Russian Journal of Coordination Chemistry, Vol. 31, No. 11, 2005, pp. 790–794. Translated from Koordinatsionnaya Khimiya, Vol. 31, No. 11, 2005, pp. 834–838.
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Studies on Mononuclear Chelates Derived from Substituted Schiff Base Ligands: Synthesis and Characterization of a New 5-Methoxysalicyliden-*p*-Aminoacetophenoneoxime and Its Complexes with Co(II), Ni(II), Cu(II), and Zn(II)

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Received December 12, 2004

Abstract—New complexes of Co(II), Ni(II), Cu(II), and Zn(II) with new Schiff bases derived by the condensation of *p*-aminoacetophenoneoxime with 5-methoxysalicylaldehyde are synthesized. The compounds are characterized by elemental analyses, magnetic susceptibility measurements, IR, ^{1}H and ^{13}C NMR spectra, electronic spectral data, and molar conductivity. The thermal stabilities of the compounds are also reported. The Schiff base acts as bidentate O,N-donor atoms, and their metal complexes are supposed to possess a tetrahedral geometry with respect to the central metal ion. The general formula of the 5-methoxysalicyliden-*p*-aminoacetophenoneoxime Co(II), Ni(II), Cu(II), and Zn(II) complexes is $Co(L)_2$, $Ni(L)_2$, $Cu(L)_2$, and $Zn(L)_2$.

There are two most important classes of ligands in the modern coordination chemistry, namely, azomethines [1] and oximes [2]. A large number of the Schiff bases and their complexes have been studied in the past because of their wide application and interesting and important properties [3–5]. Metal complexes of the Schiff bases derived from substituted salicylaldehydes and various amines have been widely investigated [4, 5]. They can serve as models of biologically important species and find applications in biomimetic catalytic reactions, materials chemistry, and industry [5–7].

There is a considerable interest in the chemistry of transition-metal complexes of ligands containing oxygen and nitrogen donor atoms due to the carcinostatic, antitumor, antiviral, antifungal, and antibacterial activity and industrial uses of complexes derived from them [3, 8–10].

Many anticancer and/or antibacterial medicines are known, on the one hand, to behave as versatile, some of which exhibit increased anticancer activity when administrated in the complex form with metal ions [11–13]. On the other hand, the Schiff base complexes are known to show antifungal activity, which is increased in the presence of a hydroxy group in the ligand [14]. The presence of transition metals in human blood plasma indicates their importance in the mechanism for accumulation, storage, and transport of transition metals in living organisms [15]. We have prepared and characterized several metal complexes of the Schiff base ligands. However, no work has been found concerning 5-methoxysalicyliden-*p*-aminoacetophenoneoxime and complexes of this compound. We now report the synthesis and characterization of this O,N-type Schiff base, as well as its complexes with cobalt, nickel, copper, and zinc.

EXPERIMENTAL

The preparation of *p*-aminoacetophenoneoxime has been described previously [16]. Elemental analyses (C, H, N) were carried out using LECO-932 CHNSO at the Technical and Scientific Research Council of Turkey, TUBITAK. IR spectra were recorded on a Mattson 1000 FT-IR spectrometer as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on Bruker GmbH Dpx-400 MHz high-performance digital FT-NMR spectrometers. Electronic spectra were recorded on a Shimadzu 1240 UV spectrometer at the Hacettepe University. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (model MK1) at room temperature using $Hg[Co(SCN)_4]$ as a standard; diamagnetic corrections were calculated from Pascal's constants. The melting points were determined on a Gallenkamp melting point apparatus. Molar conductances of the Schiff base ligand and its transition-metal complexes were determined at room temperature using a CMD 750 WPA conductivity meter. TGA curves were recorded on a Shimadzu TG-50 thermobalance.

5-Methoxysalicyliden-*p*-aminoacetophenoneoxime (HL). To a solution of *p*-aminoacetophenoneoxime (1.502 g, 10 mmol) in absolute EtOH (20 ml), 5-methoxysalicylaldehyde (1.520 g, 10 mmol) and *p*-toluenesulfonic acid (0.01 mg) dissolved in absolute EtOH (25 ml) were added dropwise at 60°C with continuous stirring and monitoring of the course of the reaction with IR. The precipitate was filtered, washed with cold EtOH and Et_2O several times, crystallized from acetone–water, and dried at 60°C to a constant weight.

