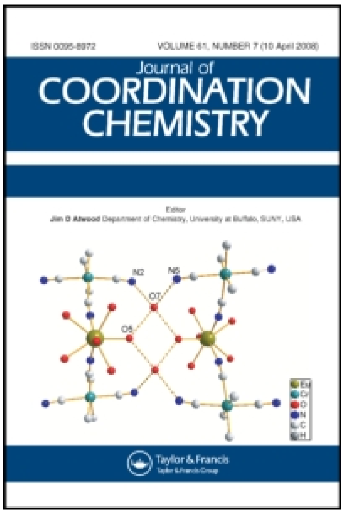


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and Characterization of Ni(II), Cu(II), Zn(II) and Cd(II) Complexes of a New Vic-Dioxime Ligand

Erdal Canpolat[a]; Mehmet Kaya[a]
[a] Department of Chemistry, Faculty of Arts and Sciences, University of Firat Elaziğ, Elaziğ, Turkey

To cite this Article Canpolat, Erdal and Kaya, Mehmet(2002) 'Synthesis and Characterization of Ni(II), Cu(II), Zn(II) and Cd(II) Complexes of a New Vic-Dioxime Ligand', Journal of Coordination Chemistry, 55: 12, 1419 — 1426
To link to this Article: DOI: 10.1080/0095897021000068834
URL: http://dx.doi.org/10.1080/0095897021000068834

J. Coord. Chem., 2002, Vol. 55, No. 12, pp. 1419–1426

Taylor & Francis
Taylor & Francis Group

SYNTHESIS AND CHARACTERIZATION OF Ni(II), Cu(II), Zn(II) AND Cd(II) COMPLEXES OF A NEW VIC-DIOXIME LIGAND

ERDAL CANPOLAT and MEHMET KAYA*

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

(Received 24 August 2001; Revised 5 February 2002; In final form 13 June 2002)

In this study, 1,2-dihydroxyimino–3,7-di-aza-9,10-*O*-α-methyl benzal decane (LH_2) was synthesized starting from 1,2-*O*-α-methyl benzal-4-aza-7-amino heptane (RNH_2) and antichloroglyoxime. With this ligand, complexes were synthesized using Ni(II) and Cu(II) salts with a metal : ligand ratio of 1 : 2. However, the reaction of the ligand with salts of Zn(II) and Cd(II) gave products with metal : ligand ratio of 1 : 1. Structures of the ligand and its complexes are proposed based on elemental analyses, IR, ^{13}C- and ^{1}H-NMR spectra, magnetic susceptibility measurements and thermogravimetric analyses (TGA).

Keywords: Vic-dioxime; Transition metal complexes; Nickel(II); Copper(II); Zinc(II); Cadmium(II)

INTRODUCTION

Vic-dioximes have great importance since they are used as chelating agents to form stable complexes with transition metals [1]. Recently, due to the increasing use of coordination compounds in analytical, biological, pigment, and medicinal chemistry, many investigators have studied the important role of complexes of vic-dioximes in coordination chemistry [2]. The synthesis of vic-dioximes and their various derivatives have been a subject of study for a long period of time [3–8]. Vic-dioximes and monooximes are amphoteric materials containing weakly acidic OH groups and basic C=N groups. The geometrical isomers of vic-dioximes and their derivatives, depending on the position of the OH groups in the molecule, are syn-, anti-, and amphi- structures [9], usually, the stability order of these is anti > amphi > syn configuration [10], but there are some exceptions [11,12]. The anti- and amphi- forms give two different colored complexes with the same metal but the syn-form does not form complexes [11].

Several mono- and disubstituted aminoglyoximes have been synthesized from anti-chloroglyoxime, anti-chlorophenylglyoxime or anti-dichloroglyoxime with corresponding amines and their transition metals complexes have been isolated [13–19]. The exceptional stability and unique electronic properties of these complexes can be

---

*Corresponding author. Tel.: 424 237 00 00 3405. Fax: 424 233 0062. E-mail: kayam08@yahoo.com

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897021000068834

attributed to their planar structure, which is stabilized by hydrogen bonding [20]. In the present article, we report the synthesis and characterization of a new vic-dioxime ligand and its complexes with Ni(II), Cu(II), Zn(II), and Cd(II) ions. As far as we know, this is the first report on this ligand.

