Polish J. Chem., **76**, 907–914 (2002) **INORGANIC CHEMISTRY**

Synthesis and Characterization of Cu(II), Co(II), Ni(II) and Zn(II) Schiff Base Complexes from 1-Amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one with Salicylaldehyde

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(Received January 3rd, 2002; revised manuscript February 19th, 2002)

Cu(II), Co(II), Ni(II) and Zn(II) metal complexes of new heterocyclic Schiff base derived from 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one with salicylaldehyde have been synthesized and characterized by elemental analyses, mass, electronic, IR and ^{1}H NMR spectra, and also by molar conductivity measurements, magnetic moment measurements and thermogravimetric analyses (TGA). It has been found that the Schiff bases behave as a neutral bidentate (NO) and tridentate (ONO) ligands forming chelates with 1:2 (metal:ligand) stoichiometry. Octahedral environment is suggested for metal complexes. The conductivity data for the Ni(II) complexes are consistent with those expected for an electrolyte.

Key words: Schiff bases complexes, salicylaldehyde, 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one

Schiff bases are an important class of ligands in coordination chemistry and find extensive application in different fields [1–3]. Schiff bases derived from the salicylaldehydes are well known polydentate ligands [4,5] coordinating in neutral forms. In recent years, metal complexes of Schiff bases have attracted considerable attention due to their remarkable antifungal, antibacterial and antitumor activities [6–8]. Schiff base complexes derived from 4-hydroxysalicylaldehyde and amines have strong anticancer activity [9].

The present paper reports the synthesis of new Schiff base ligand (Figure 1) containing a ring of the pyrimidine and their metal complexes. Spectral and magnetic studies have been used to characterize the structure of each of these complexes. IR, mass, ^{1}H NMR and ^{13}C NMR spectra were obtained to determine the structure of the ligand LH.

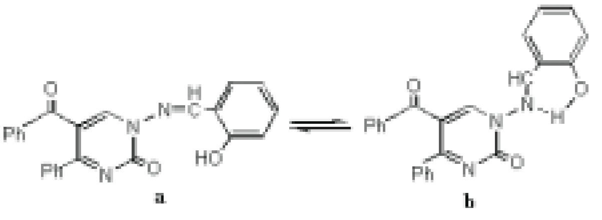

Figure 1. Structure of the ligand LH.

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EXPERIMENTAL

MeOH, EtOH, $CHCl_3$, DMF, toluene, diethylether, n-heptane and salicylaldehyde were obtained from Fluka and Aldrich. The metal salts $Cu(AcO)_2 \cdot H_2O$, $Co(AcO)_2 \cdot 4H_2O$, $Zn(AcO)_2 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$ were obtained from E. Merck. All solvents were dried and purified before use. 1-Amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one was prepared as described previously [10].

Physical measurements: Elemental analyses (C, H, N) were performed by using a Carlo Erba 1106 elemental analyzer. The IR spectra were obtained using KBr discs 4000–400 cm^{-1} on a Bio-Rad-Win-IR spectrophotometer. The electronic spectra in the 200–900 nm range were obtained in DMF on a Unicam UV2- 100 UV/Visible spectrophotometer. Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as a calibrant. Molar conductance of the Schiff base ligand and their transition metal complexes were determined in DMF at room temperature by using a Jenway model 4070 conductometer. The ^1H NMR spectra of the Schiff base were recorded with a Varian XL-200 NMR instrument. Mass spectra of the ligand were recorded on a Hewlett-Packard MS 5988 mass spectrometer. TGA measurements were carried out by a Shimadzu-50 thermal analyzer.

Preparation of the Schiff base (LH): The Schiff base ligand was prepared by the condensation of the 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one (0.2910 g, 1 mmole) with the salicylaldehyde (0.1220 g, 1 mmole) in ethanol (40 ml) achieved by boiling the mixture under reflux for 2 h. The precipitated ligand was filtered off, recrystallized from EtOH and dried in a vacuum dessicator.

Preparation of the Schiff base complexes: 0.79 g (2.00 mmole) of the ligand was dissolved in 30 ml of chloroform, and a solution of 1.00 mmole of the metal salt [$Cu(AcO)_2 \cdot H_2O$ (0.20 g), $Co(AcO)_2 \cdot 4H_2O$ (0.25 g), $Zn(AcO)_2 \cdot 2H_2O$ (0.22 g) and $NiCl_2 \cdot 6H_2O$ (0.24 g)] in 15 ml methanol was added dropwise with continuous stirring. The mixture was stirred further for 1.5–2.5 h at 80°C. The precipitated solid was then filtered off, washed with diethylether, followed by cold ethanol and dried in a vacuum dessicator.