IR spectrum (ν, cm^{-1}): 3350–3400 (oxime O–H), 3250–3295 (phenolic O–H), 1625 (phenolic CH=N), 1595 (oxime C=N), 1265 (C–O), 1005 (N–O); ^1H NMR ($CDCl_3$–DMSO-d_6, δ, ppm): 13.10 (s, 1H, phenolic OH), 10.91 (s, 1H, oxime OH), 8.67 (s, 1H, azomethine CH=N), 7.67 (d, 2H, H_{ar}^{5}), 7.25 (d, 1H, H_{ar}^{4}), 6.97 (d, 1H, H_{ar}^{13}), 6.93 (d, 2H, H_{ar}^{14}), 6.82 (s, 1H, H_{ar}^{11}), 3.72 (s, 3H, OCH_3), 2.17 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$–DMSO-d_6, δ, ppm): 162.36 (CH=N), 154.83 (C–OH), 152.54 (C–N), 151.89 (C^{12}), 148.02 (C^2), 135.66 (C^3), 133.88 (C^4 and C^8), 126.29 (C^{13}), 121.00 (C^{11}), 120.40 (C^5 and C^7), 115.05 (C^{10}), 110.15 (C^{14}), 55.48 ($-OCH_3$), 11.34 (C^1); λ_{max} (ε, l/(mol cm)): 375 (2.01×10^3) (azomethine $n \longrightarrow \pi^*$).

Bis(*p*-aminoacetophenoneoxime-5-methoxysalicylaldiminato)cobalt(II) Co(L)$_2$. A solution of $Co(AcO)_2 \cdot 4H_2O$ (0.125 g, 0.50 mmol) in absolute EtOH (20 ml) was added to a hot (50°C) solution of the HL (0.285 g, 1.00 mmol) in absolute EtOH (20 ml) under an argon atmosphere. The complex was obtained immediately upon the addition of the metal salt solution. The precipitated complex was filtered off, washed with H_2O, cold EtOH, and cold Et_2O several times, and dried *in vacuo*. IR spectrum (ν, cm^{-1}): 3350–3400 (oxime O–H), 1605 (phenolic C=N), 1595 (oxime C=N), 1280 (C–O), 1005 (N–O); λ_{max} (ε, l/(mol cm)): 676 (189) (*d–d*), 434 (2.11×10^3) (*C–T*), 370 (4.43×10^3) (azomethine $n \longrightarrow \pi^*$).

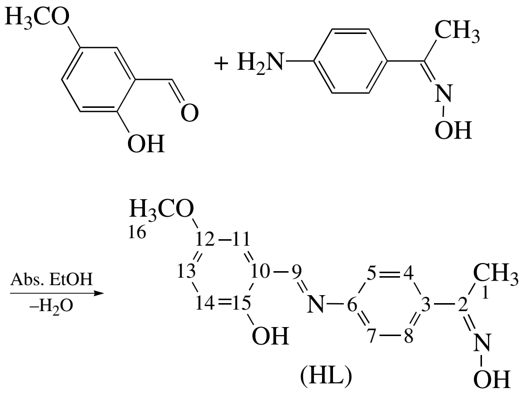
Bis(*p*-aminoacetophenoneoxime-5-methoxysalicylaldiminato)nickel(II) Ni(L)$_2$. Ni(L)$_2$ was prepared following the same procedure as that described for Co(L)$_2$, starting from HL (0.285 g, 1.00 mmol) and $Ni(AcO)_2 \cdot 4H_2O$ (0.124 g, 0.50 mmol). IR spectrum (ν, cm^{-1}): 3350–3400 (oxime O–H), 1610 (phenolic C=N), 1595 (oxime C=N), 1275 (C–O), 1005 (N–O); λ_{max} (ε, l/(mol cm)): 640 (195) (*d–d*), 418 (3.00×10^3) (*C–T*), 360 (2.30×10^3) (azomethine $n \longrightarrow \pi^*$).

Bis(*p*-aminoacetophenoneoxime-5-methoxysalicylaldiminato)copper(II) Cu(L)$_2$. Cu(L)$_2$ was prepared following the same procedure as that described for Co(L)$_2$, starting from HL (0.285 g, 1.00 mmol) and $Cu(AcO)_2 \cdot H_2O$ (0.100 g, 0.50 mmol). IR spectrum (ν, cm^{-1}): 3350–3400 (oxime O–H), 1610 (phenolic C=N), 1595 (oxime C=N), 1285 (C–O), 1005 (N–O); λ_{max} (ε, l/(mol cm)): 597 (163) (*d–d*), 418 (1.11×10^3) (*C–T*), 374 (3.77×10^3) (azomethine $n \longrightarrow \pi^*$).