EXPERIMENTAL

The preparation of anti-chloroglyoxime has been described previously [21]. All the reagents used were purchased from Merck or Fluka or Sigma Company and are chemically pure.

Elemental analyses (C, H, N) were performed on a LECO-932 CHNSO elemental analysis apparatus. IR spectra were recorded on a Mattson 1000 FTIR Spectrometer as KBr pellets and NaCl cell. ^{13}C- and ^{1}H-NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR and a Jeol FX 90 Q FT-NMR spectrometers. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20°C) using $Hg[Co(SCN)_2]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [22]. The metal contents of the complexes were determined with an Ati Unicam (Model 929) atomic absorption spectrophotometer in solutions prepared by decomposition of the compounds in conc. HCl and conc. HNO_3 (3 : 1) solution followed by dilution in water. TGA curves were recorded on a Shimadzu TG-50 thermobalance.

Synthesis of 1-Chloro-2,3-*O*-α-methyl benzal propane (1)

15–20 drops of borontrifluoride etherate, were added dropwise to 60.05 g (500 mmole) of purified acetophenone. Then 23.15 g (250 mmole) of epichlorohydrine was added dropwise to the mixture at 15–20°C while it was stirred. After addition of epichlorohydrine, the reaction mixture was further stirred for 5 h at 20°C. The liquid product was distilled at 88–90°C and 4 mm-Hg in vacuum. Characteristic IR bands (NaCl cell, cm^{-1}) and ^{1}H-NMR bands (DMSO-d_6, δ ppm, 90 MHz) are in Tables I and II. Characteristic ^{13}C-NMR bands (DMSO-d_6, δ ppm, 90 MHz): 125.08 (C_1), 131.02 (C_2), 126.04 (C_3), 131.65 (C_4), 28.90 (C_5), 110.11 (C_6), 68.07 (C_7), 76.03 (C_8), 46.00 (C_9).

TABLE I Characteristic IR bands (cm^{-1}) of the ligand and complexes as KBr pellets

Compounds	*υ(O–H)*	*υ(N–H)*	*υ(N–O)*	*υ(C=N)*	*Others*
R–Cl (**1**)	–	–	–	–	760 υ(C–Cl)
R–NH_2 (**2**)	–	3380	–	–	1090 δ(C–O–C)
LH_2 (**3**)	3391–3259	3364	977	1639	–
$[(LH)_2Ni]$	–	3320	961	1604	1736 δ(O–H$\cdots$O)
$[(LH)_2Cu]$	–	3340	965	1610	1729 δ(O–H$\cdots$O)
$[(LH)Cl(H_2O)Zn]$	3238	3380	985	1630	3430 (H_2O)
$[(LH)Cl(H_2O)Cd]$	3236	3370	990	1625	3440 (H_2O)

$\nu(C\text{–}H)_{Aliphatic} = 2992\text{–}2876$, $\nu(C\text{–}H)_{Aromatic} = 3088\text{–}3040$, cm^{-1} for all the compounds.

TABLE II ^{1}H-NMR spectra of the ligand and the complexes in DMSO-d_6 in δ (ppm)