RESULTS AND DISCUSSION

The newly synthesized Schiff base ligand and its complexes are very stable at room temperature in the solid state. The ligand is soluble in common organic solvents. But, its metal complexes are generally soluble in DMF and DMSO. The mass spectra of the ligand showed the highest mass peak at m/e 395, which agree with the formula weight of the ligand ($C_{24}H_{17}N_3O_3$ = 395 g/mole). The elemental analytical data of the complexes reveal that the compounds have a metal:ligand anion stoichiometry of 1:2 corresponding to the general formulae of $[M(L)_2] \cdot mH_2O$ and $[Ni(L)_2Cl_2] \cdot 2H_2O$, where L is the anion of LH. The analytical data are in good agreement with the proposed stoichiometry of the complexes. The colors, yields, melting points, IR and electronic absorption spectral data of all the compounds are presented in Table 1. Molar conductance value of the Ni(II) complex is 35.20 Ω^{-1} cm^2 $mole^{-1}$. The Ni(II) complex, which contains coordinated chloride ions, is non-conducting or shows a certain degree of conductivity, which would be due to their replacements by DMF solvent molecules [11]. The other complexes did not show electrolytic properties (0.8–2.8 Ω^{-1} cm^2 $mole^{-1}$). Condensation of the salicylaldehyde with 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one readily gives rise to the corresponding imines, which were easily identified by their IR, mass, ^1H NMR spectra (Figure 2).

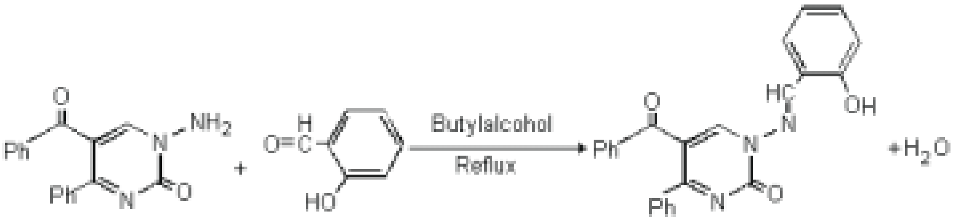

Figure 2. Scheme for the preparation of the ligand LH.

Table 1. Physical data, IR and electronic absorption spectral data of the ligands and their metal complexes.

Compounds	Yield %	μ_{eff} [B.M]	Color	M.p (°C)	C=O	C=N	C–O	M–N	M–O	λ_{max} (ε_{max}, M^{-1} cm^{-1})
LH	80	–	Light yellow	190	1691 1645	1625	1273	–	–	390 (3470), 348 (27000)
$[Cu(L)_2]$	70	1.71	Dark green	243	1676	1610	1268	470	426	715 (184), 580 (2100), 493 (1190), 359 (11700), 293 (25500)
$[Co(L)_2]\cdot H_2O$	68	4.45	Brown	285	1680 1656	1614	1268	452	420	710 (50), 510 (110), 445(890), 330 (14500), 286 (23700)
$[Ni(LH)_2Cl_2]\cdot 2H_2O$	68	3.81	Orange	145	1680 1643	1612	1273	445	420	675 (210), 517 (4200), 434 (4380), 340 (8650)
$[Zn(L)_2]\cdot 2H_2O$	65	Dia	Red	260	1678 1650	1610	1265	447	420	414 (6400), 258 (18000)

Tridentate and bidentate complexes were obtained from 1/2 molar ratio reactions with metal ions and LH ligand. The ligand LH, on reaction with $Co(CH_3COO)_2\cdot 4H_2O$, $Cu(CH_3COO)_2\cdot H_2O$, $Zn(CH_3COO)_2\cdot 2H_2O$, and $NiCl_2\cdot 6H_2O$ salts yields complexes corresponding to the general formula $[Co(L)_2]\cdot H_2O$, $[Cu(L)_2]$, $[Zn(L)_2]\cdot 2H_2O$, and $[Ni(LH)_2Cl_2]\cdot 2H_2O$. The complexes were prepared by the general reaction shown below.