Bis(*p*-aminoacetophenoneoxime-5-methoxysalicylaldiminato)zinc(II) Zn(L)$_2$. Zn(L)$_2$ was prepared following the same procedure as that described for Co(L)$_2$, starting from HL (0.285 g, 1.00 mmol) and $Zn(AcO)_2 \cdot 2H_2O$ (0.110 g, 0.50 mmol). IR spectrum (ν, cm^{-1}): 3350–3400 (oxime O–H), 1615 (phenolic CH=N), 1595 (oxime C=N), 1290 (C–O), 1005 (N–O); ^1H NMR ($CDCl_3$–DMSO-d_6, δ, ppm): 10.90 (s, 2H, oxime OH), 8.53 (s, 2H, azomethine CH=N), 6.83–7.64 (m., 14H, H_{ar}), 3.74 (s, 6H, OCH_3), 2.18 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$–DMSO-d_6, δ, ppm): 172.00 (CH=N), 159.29 (C–OH), 157.06 (C–N), 152.06 (C^{12}), 148.28 (C^2), 135.38 (C^3), 134.15 (C^4 and C^8), 126.70 (C^{13}), 120.94 (C^{11}), 120.39 (C^5 and C^7), 115.16 (C^{10}), 110.26 (C^{14}), 55.66 (C^{16}), 11.51 (C^1); λ_{max} (ε, l/(mol cm)): 430 (3.52×10^3) (*C–T*), 368 (1.64×10^3) (azomethine $n \longrightarrow \pi^*$).

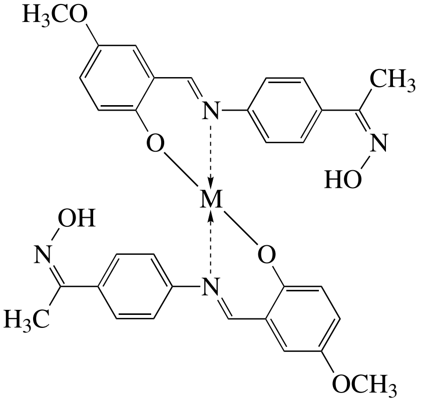
RESULTS AND DISCUSSION

The new Schiff base 5-methoxysalicyliden-*p*-aminoacetophenoneoxime (HL) was synthesized by the condensation of *p*-aminoacetophenoneoxime [16] and 5-methoxysalicylaldehyde:



(HL)

In general, reactions of the ligand with metal salt occurred at a high rate with good yield of mononuclear complexes corresponding to the general formula M(L)$_2$:



M(L)$_2$, M = Co(II), Ni(II), Cu(II), and Zn(II)

These complexes are stable at room temperature and soluble in DMSO and DMF. Microanalytical, molar

Table 1. Analytical and physical data for the ligand and complexes

Compounds	Empirical formula (fr wt, g/mol)	Color	Mp, °C	μ_{eff}, μ_B	Λ_M, Ω^{-1} cm^2 mol^{-1}	Yield, %	Content (calcd/found), %		
							C	H	N
HL	$C_{16}H_{16}N_2O_3$ (284.31)	Orange	194		2.5	74	67.44/67.59	5.55/5.67	10.11/9.85
Co(L)$_2$	$C_{32}H_{30}CoN_4O_6$ (625.54)	Light brown	174	3.97	2.8	59	61.21/61.44	5.05/4.83	9.27/8.96
Ni(L)$_2$	$C_{32}H_{30}NiN_4O_6$ (625.30)	Dark green	>300	2.89	5.3	63	61.23/61.47	4.95/4.84	8.76/8.96
Cu(L)$_2$	$C_{32}H_{30}CuN_4O_6$ (630.15)	Mustard yellow	>300	1.75	4.2	69	60.71/60.99	4.99/4.80	9.00/8.89
Zn(L)$_2$	$C_{32}H_{30}N_4O_6Zn$ (631.99)	Orange	192	Dia	6.1	71	60.65/60.81	4.98/4.78	9.10/8.87

conductance, and magnetic susceptibility data of the complexes are given in Table 1. The reactions of the transition-metal salts with the Schiff base are described by the following equation:

$$2HL + M(CH_3COO)_2 \cdot nH_2O$$
$$\longrightarrow M(L)_2 + 2CH_3COOH + nH_2O,$$
$$M = Co, Ni, Cu, Zn \quad (n = 4, 4, 1, 2, \text{respectively}).$$