Compounds	*R–Cl* (**1**)	*R–NH$_2$* (**2**)	*LH$_2$* (**3**)	*[(LH)$_2$Ni]*	*[(LH)Cl(H$_2$O)Zn]*	*[(LH)Cl(H$_2$O)Cd]*
N–H^a	–	2.05(3H)^s	6.40–5.90(2H)^s	6.31–6.05(4H)^s	6.42–5.94(2H)^s	6.43–5.95(2H)^s
N–CH$_2$^{b}	–	2.93–2.51(6H)^m	3.33–2.47(6H)^m	3.52–2.81(12H)^m	3.46–2.24(6H)^m	3.44–2.25(6H)^m
–CH$_2$–	–	1.67(2H)^m	1.80–1.70(2H)^m	1.90–1.60(4H)^m	1.81–1.72(2H)^m	1.81–1.72(2H)^m
–CH$_3$	1.71(3H)^s	1.69(3H)^s	1.64(3H)^s	1.65(6H)^s	1.66(3H)^s	1.66(3H)^s
C–H$_{arom.}$	7.72–7.20(5H)^m	7.56–7.18(5H)^m	7.70–7.11(5H)^m	8.11–7.54(10H)^m	7.82–7.17(5H)^m	7.92–7.17(5H)^m
–CH–O	4.54–4.23(1H)^m	4.49–3.89(1H)^m	4.08–3.78(1H)^m	4.23–3.94(2H)^m	3.93–3.83(1H)^m	4.03–3.84(1H)^m
–CH$_2$–O	4.17–3.94(2H)^m	3.82–3.60(2H)^m	3.91–3.62(2H)^m	4.11–3.85(4H)^m	3.96–3.79(2H)^m	3.96–3.77(2H)^m
N–OH^{a,b}	–	–	9.89–9.41(2H)^s	–	9.93–9.47(1H)^s	9.91–9.45(1H)^s
N=C–H	–	–	7.73(1H)^s	8.04(2H)^s	8.41(1H)^s	8.50(1H)^s
(O–H···O)	–	–	–	14.80(2H)^s	–	–
H$_2$O	–	–	–	–	3.33(2H)^s	3.33(2H)^s
CH$_2$–Cl	3.50–3.03(2H)^m	–	–	–	–	–

^{s}singlet; ^{m}multiplet; ^{a}deuterium exchangeable; ^{b}broad bands.

Synthesis of 1,2-*O*-α-Methyl benzal-4-aza-7-aminoheptane (2)

In a reaction flask, a $CaCl_2$ drying tube and a dropping funnel, 16.74 mL (200 mmole) of 1,3-diamino propane, 6.95 mL (50 mmole) of triethylamine and 80 mL of absolute toluene were mixed and heated to 80°C. To this mixture, a solution of 10.66 g (50 mmole) of 1-chloro-2,3-*O*-α-methyl benzal propane (**1**) in 40 mL toluene was added dropwise, refluxed for 45 h and cooled to room temperature. The mixture was filtered and the filtrate evaporated to remove the excess 1,3-diamino propane. The compound was distilled at 175–180°C at 3 mm-Hg in vacuum. Characteristic IR bands (NaCl cell, cm^{-1}) and ^1H-NMR bands (DMSO-d_6, δ ppm, 90 MHz) are in Tables I and II. Characteristic ^{13}C-NMR bands (DMSO-d_6, δ ppm, 90 MHz): 125.88 (C_1), 128.03 (C_2), 126.72 (C_3), 129.07 (C_4), 28.89 (C_5), 110.64 (C_6), 67.81 (C_7), 75.62 (C_8), 52.67 (C_9), 48.26 (C_{10}), 41.11 (C_{11}), 34.53 (C_{12}).

Synthesis of the Ligand LH_2 (3)

A solution of $NaHCO_3$ 3.39 g (40 mmole) was added to a solution of 1,2-*O*-α-methyl benzal-4-aza-7-aminoheptane 5.04 g (20 mmole) in 50 mL absolute ethanol, then a solution of anti-chloroglyoxime 2.47 g (20 mmole) in 40 mL absolute ethanol, which is synthesized by the method described previously [21] was added dropwise to the mixture at room temperature over 5 h, the mixture was stirred on a water bath at 60–70°C for 10 h. The mixture was filtered and excess ethanol was removed by evaporation. The product was crystallized by addition of diethyl ether. Obtained product was filtered off, washed with diethyl ether and water several times and dried in vacuum for 30 h. The purified ligand (LH_2) is soluble in common solvents such as C_3H_6O, $CHCl_3$, DMSO, and DMF. Characteristic IR bands (KBr pellet, cm^{-1}) and ^1H-NMR bands (DMSO-d_6, δ ppm, 400 MHz) are shown in Tables I and II. Characteristic ^{13}C-NMR bands (DMSO-d_6, δ ppm, 400 MHz): 129.52 (C_1), 128.31 (C_2), 130.01 (C_3), 131.11 (C_4), 109.60 (C_6), 25.72 (C_5), 76.08 (C_7), 82.4 (C_8), 52.88 (C_9), 46.97 (C_{10}), 28.25 (C_{11}), 37.01 (C_{12}), 150.70 (C_{13}), 145.30 (C_{14}).