$$2LH + M(CH_3COO)_2\cdot nH_2O \xrightarrow{\text{methanol/chloroform}} [M(L)_2]\cdot mH_2O + 2CH_3COOH + xH_2O$$

$M = Co(II),\ Cu(II),\ Zn(II)$ $LH = C_{24}H_{17}N_3O_3$

M =	Co(II)	Cu(II)	Zn(II)
n =	4	1	2
m =	1	–	2
x =	3	1	–

$$2LH + NiCl_2\cdot 6H_2O \xrightarrow{\text{methanol/chloroform}} [Ni(LH)_2CL_2]\cdot 2H_2O + 4H_2O$$

The metal-to-ligand ratio of the Co(II), Cu(II) and Zn(II) complexes was found to be1:2. But the Co(II) and Zn(II) complexes have one and two additional molecule of water of crystallization.

Mass spectral study: The mass spectra of compound (LH) were recorded. For compound (LH) the molecular ion peak 395.0 (M^+) is observed.

Infrared spectral study: Table 1 presents the most important IR spectral bands of the ligand LH with all the metal complexes. The IR spectra of Schiff base ligand, derived from salicylaldehyde (LH), showed a broad band at 3460 cm^{-1}, which may be due to ν(OH). The free ν(OH) is generally observed between 3500 and 3650 cm^{-1} [12,16]. The observed low value of this band is due to intramolecular hydrogen bonding between H of OH and azomethine nitrogen suggesting the presence of structure **b** at least in the solid state (Figure 1).

The intense band at 1273 cm^{-1} present in the IR spectrum of the Schiff base ligand may be assigned to phenolic (C–O) stretching mode, according to the previous assignments. The pyrimidine ring shows characteristic stretching absorption bands at the 3060 cm^{-1}. The phenyl group shows C–H stretching at 3030 cm^{-1} and C=C stretching at 1540 cm^{-1}. The bands at 1590 cm^{-1} can be very safely assigned to ν(C=N) (pyrimidine) [15]. A strong band at l691–1645 cm^{-1} and 1625 cm^{-1} in the IR spectra of the free ligand assigned to ν(C=O) and ν(C=N) [11,15] is changed by ±10–30 cm^{-1} in the spectra of complexes, indicating coordination through azomethine nitrogen, phenolic oxygen and carbonyl oxygen of Schiff base (Figure 2). In the spectra of metal complex as Ni(II), 1273 cm^{-1} for the phenolic group did not shift, suggesting that this oxygen atom of the phenolic group is not coordinated to the metal ion [16]. It is suggested they are bidentate complexes from that the oxygen atom of this carbonyl group and the nitrogen atom of the azomethine group are coordinated to the metal ion (Figure 3). In the spectra of the Cu(II), Ni(II), Co(II) and Zn(II) complexes, the bands observed in the 445–470 and 420–426 cm^{-1} region may be due to ν(M–N) and ν(M–O), respectively [16]. Broad bands of the Cu(II), Ni(II), Co(II) and Zn(II) complexes in the 3240–3350 cm^{-1} region are assigned to the ν(OH) vibration of the water molecules [16].

Proton and carbon nuclear magnetic resonance spectra: Chloroform was used as a deuterated solvent to measure the ^{1}H-NMR spectra of the ligand and its Zn(II) complex except those of Cu(II), Co(II) and Ni(II) because of their paramagnetic behaviour. The sharp singlet was observed at about δ 10.28 ppm due to phenolic proton of the ligand. The singlet at δ 9.59 ppm and 8.35 ppm is due to azomethine proton and pyrimidine ring (C–H) proton, respectively, in the spectrum of the ligand. In the spectra of the Schiff base the phenyl multiplet was observed between δ 7.02 and 7.71 ppm. The ^{1}H-NMR spectra of Zn(II) complex show approximately the same peaks identical to those of the free ligand with exception that the peak due to the (2-OH) phenolic group resonance is absent. This is considered as an additional evidence for the deprotonation of OH phenolic.

Chloroform was used as a deuterated solvent to measure the ^{1}H-NMR spectra of the ligand. The ^{13}C NMR spectra of the ligand LH are characterized by the presence of a cluster of peaks at 193.5 and 197.4 ppm, due to carbonyl carbons. The spectrum of the ligand shows a peak at 165.8 ppm, which may be attributed to the CH=N group. The spectrum of the ligand shows a peak at 149.4 ppm, which may be attributed to the pyrimidine ring (C=N) group. The spectrum of the ligand shows a peak in the region 122.6–138.0 ppm, due to aromatic carbons.