IR spectra of the free Schiff base ligand and the complexes exhibit various bands in the 400–4000 cm^{-1} region. The phenolic O–H stretching frequency of the free ligand is expected at 3250–3295 cm^{-1}; however, this frequency is generally displaced to 2600 cm^{-1} due to the internal hydrogen bridge OH···N=C [17]. The band becomes broader and sometimes is not detected as the hydrogen bond becomes stronger. Hydrogen bonds in the Schiff base are usually very strong. The ligand is relatively planar with adequate intramolecular distances that favor the formation of the hydrogen bond. The presence of an electron-donating group on the nitrogens also favors intramolecular hydrogen bond formation [18].

An electron-donating group in the phenolic ring increases the electron density on the hydroxyl oxygen making the phenolic O–H bond stronger, and the absorption usually appears as a broad band in the IR spectrum. The phenolic O–H stretching appears as two bands in the spectrum of the free ligand HL: the sharp, weaker band at 3250 cm^{-1} is tentatively assigned to the free O–H stretching frequency, and the broader, more intense band at 3295 cm^{-1} is attributed to the intermolecular hydrogen bonded phenolic O–H stretching [19]. The C=N stretching frequency for the ligand is assigned at 1625 cm^{-1} in agreement with the assignments reported [20, 21] for this band. An electron-donating group in the phenolic ring increases the electron density on the hydroxyl oxygen more than the azomethine nitrogen. A third characteristic band, due to the C–O stretching frequency, appears as a weak band within the 1265 cm^{-1} reported for similar ligands [22, 23].

The infrared spectrum of HL bands at ca. 3350–3400 and 1595 cm^{-1} are assigned to O–H (oxime) and C=N (oxime) [24–27]. Coordination of the Schiff base to the Co(II), Ni(II), Cu(II), and Zn(II) ion through the azomethine nitrogen atom is expected to reduce the electron density in the azomethine link and, thus, to lower the C=N absorption frequency. Hence, this band undergoes a shift to lower frequency to 1605–1615 cm^{-1} after complexation indicating the coordination of the azomethine nitrogen [28] to Co(II), Ni(II), Cu(II), and Zn(II). A medium-intensity band at 3250–3295 cm^{-1} in the spectra of the free ligands due to phenolic O–H was absent in the spectra of all the complexes, indicating the deprotonation of the Schiff base prior the coordination through its oxygen atom. This is further supported by an increase in the absorption frequency of the phenolic C–O band from 1265 cm^{-1} in the spectra of the free ligand to 1275–1290 cm^{-1} in the spectra of the complexes, indicating that the other coordination site of the Schiff base is the phenolic oxygen [29, 30]. The practically unchanged O–H and C=N of the oxime group itself do not coordinate to metal atoms by neither oxygen nor nitrogen atoms.

^{1}H and ^{13}C NMR spectra. In order to identify structures of the Schiff base ligand and complexes in solution, the ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$–DMSO-d_6. The ^{1}H and ^{13}C NMR assignments are also given in Experimental. Similar spectra were obtained for the ligand. It is important to emphasize the ^{1}H NMR resonance of the OH group at 13.10 ppm, due to the presence of intramolecular hydrogen bonding [31]. The singlet at 10.91 ppm can be assigned to the proton of the oxime OH proton [32, 33]. The signal due to the OH protons disappears in a D_2O solution. The single-proton resonance in the ^{1}H NMR spectra of the ligand accruing near 8.67 ppm has been assigned to the azomethine group proton. The multiplets at 6.82–7.67 ppm can be assigned to the protons of the aromatic ring. In addition, the proton of the methoxy group is observed at 3.72 ppm as a singlet.

