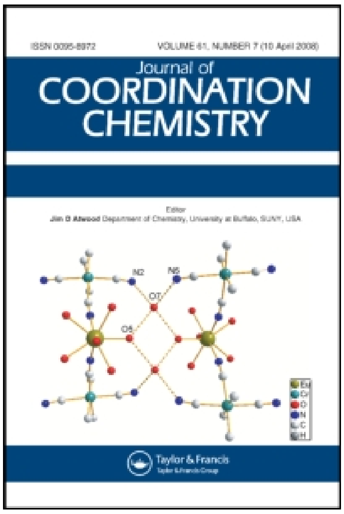


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Studies on mononuclear chelates derived from substituted Schiff-base ligands (Part 10): synthesis and characterization of a new 4-hydroxysalicyliden-<i>p</i>-aminoacetophenoneoxime and its complexes with Co(II), Ni(II), Cu(II) and Zn(II)

Erdal Canpolat[a]; Ayşegül Yazici[a]; Mehmet Kaya[a]
[a] Faculty of Arts and Sciences, University of Firat, Department of Chemistry, Elazığ-23119, Turkey

To cite this Article Canpolat, Erdal , Yazici, Ayşegül and Kaya, Mehmet(2007) 'Studies on mononuclear chelates derived from substituted Schiff-base ligands (Part 10): synthesis and characterization of a new 4-hydroxysalicyliden-**<i>p</i>**-aminoacetophenoneoxime and its complexes with Co(II), Ni(II), Cu(II) and Zn(II)', Journal of Coordination Chemistry, 60: 4, 473 — 480

To link to this Article: DOI: 10.1080/00958970600882555

URL: http://dx.doi.org/10.1080/00958970600882555

Journal of Coordination Chemistry
Vol. 60, No. 4, 20 February 2007, 473–480

Taylor & Francis
Taylor & Francis Group

Studies on mononuclear chelates derived from substituted Schiff-base ligands (Part 10): synthesis and characterization of a new 4-hydroxysalicyliden-*p*-aminoacetophenoneoxime and its complexes with Co(II), Ni(II), Cu(II) and Zn(II)

ERDAL CANPOLAT, AYŞEGÜL YAZICI and MEHMET KAYA*

Faculty of Arts and Sciences, University of Firat, Department of Chemistry
Elazığ-23119, Turkey

(*Received 17 February 2006; revised 2 May 2006; in final form 5 May 2006*)

In this study, 4-hydroxysalicylaldehyde-*p*-aminoacetophenoneoxime (LH) was synthesized starting from *p*-aminoacetophenoneoxime and 4-hydroxysalicylaldehyde. Complexes of this ligand with Co(II), Ni(II), Cu(II) and Zn(II) were prepared with a metal : ligand ratio of 1 : 2. The ligand and its metal complexes have been characterized by elemental analyses, IR, ^{1}H- and ^{13}C-NMR spectra, magnetic susceptibility measurements and thermogravimetric analyses (TGA).

Keywords: Schiff bases; Transition metal complexes; Thermogravimetric analyses

1. Introduction

Schiff bases derived from an amine and any aldehyde are an important class of compounds which coordinate to metal ions via the azomethine nitrogen [1]. Schiff bases and their metal complexes play a key role in our understanding of the coordination chemistry of transition metal ions [2]. There is considerable interest in the chemistry of transition metal complexes of ligands containing oxygen, nitrogen and sulfur donor atoms due to the carcinestatic, antitumour, antiviral, antifungal and antibacterial activity and industrial uses [2–4]. In addition, the presence of nitrogen and oxygen donor atoms in the complexes makes these compound effective and stereospecific catalysts for oxidation, reduction hydrolysis and may also show biological activity and other transformations of organic and inorganic chemistry [2–5]. It is well known that some drugs have increased activity when administered as metal complexes [2, 3].

In our previous studies we investigated the synthesis and characterization of various transition metal complexes of novel Schiff bases [6–14]. In this study, we report

---

*Corresponding author. Email: ecanpolat@firat.edu.tr

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970600882555

the synthesis and characterization of cobalt(II), nickel(II), copper(II) and zinc(II) complexes with 4-hydroxysalicyliden-*p*-aminoacetophenoneoxime (LH). All compounds were characterized by elemental analyses, IR, ^{1}H- and ^{13}C-NMR spectra, magnetic susceptibility measurements and thermogravimetric analyses (TGA).