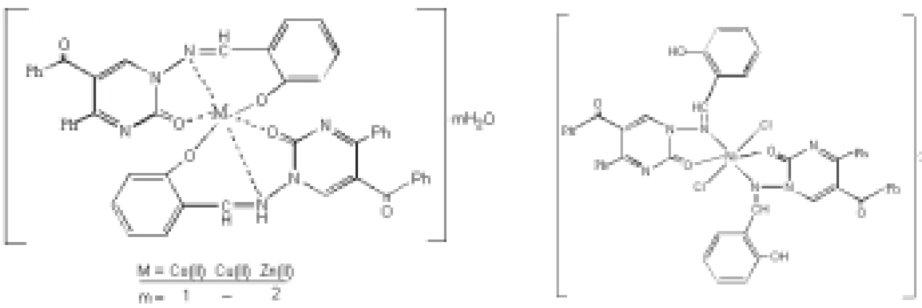

Figure 3. Suggested structure of the octahedral complexes of the ligand LH.

Electronic spectra and magnetic measurements: The electronic absorption data of the compounds, which are dissolved in DMF are given in Table 1. In the spectra of the ligands, the bands in the 390–348 nm range are assigned to the n→π* transitions of the azomethine group. During the formation of the complexes, these bands are shifted to lower wavelengths, suggesting that the nitrogen atom of the azomethine group is coordinated to the metal ion. The values in the 300–250 nm range are attributed to the π→π* transition of the benzenoid and pyrimidine rings. In the spectra of the complexes, these bands are slightly shifted to lower wavelength. The electronic spectra of the Zn(II) complex, which is diamagnetic, have bands in the 280–250 nm range and these bands may be due to the n→π* and π→π* transitions of the benzene, pyrimidine rings and azomethine group. In the spectra of the complexes, the less intense and broad bands in the 445–250 nm range result from the overlap of the low energy π→π* transitions mainly localized within the imine chromophore and the LMCT (ligand to metal charge-transfer bands) transition from the lone pairs of the phenolate oxygen donor to the M(II) ions.

The first spectrum of $[Cu(L)_2]$, which occurs at frequencies above 490 nm, represents the L→M charge-transfer band. The second one at the range 715–580 nm corresponds to the d-d transition band. The spectra of tetragonally distorted octahedral chelates should consist of three bands corresponding to transitions: $^2B_{1g}\rightarrow{}^2A_{2g}\rightarrow{}^2B_{2g}$ and ^2E_g in order of increasing energy. But generally, such chelates exhibit a broad structureless band with or without shoulder between 715–520 nm depending upon the strength of the field of ligand. The obtained values of the effective magnetic moment (1.71 B.M.) is typical for distorted octahedral Cu(II) chelates.

$[Ni(LH)_2Cl_2]\cdot 2H_2O$ shows d-d transition at 517 and 675 nm corresponding to $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}\rightarrow{}^3T_{2g}(F)$ respectively, which suggests mostly octahedral geometry. The magnetic moment values for the Ni(II) complex of the Schiff base ligand at room temperature was found to be in the normal range (2.8-3.5 B.M.) [17]; *e.g.* $[Ni(LH)_2Cl_2]\cdot 2H_2O$ showed magnetic moment value of 3.81 B.M. Zinc(II) complex is diamagnetic as expected for the d^{10} configuration.

The magnetic moment values for the $[Co(L)_2]\cdot H_2O$ complex of the ligand is near the spin only value for high spin octahedral complexes. The electronic spectrum shows two bands at 650 and 510 nm attributed to $^4T_{1g}\rightarrow{}^4A_{2g}$ (ν_2) and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ (ν_3) transitions respectively, in an octahedral geometry around the Co(II) ion. The band at 445 nm is due to a charge-transfer transition [17].

Single crystals of the complexes could not be isolated from any solutions, thus, no definitive structure can be described. However, the analytical, spectroscopic and magnetic data enable us to predict possible structures as shown in Figures 2 and 3.

Conductivity: The complexes are non-electrolytes as shown by their molar conductivity (Λ_M) in DMF, which are in the range 0.8–35.2 Ω^{-1} cm^2 mol^{-1} [11,17–23].