Synthesis of the Ni(II) and Cu(II) Complexes

A quantity of 0.337 g (1 mmole) of the ligand was dissolved in 10 mL absolute methanol. A solution of 0.5 mmole metal salts [$NiCl_2 \cdot 6H_2O$ (0.120 g) and $CuCl_2 \cdot 2H_2O$ (0.087 g)] in 5 mL absolute methanol was added dropwise with continuous stirring. The apparent pH of the solutions was adjusted to 5.0–5.5 by the addition of a 1 M NaOH solution in methanol. Every mixture was stirred 1 h more at 30°C, and the complexes thus precipitated were kept on a water bath for 35 min at 40°C, filtered and the precipitate washed with diethyl ether and water. The precipitate was dissolved in methanol and precipitated in diethyl ether (1/10) and dried in vacuum at 60°C. The complexes are soluble in THF, DMF, and DMSO. Characteristic IR bands (KBr pellet, cm^{-1}) and ^1H-NMR peaks (DMSO-d_6, δ ppm, 400 MHz) are shown in Tables I and II.

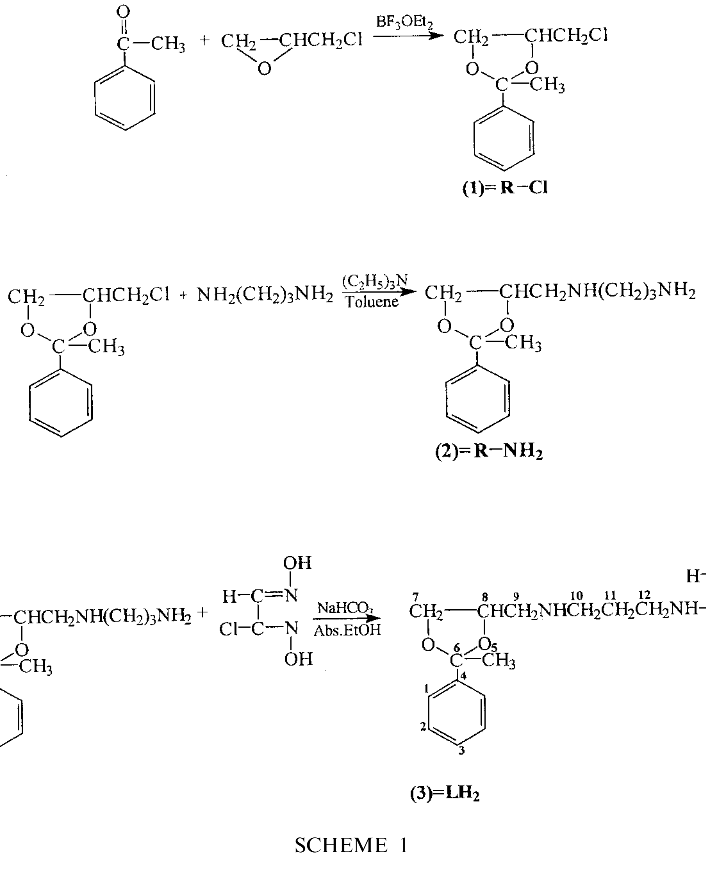
Synthesis of the Zn(II) and Cd(II) Complexes