2. Experimental

The preparation of *p*-aminoacetophenoneoxime has been described previously [6]. Elemental analyses (C, H, N) were carried out using LECO-932 CHNSO by 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 a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR Spectrometer. Electronic spectra were obtained on a Shimadzu 1240 UV Spectrometer at 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 calibrant; diamagnetic corrections were calculated from Pascal's constants. TGA curves were recorded on a Shimadzu TG-50 thermo balance.

2.1. *Preparation of the ligand (LH)*

To a solution of (1.50 g, 0.01 mol) *p*-aminoacetophenoneoxime in 10 mL absolute EtOH, 4-hydroxysalicylaldehyde (1.38 g, 0.01 mol) and (0.01 mg) *p*-toluene sulfonic acid dissolved in 20 mL absolute EtOH were added dropwise at 60°C with continuous stirring and monitoring in the course of the reaction with IR. The precipitate was filtered, washed with cold EtOH and Et_2O several times and crystallized from acetone–water and dried at 60°C to a constant weight.

[LH: % calculated C, 66.65; H, 5.22; N, 10.36, found C, 66.44; H, 4.86; N, 9.98].

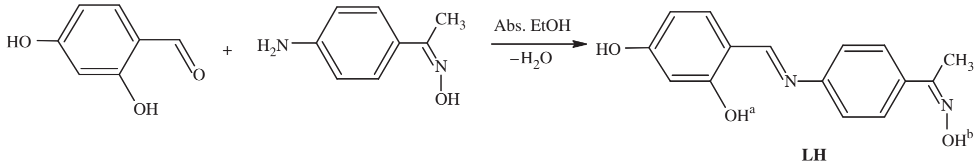
2.2. *Preparation of the Co(II), Ni(II), Cu(II) and Zn(II) complexes*

A sample of ligand (0.27 g, 0.001 mol) was dissolved in absolute ethanol (10 mL). A solution (0.002 mol) of the acetate salt of metal [$Co(AcO)_2 \cdot 4H_2O$ (0.05 g), $Ni(AcO)_2 \cdot 4H_2O$ (0.05 g), $Cu(AcO)_2 \cdot H_2O$ (0.04 g) and $Zn(AcO)_2 \cdot 2H_2O$ (0.06 g)] in 20 mL of absolute ethanol was added dropwise to the ligand solution with continuous stirring at 55°C. The complex started to from immediately upon 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*.

[For $Co(L)_2$: % calculated C, 60.31; H, 4.39; N, 9.38, found C, 59.96; H, 3.99; N, 9.57. For $Ni(L)_2$: % calculated C, 60.33; H, 4.39; N, 9.38, found C, 59.99; H, 4.77; N, 9.55. For $Cu(L)_2$: % calculated C, 59.84; H, 4.35; N, 9.31, found C, 60.05; H, 4.72; N, 9.66. For $Zn(L)_2$: % calculated C, 59.66; H, 4.34; N, 9.28, found C, 59.88; H, 3.99; N, 8.95].

3. Results and discussion

The ligand (LH) was prepared by reacting equimolar amounts of 4-hydroxysalicylaldehyde with *p*-aminoacetophenoneoxime in absolute ethanol (scheme 1). The structures of the ligand and the complexes were established from their IR, ^{1}H- and ^{13}C-NMR spectra, elemental analyses, magnetic susceptibility measurements and thermogravimetric analyses (tables 1–5). All metal complexes with the ligand were prepared by the stoichiometric reaction of the corresponding metal(II) acetate with LH in the molar ratio M : L = 1 : 2. The complexes are intensely coloured stable solids.



Scheme 1. Structure of the ligand.

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

Compounds	Formula (F.W.) (g mol^{-1})	Colour	μ_{eff} (BM)	M.p. (°C)	Yield (%)	λ_{max} d–d	C–T	n → π* azomethine
LH	$C_{15}H_{14}N_2O_3$ (270.28)	Orange	–	240	67	–	–	377
Co(L)$_2$	$CoC_{30}H_{26}N_4O_6$ (597.48)	Dark yellow	3.95	295	55	688	425	382
Ni(L)$_2$	$NiC_{30}H_{26}N_4O_6$ (597.24)	Tile red	2.90	284	61	656	415	395
Cu(L)$_2$	$CuC_{30}H_{26}N_4O_6$ (602.10)	Brown	1.82	278	59	579	435	386

Table 2. Characteristic IR bands of the ligand and the complexes (in cm^{-1}).