Thermal studies: The thermal stability of the complexes was investigated using TGA. The TGA curves were obtained at a heating rate of 10°C/min in N_2 atmosphere over the temperature range of 25–850°C.

The Cu(II) complex was stable up to 275°C and its decomposition started at this temperature and was completed at 663°C. The Cu(II) complex decomposed and produced CuO as residue [(calculated/found) %: 9.75/9.63] in three steps in the temperature ranges 275–320, 320–468 and 468–663°C. In the decomposition process of Cu(II) complex, the mass losses corresponded to Ph–C=O–, Ph– and the other organic moieties leaving in the first, second and third stages of the decomposition, respectively. The three stages of the decomposition of Cu(II) complex were irreversible.

The Ni(II) complex was stable up to 25°C and its decomposition started at this temperature and was completed at 671°C. The (Ni) complex decomposed and produced NiO as residue [(calculated/found) %: 7.82/7.97] in four steps in the temperature ranges 25–70, 70–272, 272–358 and 358–671°C. In the decomposition process of the Ni(II) complex, the mass losses corresponded to H_2O, Cl, Ph–C=O– and Ph– and the other organic moieties leaving in the first, second, third and fourth stages of the decomposition, respectively. The four stages of decomposition of Ni(II) complex were irreversible.

The Co(II) complex was stable up to 36°C and its decomposition started at this temperature and was completed at 565°C. The Cu(II) complex decomposed and produced CoO as residue [(calculated/found) %: 8.85/10.85] in four steps in the temperature ranges 36–110, 110–318, 318–472 and 472–565°C. In the decomposition process of Co(II) complex, the mass losses corresponded to H_2O, Ph–C=O–, Ph– and the other organic moieties leaving in the first, second, third and fourth stages of the decomposition, respectively. The four stages of the decomposition of Co(II) complex were irreversible.

The Zn(II) complex was stable up to 32°C and its decomposition started at this temperature and was completed at 572°C. The Zn(II) complex decomposed and produced ZnO as residue [(calculated/found) %: 9.17/9.28] in four steps in the temperature ranges 32.0–250.2, 250.2–303.0, 303.0–512.0 and 512.0–572.0°C. In the decomposition process of the Zn(II) complex, the mass losses corresponded to H_2O, Ph–, Ph–C=O– and the other organic moieties leaving in the first, second, third and fourth stages of the decomposition, respectively. The four stages of decomposition of Zn(II) complex were also irreversible.

The Cu(II) complex is thermally stable up to 275°C, whereas the Ni(II), Co(II), and Zn(II) complexes are thermally stable up to 25°C, 36°C, and 32°C, respectively. In the TGA curve of the Ni(II) complex, 3.80% weight loss was observed at 70°C. In the TGA curve of the Co(II) complex, 2.10% weight loss was observed at 110°C. In the TGA curve of the Zn(II) complex, 4.16% weight loss was observed at 250.2°C. This shows that the complexes contain 2, 1, and 2 mole of water of crystallization per complex molecule, respectively. The IR spectra of the complexes are characterized by the appearance of a broad band in the region 3240–3350 cm^{-1}, due to the υ(O–H) frequency of water of crystallization [18–26]. This water content was also identified by the elemental analyses. These decomposition processes of Cu(II), Ni(II), Co(II) and Zn(II) complexes were also confirmed by TGA data. As it can be seen in Table 3, the most stable complex forms Cu(II).

The weight losses for Cu(II), Ni(II), Co(II) and Zn(II) complexes were found to be approximately the same, when expressed as the percentages calculated stoichiometrically from their chemical formulas given in Tables 1, 2 and 3. All of these complexes undergo complete decomposition to the corresponding metal oxides, CuO, NiO, CoO or ZnO [18–25,26] (Table 2).

Table 2. TGA data of the complexes.

Compounds	First Step, °C	Second Step, °C	Third Step, °C	Fourth Step, °C	Residue, Calculated (found) %
$[Cu(L)_2]$	275.0–320.0	320.0–468.0	468.0–663.0	–	CuO 9.75 (9.63)
$[Ni(LH)_2Cl_2]\cdot 2H_2O$	25.0–70.0	70.0–272.0	272.0–358.0	358.0–671.0	NiO 7.82 (7.97)
$[Co(L)_2]\cdot H_2O$	36.0–110.0	110.0–318.0	318.0–472.0	472.0–565.0	CoO 8.85 (10.85)
$[Zn(L)_2]\cdot H_2O$	32.0–250.2	250.2–303.0	303.0–512.0	512.0–572.0	ZnO 9.17 (9.28)

Table 3. TGA data of the complexes [weight loss %, calculated (found)].