The ^{13}C NMR spectral data of the ligand confirms the results of the ^{1}H NMR spectra. The carbon atoms of the CH=N, C–OH, and C–N are observed in the extensive 162.36, 154.83, and 152.54 ppm ranges. The signal at 55.48 ppm can be attributed to the carbon atom of the methoxy (–OCH_3) group. As can be seen in the ^{1}H NMR spectra of the Zn(II) complex, there is no OH

Table 2. *TGA* data of Co(II), Ni(II), Cu(II), and Zn(II) complexes with HL

complexes	Decomposition step temperature range, °C	weight loss (calcd/found), %	temperature range, °C	weight loss (calcd/found), %	final product	residue (calcd/found), %
Co(L)$_2$	271–313	12.5/12.8	313–597	75.6/76.2	CoO	11.9/11.0
Ni(L)$_2$	230–296	12.4/13.1	296–555	75.8/75.5	NiO	11.8/11.4
Cu(L)$_2$	247–299	12.3/12.5	299–500	75.1/75.5	CuO	12.6/12.0
Zn(L)$_2$	243–335	21.7/22.6	335–688	65.4/65.3	ZnO	12.9/12.1

peaks expected. The absence of the phenolic OH proton signal (at 13.10 ppm in the ligand HL) in the Zn(II) complex indicates the coordination by the phenolic oxygen to the metal ion after deprotonation. The coordination of the azomethine nitrogen is inferred by the upfield shift of the CH=N proton signal from 8.67 ppm in the ligand to 8.53 ppm in the complex [34]. The aromatic proton signals and –OCH$_3$ proton signal are seen at 6.83–7.64 and 3.74 ppm, respectively.

Thus, the ^{1}H NMR data confirm the monobasic bidentate (ON) nature of the ligand, which already has been suggested from the IR spectral data. ^{13}C NMR spectrum of the Zn(II) complex for the CH=N, C–OH, and C–N carbon atoms are observed at 172.00, 159.29, and 157.06 ppm, respectively. The rest of carbon atoms likewise showed similar diagnostic features for the free ligand, as well as its complex as expected. The signals corresponding to the N–OH proton and C=N–OH carbon (both in oxime) [35–38] groups are unchanged in the ^{1}H and ^{13}C NMR spectra of the complexes indicating that these oxime groups do not take part in complexation.

Elemental analyses and molar conductance. The general characteristic properties of the complexes and the Schiff base are shown in Table 1. The elemental analysis results agree with the calculated values showing that the complexes have the 1 : 2 metal/ligand ratios. The elemental analyses confirmed the compositions of the above-synthesized compounds.

The observed molar conductance of the complexes in 10^{-4} molar solutions in DMSO lies in the range 2.8–6.1 cm^2/(Ω mol). This is consistent with the nonelectrolytic nature of these complexes [39].

UV–Vis spectra and magnetic moment. A solution spectrum (DMF) of Schiff base ligand and its complexes, as well as *d–d* bands in solution, is presented in Experimental. HL exhibits a band at 270 nm assigned to the phenyl ring transition $\pi \longrightarrow \pi^*$, which remains nearly unchanged in the spectra of its metal complexes. The intense band at 375 nm ($\varepsilon = 2.01 \times 10^3$ l/(mol cm)) in the spectrum of the ligand is assigned to the $n \longrightarrow \pi^*$ transition, which shifted to higher energy on complexation [40]. The electronic spectra of the Co(II) complex in DMF solution are similar and show the main band at 676 nm ($\varepsilon = 189$ l/(mol cm)) assigned to the $^4A_2 \longrightarrow {}^4T_1$ (*P*) transition in a tetrahedral ligand field [41]. Also, the value of the magnetic moment (3.97 μ_B) is additional evidence for a tetrahedral structure around the Co^{2+} ion.

The magnetic moment value of the Ni(II) complex in the 2.89 μ_B corresponds to two unpaired electrons and suggests a four-coordinate tetrahedral structure. The spectra of the Ni(II) complex show a less intense shoulder at 640 nm ($\varepsilon = 195$ l/(mol cm)), which is assigned to *d–d* transition of the metal ion. The former band is probably due to the $^3A_2 \longrightarrow {}^3T_2$ (*F*) transition of tetrahedral geometry [42]. The Cu(II) complex exhibits a magnetic moment value close to the spin-only value for an unpaired at 1.73 μ_B. In visible region, the Cu(II) complex exhibits a high-intensity shoulder at 418 nm ($\varepsilon = 1.11 \times 10^3$ l/(mol cm)) and a weak broad shoulder at 597 nm ($\varepsilon = 163$ l/(mol cm)) assignable to charge transfer (*C–T*) and $^2T_2 \longrightarrow {}^2E$ (*G*) in a tetrahedral field, respectively [43]. The Zn(II) complex was found to be diamagnetic as expected. The Zn(II) complex shows an intense band at 368 nm ($\varepsilon = 1.64 \times 10^3$ l/(mol cm)), which is assigned to $n \longrightarrow \pi^*$ transition associated with azomethine linkage. The spectra of the Zn(II) complex show an intense band at 430 nm ($\varepsilon = 3.52 \times 10^3$ l/(mol cm)), which can be assigned to *C–T* transition of tetrahedral geometry [44].