Compounds	υ(O–H)	υ(C=N) azomethine	υ(C=N) oxime	υ(C–O)	υ(N–O)
LH	3400–3250	1639	1597	1208	1005
Co(L)$_2$	3400–3275	1614	1597	1245	1005
Ni(L)$_2$	3400–3275	1630	1598	1273	1004
Cu(L)$_2$	3400–3275	1610	1597	1230	1005
Zn(L)$_2$	3400–3275	1623	1597	1252	1004

Table 3. ^{1}H-NMR spectral data of the ligand and the Zn(II) complex (in ppm).

Compounds	CH$_3$	Ar–H	4-OH	CH=N	=N–OH	C–OH
LH	2.18 (s, 3H)	6.33–7.72 (m, 7H)	10.28 (s, 1H)	8.83 (s, 1H)	11.20 (s, 1H)	13.51 (s, 1H)
Zn(L)$_2$	2.18 (s, 6H)	6.31–7.72 (m, 14H)	10.28 (s, 2H)	8.66 (s, 2H)	11.20 (s, 2H)	–

Table 4. ^{13}C-NMR spectral data of the ligand and the Zn(II) complex (in ppm).

Compounds	C^1	C^2	C^3	C^4–C^8	C^5–C^7	C^6	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	C^{15}
LH	11.90	148.70	134.97	127.06	121.52	152.92	163.62	112.58	135.28	108.46	163.11	102.91	162.97
$Zn(L)_2$	11.91	148.76	135.00	128.00	121.55	155.06	165.72	112.63	135.31	108.45	163.08	102.88	166.40

Table 5. TGA data of the ligand and the complexes.

	Decomposition temperature (%) calculated (found)				
Compounds	First step	Second step	Weight loss (%) calculated (found)	Residue (%) calculated (found)	Final product
LH	210–238, 21.48 (20.97)	238–670, 78.52 (78.13)	(99.01)	(0.90)	–
$Co(L)_2$	190–320, 22.11 (22.04)	320–400, 65.35 (64.88)	87.46 (86.92)	12.54 (13.08)	CoO
$Ni(L)_2$	185–225, 27.81 (28.35)	225–416, 59.68 (58.99)	87.49 (87.34)	12.51 (12.66)	NiO
$Cu(L)_2$	212–242, 21.93 (22.54)	242–366, 64.86 (63.95)	86.79 (86.49)	13.21 (13.51)	CuO
$Zn(L)_2$	194–228, 12.94 (13.46)	228–600, 73.59 (72.89)	86.53 (86.35)	13.47 (13.65)	ZnO

3.1. *IR spectra*

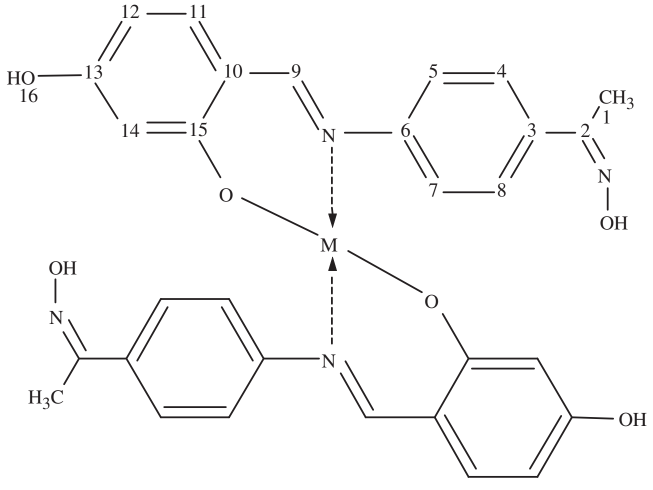
The ligand contains four potential donor sites: (1) the phenolic oxygen, (2) the azomethine nitrogen, (3) the oxime oxygen, and (4) the oxime nitrogen. In the IR spectrum of the ligand, the O–H (oxime) [9–11], O–H (phenolic), C=N (azomethine), C=N (oxime) [12–14], C–O and N–O stretching vibrations were observed at 3310, 3250, 1639, 1597, 1208 and 1005 cm^{-1} respectively. These values are in agreement with those observed for similar compounds [6–14]. The azomethine vibration of the ligand at 1639 cm^{-1} was shifted to lower frequencies after complexation, 1614, 1630, 1610 and 1623 cm^{-1} for Co(II), Ni(II), Cu(II) and Zn(II) complexes, respectively. This clearly indicates coordination of the Schiff bases through the azomethine nitrogen [7–10]. In the free ligand a strong band at 1208 cm^{-1} due to C–O (phenolic) shifts to higher frequency by 22–65 cm^{-1} in the complexes indicating coordination of the phenolic oxygen atom to the metal ion [15]. The practically unchanged O–H at 3310–3400 and C=N at 1597 cm^{-1} reveal that these oxime groups do not coordinate to metal atoms by oxygen or nitrogen atoms.

