Ni(II), Co(II) ions by (C=O) amide oxygen[13] and azomethine nitrogen[14] atoms but it is not involved in the coordination in the Zn(II) complex. The absorption of the, β'' bending in plane corresponding to the pyridinic ring does not show important shiftings to the Cu(II), Ni(II), Co(II) complexes but it appears at 647 cm^{-1} ($\Delta\nu$ = 52 cm^{-1}) in the spectrum of the Zn(II) complex. These results demonstrate the involving of the nitrogen from the pyridinic ring in the coordination to the Zn(II) ion but this atom is not coordinated in the Cu(II), Ni(II), Co(II) complexes. The symmetrical valency vibration of the pyridinic ring (ν_{sym}^{ring} – Py – A1) presents a negative variation with $\Delta\nu$ = 58 cm^{-1} to the Zn(II) complex, aspect which also sustain the coordination of the pyridinic nitrogen atom to the Zn(II) ion. The weak absorption bands from the region 473-446 cm^{-1} in the spectra of the Cu(II), Ni(II), Co(II) complexes are assigned to the ν(M-N$_{azomethine}$) vibrations. From the presented data results that the isonicotinoylhydrazone-4-benzyloxybenzaldehyde (INHBBA) ligand is neutral bidentate coordinated in the Cu(II), Ni(II), Co(II) complexes by the (C=O) amide oxygen and the (C=N) azomethine nitrogen, but in the Zn(II) complex this aroylhydrazone is monodentate coordinated by the nitrogen from the pyridinic ring.

In the ^{1}H NMR spectrum of the INHBBA (HL) ligand are observed signals at δ 12.01; δ 8.80; δ 8.42; δ 7.86 ppm which can be assigned to the H-8 (amide), H-2,6 (pyridine), H-10 (azomethine), H-3,5 (pyridine) protons. The absorption signals situated at δ 161.34; δ 150.01; δ 148.97; δ 141.00; δ 121.74 ppm in the ^{13}C NMR spectrum of the ligand are attached to the C-7 (amide), C-2,6 (pyridine), C-10 (azomethine), C-4 (pyridine), C-3,5 (pyridine) carbon atoms. The signals of the H-8 (amide), H-10 (azomethine) protons in the ^{1}H NMR spectrum of the Zn(II) complex, but also the corresponding absorptions to the C-7 (amide), C-10 (azomethine) carbon atoms from the ^{13}C NMR spectrum, suffer very small variations and thus is confirmed that the amide oxygen and azomethine nitrogen atoms are not involved in the coordination in this complex. The H-2,6 protons from the pyridinic ring present the absorption signal towards a lower field with Δ = 0.43 ppm and the absorptions of the C-2,6 and C-4 carbon atoms put in evidence shiftings with Δ = 2.41 ppm respectively Δ = 2.5 ppm, aspects which demonstrate the coordination of the pyridinic nitrogen to the Zn(II) ion.

The electronic spectra (Table-3) and the magnetic moments (Table-1) confirmed the stereochemistry of the complexes.

TABLE-3
ELECTRONIC SPECTRA OF THE COMPLEXES

Compounds	Frequencies (cm^{-1})	Assigning
[Cu(HL)$_2$Cl$_2$]	24096	n → π*
	14662	$^2E_g \rightarrow {}^2T_{2g}$
[Ni(HL)$_2$Cl$_2$]·2H$_2$O	24390	n → π*
	16000	$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)
	10050	$^3A_{2g} \rightarrow {}^3T_{2g}$ (F)
[Co(HL)$_2$Cl$_2$]	25641	n → π*
	18867	$^4T_{1g} \rightarrow {}^4T_{1g}$ (P)
	10256	$^4T_{1g} \rightarrow {}^4T_{2g}$ (F)
[Zn(HL)$_2$Cl$_2$]	25316	n → π*
	23529	CT