Thermal studies. The thermal behavior was determined by TGA curves for the Schiff base ligand and its complexes at a heating rate of 10°C/min in a nitrogen atmosphere over a temperature range of 25–800°C. The thermal stability data are listed in Table 2. Thermogravimetric studies of all the complexes showed no weight loss up to 230°C, indicating the absence of water in the complexes. The TGA curves showed that the thermal decomposition of the complexes occurs in two steps. Possibly, the different groups in the ligand affect the stability of all the complexes. Furthermore, it is known that the electronegativity and atomic radius of the central metal atom affect also the thermal stability. As a result of decomposition, the observed weight losses for all complexes are in good agreement with the calculated values. All these complexes undergo complete decomposition to the corresponding thermodynamically stable metal oxides, CoO (residue 11.0%), NiO (residue 11.4%), CuO (residue 12.0%), and ZnO (residue 12.1%). In addition, the thermal stability of all complexes increases in the order Cu < Ni < Co < Zn [45, 46].

ACKNOWLEDGMENTS

The support of the Management Unit of Scientific Research Projects of Firat University (FUBAP) under research project no. 835 is gratefully acknowledged.

REFERENCES

1. Vigato, P.A. and Tamburini, S., *Coord. Chem. Rev.*, 2004, vol. 248, nos. 21–24, p. 1717.
2. Kukiskin, V.Yu. and Pombeiro, A.J.L., *Coord. Chem. Rev.*, 1999, vol. 181, no. 1, p. 147.
3. Mishra, A.P., Khare, M., and Gautam, S.K., *Synth. React. Inorg. Met.-Org. Chem.*, 2002, vol. 32, no. 8, p. 1485.
4. El-Ansary, A.L., Soliman, A.A., Sherif, O.E., and Ezzat, J.A., *Synth. React. Inorg. Met.-Org. Chem.*, 2002, vol. 32, no. 7, p. 1301.
5. Tuncel, M.. and Serin, S., *Synth. React. Inorg. Met.-Org. Chem.*, 2003, vol. 33, no. 6, p. 985.
6. Çelik, C., Tümer, M., and Serin, S., *Synth. React. Inorg. Met.-Org. Chem.*, 2002, vol. 32, no. 10, p. 1839.
7. Temel, H., Ilhan, S., Şekerci, M., and Ziyadanoğullar, R., *Spectrosc. Lett.*, 2002, vol. 35, no. 2, p. 219.
8. Sengupta, P., Ghosh, S., and Mak, T.C.W., *Polyhedron*, 2001, vol. 20, nos. 9–10, p. 975.
9. Boghaei, D.M. and Mohebi, S., *Tetrahedron,* 2000, vol. 58, no. 26, p. 5357.
10. Maurya, R.C., Patel, P., and Rajput, S., *Synth. React. Inorg. Met.-Org. Chem.*, 2003, vol. 33, no. 5, p. 817.
11. Hassan, M., Chohan, H.Z., and Supuran, C.T., *Synth. React. Inorg. Met.-Org. Chem.*, 2002, vol. 32, no. 8, p. 1445.
12. Campbell, M.J.M., *Coord. Chem. Rev.,* 1975, vol. 15, nos. 2–3, p. 279.
13. Williams, D.R., *Chem. Rev.*, 1972, vol. 72, no. 3, p. 203.
14. Temel, H., Cakr, U., Ugras, H.I., and Şekerci, M., *J. Coord. Chem.*, 2003, vol. 56, no. 11, p. 943.
15. Joshi, J.D., Sharma, S., Patel, G., and Uora, J.J., *Synth. React. Inorg. Met.-Org. Chem.*, 2002, vol. 32, no. 10, p. 1729.