3.2. *^{1}H- and ^{13}C-NMR spectra*

The NMR spectra of the ligand (LH) and its diamagnetic Zn(II) complex were recorded in $CDCl_3/DMSO\text{-}d_6$ and data are given in tables 3–4. Comparison of the chemical shifts of the ligand with those of the complex shows that the signal due to the phenolic proton (OH) is absent in the complex, suggesting the coordination of the phenolic oxygen to the metal ion after deprotonation [2, 16]. The azomethine proton (CH=N) undergoes a significant shift, indicating coordination of the azomethine nitrogen to the metal ion [16]. More detailed information about the structure of the ligand was provided by ^{13}C-NMR spectral data. C–OH, CH=N and C–N carbon atoms are observed at 162.97, 163.62 and 152.92 ppm, respectively for LH. The detailed ^{13}C-NMR spectral data are given in table 4. ^{13}C-NMR spectrum of Zn(II) complex C–OH, CH=N and C–N carbon atoms are observed at 166.40, 165.72 and 155.06 ppm respectively. These signals are shifted to higher field after complexation, which means that the shifts are due to coordination of the ligand to metal atom by the azomethine nitrogen and phenolic oxygen [17, 18]. The signals corresponding to the H^b proton and C$_2$ carbon (both in oxime) 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. The results confirm the proposed structure of Zn(II) complex (figure 1).

3.3. *Electronic spectra*

The electronic spectra of the ligand and the Co(II), Ni(II) and Cu(II) complexes were recorded in DMF at room temperature. The UV spectral data of the ligand and its complexes are given in table 1. The aromatic band of the ligand at 280 nm is attributed to a benzene $\pi \rightarrow \pi^*$ transition. The band around 377 nm is due to the $n \rightarrow \pi^*$ transition of the non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base. The complexes of Co(II), Ni(II) and Cu(II) show less intense shoulders at ca 579–688 nm, which are assigned as d–d transitions of the metal ions. The former band is probably due to the $^4A_2 \rightarrow {}^4T_1$ (P) for Co(L)$_2$, $^3A_2 \rightarrow {}^3T_2$ (F) for Ni(L)$_2$ and $^2T_2 \rightarrow {}^2E$ (G) for Cu(L)$_2$ transitions of tetrahedral geometry [19]. All the complexes show an intense band at ca 380–395 nm which is assigned to the $n \rightarrow \pi^*$ transition associated with an azomethine linkage [20]. The spectra of the complexes show an intense band at ca 415–445 nm, which can be assigned to a charge transfer (CT) transition of tetrahedral geometry [21–23] in table 4.



M(L)$_2$

M = Co(II), Ni(II), Cu(II) and Zn(II)

Figure 1. Suggested structure of the tetrahedral complexes.

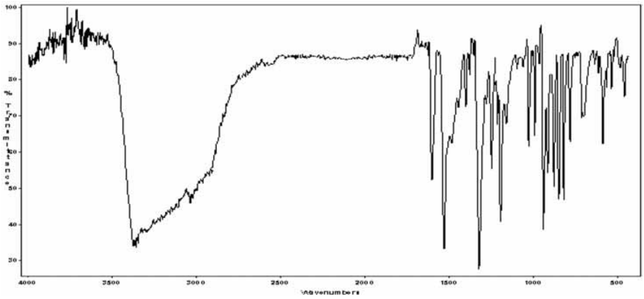


Figure 2. IR spectrum of Zn(II) complex.