In the UV-Vis spectrum of the INHBBA aroylhydrazone is observed an intense band at 27027 cm^{-1} (370 nm) which correspond to the n → π* transition. This band is recognized also in the electronic spectra of the complexes but it is situated towards the lower wave numbers, aspect which indicate the coordination of the ligand to the metallic ions. For the [Cu(HL)$_2$Cl$_2$] complex is remarked a broad and intense band at 14662 cm^{-1} (682 nm), which characterizes the Cu(II) ion in a weak distorted octahedral surrounding and it can be assigned to the $^2E_g \rightarrow {}^2T_{2g}$ transition. The ^2E_g and $^2T_{2g}$ states of the Cu(II) (d^9) ion in the octahedral symmetrie are splitting due to the tetragonal distortion and theoretically can appear three transitions noted as follows: $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2A_{1g}$. These transitions remain unresolved in the electronic spectrum because its energies are closed[15]. The magnetic moment of 1.81 BM belongs to the range of the Cu(II) octahedral complexes. In the spectrum of the [Ni(HL)$_2$Cl$_2$]·2H$_2$O complex are observed two bands of absorption at 16000 cm^{-1} (625 nm) and 10050 cm^{-1} (995 nm) which correspond to the $^3A_{2g} \rightarrow {}^3T_{1g}$(F) ($\nu_2$) and $^3A_{2g} \rightarrow {}^3T_{2g}$(F) ($\nu_1$) transitions, respectively. These transitions releave the octahedral stereochemistry for the Ni(II) ion[16]; the magnetic moment of 3.16 BM sustain this geometry. The ratio ν_2/ν_1 has the value of 1.59 and it is situated in the range of the Ni(II) octahedral complexes. The Dq, B, β parameters were calculated and these correspond to the Dq = 1005 cm^{-1}, B = 778 cm^{-1}, β = 0.75 values. The [Co(HL)$_2$Cl$_2$] complex presents the electronic spectrum bands at 18867 cm^{-1} (530 nm) and 10256 cm^{-1} (975 nm) which can be assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}$(P) ($\nu_2$) and $^4T_{1g} \rightarrow {}^4T_{2g}$(F) ($\nu_1$) transitions, respectively. These bands are characteristics to the Co(II) ion in the octahedral coordination[17] and the magnetic moment of 4.94 BM confirm this symmetry. The ratio ν_2/ν_1 = 1.83 sustain the octahedral configuration. In the reflection spectrum of the [Zn(HL)$_2$Cl$_2$] complex is releaved an intense absorption at 23529 cm^{-1} (425 nm). This band is assigned to the charge transfer transition L → M[18] and the complex is diamagnetic. From the electronic spectrum of the complex the geometry of the metallic ion can not be assigned but taking in consideration that the ligand functions in a monodentate form as well as the tendency of the Zn(II) ion for the tetrahedral stereochemistry in the tetra coordination complexes.

The ESR spectrum for the $[Cu(HL)_2Cl_2]$ complex was investigated at the room temperature. This complex releave an intense broad and isotropic signal in which the g" parameter presents only one value ($g_{isotropic} = 2.1138$). The symmetry of the ESR signal toghether with the g" parameter represent characteristics for a weak deformed octahedral geometry.

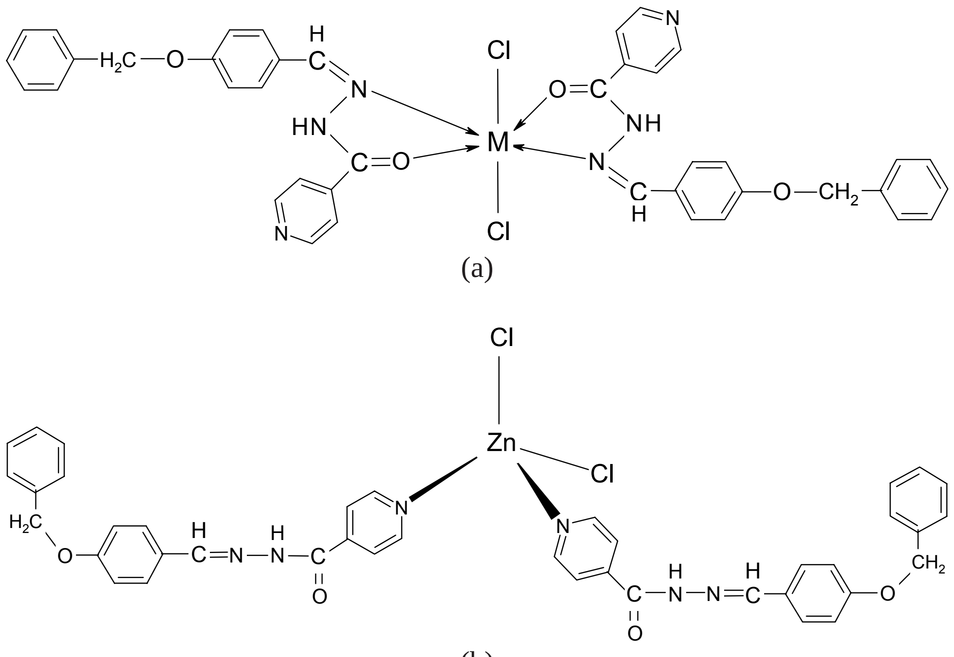
The thermal behaviour of the Cu(II), Ni(II), Co(II), Zn(II) complexes was studied in air at temperature range of 25-700 ºC and the obtained data are presented in the Table-4.

TABLE-4
THERMAL ANALYSIS FOR THE COMPLEX COMBINATIONS

Complexes	Total mass losses		Temp. (ºC)	Loss (%)
	Theoretical (%)	Experimental (%)		
$[Cu(HL)_2Cl_2]$	89.99	89.59	195-434 434-650 650-700	44.38 45.21 10.23 exp./res. 9.98 calc./res.
$[Ni(HL)_2Cl_2].2H_2O$	90.96	90.39	80-150 150-370 370-480 480-700	4.16 34.77 51.46 8.83 exp./res. 9.02 calc./res.
$[Co(HL)_2Cl_2]$	89.86	89.56	250-440 440-625 625-700	43.29 46.27 9.91 exp./res. 10.13 calc./res.
$[Zn(HL)_2Cl_2]$	89.79	89.43	250-449 449-630 630-700	41.27 48.16 10.02 exp./res. 10.19 calc./res.