16. Canpolat, E. and Kaya, M., *Pol. J. Chem.,* 2005, vol. 79, no. 6, p. 959.
17. Ianiran, J.A., Patel, K.S., and Bailar, J.C., *J. Inorg. Nucl. Chem.*, 1974, vol. 36, no. 7, p. 1547.
18. Freedman, H.H., *J. Am. Chem. Soc.*, 1961, vol. 83, no. 13, p. 2900.
19. Silverstein, R.M., Bassler, G.C., and Morril, T.C., *Identification of Organic Compounds*, New York: Wiley, 1991, p. 110.
20. Canpolat, E. and Kaya, M., *J. Coord. Chem.*, 2004, vol. 57, no. 14, p. 1217.
21. Kukushkin, Y.N., Krylov, V.K., Kaplan, S.F., *et al.*, *Inorg. Chim. Acta,* 1999, vol. 285, no. 1, p. 116.
22. Percy, G.C. and Thornton, J.J., *Inorg. Nucl. Chem.*, 1973, vol. 35, no. 7, p. 2319.
23. Felicio, R.C., *Synth. React. Inorg. Met.-Org. Chem.*, 1999, vol. 29, no. 2, p. 171.
24. Canpolat, E., Kaya, M., and Gorgulu, A.O., *Pol. J. Chem.*, 2002, vol. 76, no. 5, p. 687.
25. Canpolat, E.. and Kaya, M., *J. Coord. Chem.,* 2002, vol. 55, no. 8, p. 961.
26. Canpolat, E., Kaya, M., and Yazc, A., *Russ. J. Coord. Chem.*, 2004, vol. 30, no. 2, p. 87.
27. Canpolat, E. and Kaya, M., *Pol. J. Chem.*, 2003, vol. 77, no. 8, p. 961.
28. Patwardhan, H.A., Gopinathan, S., and Gopinathan, C., *Indian J. Chem.*, 1978, vol. 16, no. 3, p. 224.
29. Kovacic, J.E., *Spectrochim. Acta*, 1967, vol. 23, no. 1, p. 183.
30. Garg, B.S., Singh, P.K., and Sharma, J.L., *Synth. React. Inorg. Met.-Org. Chem.*, 2000, vol. 30, no. 5, p. 803.
31. Lindoy, L.F., Moody, W.E., and Taylor, D., *Inorg. Chem.,* 1977, vol. 16, no. 8, p. 1962.
32. Canpolat, E. and Kaya, M., *J. Coord. Chem.*, 2002, vol. 55, no. 12, p. 1419.
33. Canpolat, E., Kaya, M., and Gur, S., *Turk. J. Chem.*, 2004, vol. 28, no. 2, p. 235.
34. Singh, H.R. and Agarwala, B.V., *J. Indian Chem. Soc.,* 1988, vol. 65, no. 8, p. 591.
35. Gungor, O., Canpolat, E., and Kaya, M., *Pol. J. Chem.*, 2003, vol. 77, no. 4, p. 403.
36. Canpolat, E. and Kaya, M., *J. Coord. Chem.*, 2004, vol. 57, no. 1, p. 25.
37. Canpolat, E. and Kaya, M., *Transition Met. Chem. (London)*, 2004, vol. 29, no. 5, p. 550.
38. Canpolat, E., Kaya, M., and Öztürk, Ö.F., *Pol. J. Chem.*, 2004, vol. 78, no. 10, 1843.
39. Geary, W.J., *Coord. Chem. Rev.,* 1971, vol. 7, no. 1, p. 81.
40. El-Sawaf, A.K., West, D.X., El-Saied, F.A., and El-Bahnasawy, R.M., *Synth. React. Inorg. Met.-Org. Chem.*, 1997, vol. 27, no. 8, p. 1127.
41. Panda, P.K., Mishra, S.B., and Mohapatka, B.K., *J. Inorg. Nucl. Chem.*, 1980, vol. 42, no. 4, p. 497.
42. West, D.X., Nassar, A.A., El-Saied, F.A., and Ayad, M.I., *Transition Met. Chem. (London)*, 1999, vol. 24, no. 6, p. 617.
43. Atkins, R., Brewer, G., Kokot, E., *et al.*, *Inorg. Chem.*, 1985, vol. 24, no. 2, p. 127.
44. Tümer, M., Köksal, H., Sener, M.K., and Serin, S., *Transition Met. Chem. (London)*, 1999, vol. 24, no. 4, p. 414.
45. Dubler, E. and Hanggi, G., *Thermochim. Acta*, 1994, vol. 234, no. 3, p. 201.
46. Rakha, T.H., *Transition Met. Chem. (London)*, 1999, vol. 24, no. 6, p. 659.