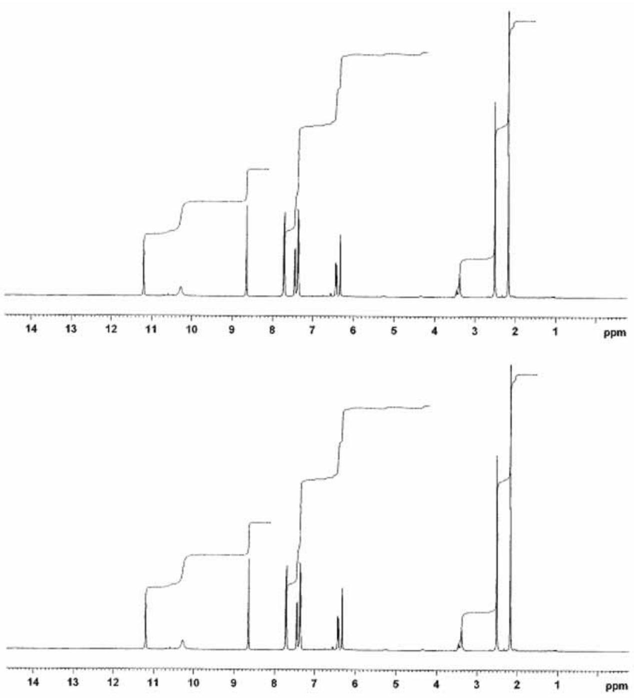


Figure 3. ^{1}H-NMR spectrum of Zn(II) complex.

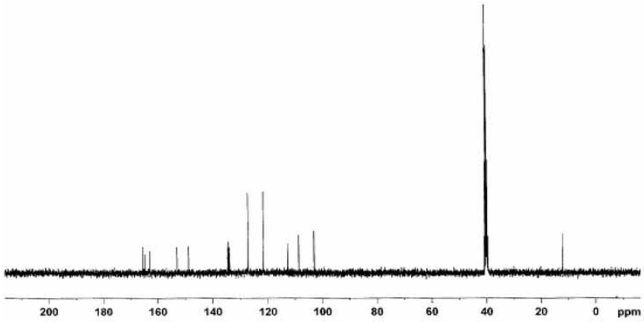


Figure 4. ^{13}C-NMR spectrum of Zn(II) complex.

3.4. *Magnetic properties*

The metal to ligand ratio of all the complexes was found to be 1 : 2 according to the elemental analyses. The magnetic moments of the complexes were measured at room temperature and are listed in table 1. The synthesized complexes are suggested to have the general structural formulas shown in figure 1. The Co(II), Ni(II) and Cu(II) complexes are paramagnetic, while the zinc(II) complex is diamagnetic, as expected for a d^{10} configuration. According to the magnetic moment calculations, Co(II), Ni(II) and Cu(II) have three, two and one unpaired electrons, respectively. The magnetic moments of the Co(II), Ni(II) and Cu(II) complexes at room temperature fall in the range 3.95, 2.90 and 1.82 BM respectively, which is characteristic for mononuclear, tetrahedral complexes [16, 24, 25]. In the Zn(II) complex, a tetrahedral structure is proposed and the diamagnetic behaviour was confirmed [16].

3.5. *Thermal studies*

Thermogravimetric (TG) curves for the complexes were obtained at a heating rate of 10°C min^{-1} with a 30 mL min^{-1} flowing nitrogen atmosphere over a temperature range of 20–800°C. Approximately 10 mg samples of the complexes were used in each case. The TG curves showed that thermal decomposition of the complexes takes place in two steps. It is possible that the different groups in the ligand lead to a decrease in the stability of all the complexes. Furthermore, electronegativity and atomic radius of the central metal atom also affect the thermal stability. Thermogravimetric studies of all the complexes showed no weight loss up to 150°C, indicating absence of water in the complexes. The inflation of the TG curves of all the complexes at a temperature under 600°C indicates the decomposition of the fully organic part of the chelate, leaving metallic oxide at the final temperature [7, 10]. In addition, the thermal stability of all complexes increases in the order: $\text{Cu} < \text{Ni} < \text{Co} < \text{Zn}$. When the complexes are heated to higher temperatures, they decompose to give oxides of the MO type [9, 12] (table 5).