Compounds	First Step, °C	Second Step, °C	Third Step, °C	Fourth Step, °C	Total
$[Cu(L)_2]$	25.75 (25.52)	18.18 (18.09)	45.62 (46.46)	–	90.25 (90.07)
$[Ni(LH)_2Cl_2]\cdot 2H_2O$	3.77 (3.80)	7.43 (7.45)	38.09 (36.84)	42.89 (43.94)	92.18 (92.03)
$[Co(L)_2]\cdot H_2O$	2.08 (2.10)	24.28 (23.46)	17.80 (17.76)	46.99 (45.83)	91.15 (89.15)
$[Zn(L)_2]\cdot H_2O$	4.06 (4.16)	17.35 (18.40)	23.66 (23.58)	45.76 (44.58)	90.83 (90.72)

Acknowledgment

We thank the Research Fund of the Yüzüncü Yıl University for financial support.

REFERENCES

1. Jungreis E. and Thabet S., *Chelates Anal. Chem*., **2,** 149 (1969).
2. Dubay S.D., Singh K. and Tandon J.P., *Synth. React. Inorg. Met.-Org. Chem*., **23,** 1251 (1993).
3. Mohand S.A., Levina A. and Muzart J., *J. Chem. Re*s (S)., **25,** 2051 (1995).
4. Holm R.H., Everett G.W. and Chakravorty A., *Prog. Inorg. Chem*., **7,** 83 (1966).
5. Hobday M.D. and Smith T.D., *Coord. Chem. Rev*., **9,** 311 (1973).
6. Usha A.K. and Chandra S., *Synth. React. Inorg. Met.-Org. Chem*., **2,** 1565 (1992).
7. Garg B.S. and Kapur L., *Inorg. Chim. Acta*, **173,** 223 (1990).
8. Chohan Z.H. and Kausar S., *Chem Pharm. Bull. (Japan),* **41**, 951 (1993).
9. Zishen W., Zhiping L. and Zhenhuan Y., *Transn. Met. Chem*., **18**, 291 (1993).
10. Altural B., Akçamur Y., Sarıpınar E., Yıldırım I. and Kollenz G., *Monatsh. Chem*., **120**, 1015 (1989)
11. Khalil S.M.E., Stefan S.L. and Bashir K.A., *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 1685 (1999).
12. Sönmez M., *Turk. J. Chem.,* **25**, 181 (2001).
13. Temel H., İlhan S., Şekerci M. and Ziyadanoğulları R., *Spectroscopy Letters,* **35**, (2002) (in press).
14. Temel H., Çakır Ü., Şekerci M. and Uğraş H.İ., *Heteroatom Chem.,* (2002) (in press).
15. Temel H. and Şekerci M., *Synth. React. Inorg. Met.-Org. Chem*., **31**, 849 (2001).
16. Bellamy L.J., *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London (1978).
17. Lever A.B.P., *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam (1984).
18. Şekerci M. and Taş E., *Heteroatom Chem*., **11,** 254 (2000).
19. Şekerci M., *Synth. React. Inorg. Met.-Org. Chem*.**,** **30,** 117 (2000).
20. Şekerci M. and Alkan C., *Synth. React. Inorg. Met.-Org. Chem*., **29,** 1685 (2001).
21. Şekerci M. and Alkan C., *J. Science and Engineering of Fırat University*., **11,** 119 (1999).
22. Şekerci M., Ph. D. Thesis, Institute of Science, University of Fırat, Elazığ, Turkey, 98 (1997).
23. Şekerci M., *S. Afr. J. Chem*., **52,** 79 (1999).
24. Şekerci M., *Synth. React. Inorg. Met.-Org. Chem*., **29,** 487 (1999).
25. Şekerci M., *Synth. React. Inorg. Met.-Org. Chem.*, **30,** 191 (2000).
26. Çukurovalı A., Yılmaz İ., Ahmedzade M. and Özmen H., *Synth. React. Inorg. Met.-Org. Chem.*, **31,** 255 (2001).