In the range 80-150 ºC, the Ni(II) complex eliminate the lattice water. All the four metal complexes are decomposed in two steps at high temperatures (t > 253 ºC) and the INHBBA ligand is lost partially. In the final step (≈ 700 ºC) is formed as a stable residue the CuO, NiO, Co_3O_4, ZnO metallic oxides. The evaluation resulted from the thermic analysis sustains the molecular formulas assigned to the complexes. According to the obtained data, we can propose for the metal complexes the following tentative of structures (Fig. 2).

The antimicrobial activity of the isonicotinoylhydrazone-4-benzyloxybenzaldehyde (INHBBA) ligand and of its complexes with Cu(II), Ni(II), Co(II), Zn(II) ions were verified on the bacterial agents *Staphylococcus aureus*, *Escherichia coli*, *Klebssiella pneumoniae* and the results are presented in the Table-5.



(a)

(b)

Fig. 2. Structural formulas of the complexes: (a) $[M(INHBBA)_2Cl_2]\cdot xH_2O$; M = Cu(II), Co(II), x = 0; M = Ni(II), x = 2; (b) $[Zn(INHBBA)_2Cl_2]$

TABLE-5
ANTIMICROBIAL ACTIVITY OF INHBBA AND ITS COMPLEXES

Compounds	Bacteria / Inhibition zone (mm)		
	S. aureus Gram-positive	*E. coli* Gram-negative	*K. pneumoniae* Gram-negative
INHBBA(HL)	5	6	5
$[Cu(HL)_2Cl_2]$	6	9	6
$[Ni(HL)_2Cl_2].2H_2O$	7	11	8
$[Co(HL)_2Cl_2]$	18	16	24
$[Zn(HL)_2Cl_2]$	12	12	13

For all the bacterial strains the Cu(II), Ni(II), Co(II), Zn(II)complexes present a higher activity comparatively with the INHBBA ligand and this effect is assigned to the donor atoms which are not involved in the coordination but become more active by the formation of the complex combinations[19]. The Co(II) complex releave a maximum action regarding the three bacterial agents. Zn(II) complex in which the INHBBA ligand is acting in a monodentate way is more active by rapport with the Cu(II), Ni(II) complexes in which the INHBBA ligand acting as bidentate[20]. The metal complexes of Cu(II), Ni(II) show the highest activity to the *E. coli* and the Co(II), Zn(II) complexes present the maximum activity to the *K. pneumoniae*.

REFERENCES

1. R.L. Dutta and M.M. Hossain, *J. Sci. Ind. Res.*, **44**, 635 (1985).
2. S.Y. Yu, S.X. Wang and Q.H. Luo, *Polyhedron*, **12**, 1093 (1993).
3. J.G. Wu, R.W. Deng and Z.N. Chen, *Transition Met. Chem.*, **18**, 23 (1993).
4. L.F. Wang, Y. Zhu and J.G. Wu, *Polyhedron*, **10**, 2477 (1991).
5. K.K. Narang and V.P. Singh, *Transition Met. Chem.*, **18**, 287 (1993).
6. N. Kaur, R. Herjinder and S.K. Sangal, *Chim. Acta Turc.*, **26**, 123 (1996).
7. L. Mitu, A. Kriza and M. Dianu, *Asian J. Chem.*, **19**, 5666 (2007).
8. L. Mitu, A. Kriza and M. Dianu, *Asian J. Chem.*, **20**, 1627 (2008).
9. C.Gh. Macarovici, Analiza Chimica Cantitativa Anorganica, (Inorganic Quantitative Chemical Analysis), Editura Academiei R.S.R., Bucuresti, p. 364 (1979).
10. R. Rajavel, M. Senthil and C. Anitha, *E - J. Chem.*, **5**, 620 (2008).
11. Y. Kumar, P.D. Sethi and C.L. Jain, *J. Indian Chem. Soc.*, **67**, 769 (1990).
12. T.L. Yang and W.W. Qin, *Polish J. Chem.*, **80**, 1657 (2006).
13. S.S. Tajudeen and M.S. Dastageer, *Asian J. Chem.*, **21**, 317 (2009).
14. A.A. Osowole, *E - J. Chem.*, **5**, 130 (2008).
15. J. Sanmartin, M.R. Bermejo and C. Lage, *Polyhedron*, **19**, 185 (2000).
16. R. Prasad, P.P. Thankachan and M.T. Thomas, *J. Indian Chem. Soc.*, **78**, 28 (2001).
17. M. Sönmez and M. Sekerci, *J. Serb. Chem. Soc.*, **72**, 259 (2007).
18. B.C.S. Radovanovic and S.S. Andjelkovic, *J. Serb. Chem. Soc.*, **63**, 379 (1998).
19. G. Vengatachalam and R. Ramesh, *Spectrochim. Acta*, **61A**, 2081 (2005).
20. M. Kurtoglu, M.M. Dagdelen and S. Toroglu, *Transition Met. Chem.*, **31**, 382 (2006).

(*Received*: 3 February 2009; *Accepted*: 30 April 2009) AJC-7531