4. Conclusions

Our group has been heavily engaged in synthesis of substituted oximes and their Schiff-base derivatives. Many Schiff-base derivatives, containing substituted oximes, were synthesized, characterized in detail and used for complexation with some transition metal salts. Functional groups, such as oxime, on the complexes have no effect. These functional groups are very far from the pendants taking part in the complexation. The Schiff-base ligand and its Co(II), Ni(II), Cu(II) and Zn(II) metal complexes were synthesized and characterized by elemental analyses, IR, ^{1}H- and ^{13}C-NMR spectra, magnetic susceptibility measurements and thermogravimetric analyses (TGA). All complexes are mononuclear and tetrahedral. According to results obtained from TGA, IR and elemental analyses, there are no lattice/coordinated water molecules in the complexes. For these complexes, additional analytical and physical data are given in tables 1–5. The suggested modes of coordination are shown in figure 1.

Acknowledgements

The support of the Management Unit of Scientific Research Projects of Firat University (FUBAP) under Research Project No. 874 is gratefully acknowledged.

References

[1] K. Arora, K.P. Sharma. *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 913 (2002).
[2] C. Çelik, M. Tümer, S. Serin. *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 1839 (2002).
[3] R. Ramesh, M. Sivagamasundari. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 899 (2003).
[4] R.C. Maurya, R. Verma, T. Singh. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 309 (2003).
[5] I. Sheikhshoaei. *J. Coord. Chem.*, **56**, 463 (2003).
[6] L.F. Lindoy, W.E. Moody, D. Taylor. *Inorg. Chem.*, **16**, 1962 (1977).
[7] H.A. Patwardhan, S. Gopinathan, C. Gopinathan. *Indian J. Chem.*, **16**, 224 (1978).
[8] R.C. Maurya, P. Patel, S. Rajput. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 817 (2003).
[9] E. Canpolat, M. Kaya. *J. Coord. Chem.*, **57**, 1217 (2004).
[10] S.A. Shama, H. Omara. *Spectrosc. Lett.*, **34**, 49 (2001).
[11] S. Satapathy, B. Sahoo. *J. Inorg. Nucl. Chem.*, **32**, 2223 (1970).
[12] K.P. Deepa, K.K. Aravindakshan. *Synth. React. Inorg. Met.-Org. Chem.*, **30**, 1601 (2000).
[13] E. Canpolat, M. Kaya. *J. Coord. Chem.*, **58**, 1063 (2005).
[14] M.A. Hundekar, D.N. Sen. *Indian J. Chem. Sec. A*, **23**, 477 (1984).
[15] A. Saxena, J.P. Tandon. *Polyhedron*, **3**, 681 (1984).
[16] R.C. Maurya, P. Patel, S. Rajput. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 817 (2003).
[17] J.D. Joshi, S. Sharma, G. Patel, J.J. Uora. *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 1729 (2002).
[18] C. Jayabakalakrishnan, R. Karvembu, K. Natarajan. *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 1099 (2002).
[19] R. Atkins, G. Brewer, E. Kokot, G.M. Mockler, E. Sinn. *Inorg. Chem.*, **24**, 127 (1985).
[20] J.C. Rasmussen, H. Toftlund, A.N. Nivorzhkin, J. Bourassa, P.C. Ford. *Inorg. Chim. Acta*, **251**, 291 (1996).
[21] S. Yamada, A. Takeuchi. *Coord. Chem. Rev.*, **43**, 187 (1982).
[22] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, Elsevier, Amsterdam (1997).
[23] M.R. Wagner, F.A. Walker. *Inorg. Chem.*, **22**, 3021 (1983).
[24] F.A. Cotton, G. Wilkinson. *Advanced Inoorganic Chemistry*, 5th Edn, p. 725, Wiley Interscience, New York (1988).
[25] M.M. Aboaly, M.M.H. Khalil. *Spectrosc. Lett.*, **34**, 495 (2001).