A solution of 0.338 g (1 mmole) of the ligand was dissolved in 10 mL absolute methanol. A solution of 1 mmole metal salts [$ZnCl_2$ (0.138 g), $CdCl_2 \cdot H_2O$ (0.203 g) in 10 mL absolute methanol was added dropwise with continuous stirring. The apparent pH of the solutions was adjusted to 5.0–5.5 by the addition of 1 M NaOH solution in methanol. The mixture was further stirred on a water bath at 50°C for 2 h in order to complete precipitation. The precipitate was filtered, washed with diethyl ether and dried in vacuum at 60°C. The complexes are soluble in acetonitrile, DMF, and DMSO. Characteristic IR bands (KBr pellet, cm^{-1}) and ^1H-NMR peaks (DMSO-d_6, δ ppm, 400 MHz) are shown in Tables I and II.

RESULTS AND DISCUSSION

The new ligand, 1,2-dihydroxyimino-3,7-di-aza-9,10-*O*-α-methyl benzal decane (LH_2) was prepared in a three-stage process as shown in Scheme 1. The characterization data of (**1**) are given in the experimental section and of (**2**) in the experimental section and Tables I–IV. The structure of LH_2 was determined by a combination of elemental analysis, IR, ^1H- and ^{13}C-NMR spectra and thermogravimetric analyses (TGA).

In the IR spectrum of (**2**), the characteristic bands are at 3380 cm^{-1}, which are assigned to υ(–NH) and υ(–NH_2) groups, and at 1090 cm^{-1}, assigned to the δ(C–O–C) group. There is no C–Cl band in the IR spectrum of (**2**). In the ^1H-NMR spectra of (**2**), a peak appears at 2.51–2.93 ppm for (N–CH_2–) and 2.05 ppm for (–NH and –NH_2) as



SCHEME 1

TABLE III TGA data and elemental analyses of the ligand and the complex

Compounds	*First step* °C	*Second step* °C	*W. Loss* %	*Residue*	*Elem. analyses* % *calculated (found)*		
					C	*H*	*N*
LH_2	98–460	460–700	99.08	–	57.12 (56.81)	7.21 (6.86)	16.66 (17.05)
$[(LH)_2Ni]$	123–476	476–605	89.76	NiO	52.68 (53.04)	6.37 (5.98)	15.36 (15.01)
$[(LH)_2Cu]$	152–340	340–652	89.17	CuO	52.33 (51.94)	6.33 (5.96)	15.26 (14.95)
$[(LH)Cl(H_2O)Zn]$	117–324	324–628	85.07	ZnO	42.30 (41.92)	5.56 (5.18)	12.34 (11.95)
$[(LH)Cl(H_2O)Cd]$	112–335	335–660	74.39	CdO	38.33 (37.96)	5.04 (4.65)	11.18 (10.81)

TABLE IV The formulas, formula weights, colors, melting points, yields and magnetic susceptibilities of the ligand and the complexes

Compounds	*f.w.* g/mol	*Color*	*m.p.* °C	*yield* %	μ_{eff} B.M
R–Cl (**1**) $C_{11}H_{13}O_2Cl$	212.50	Colorless	–	78	–
R–NH_2 (**2**) $C_{14}H_{22}N_2O_2$	250.00	Colorless	–	63	–
LH_2 (**3**) $C_{16}H_{24}N_4O_4$	336.44	White	120	60	–
$[(LH)_2Ni]$ $C_{32}H_{46}N_8O_8Ni$	729.55	Tile red	223	57	dia
$[(LH)_2Cu]$ $C_{32}H_{46}N_8O_8Cu$	734.41	Green	198	51	1.65
$[(LH)Cl(H_2O)Zn]$ $C_{16}H_{25}N_4O_5ClZn$	454.29	Yellow	193	65	dia
$[(LH)Cl(H_2O)Cd]$ $C_{16}H_{25}N_4O_5ClCd$	501.31	Yellow	227	62	dia

broad peak. The N–H and N–H_2 resonances disappeared upon the addition of D_2O. Observation of the (–O–CH_2–) peaks at 3.60 and 3.82 ppm, as multiplets in each case, indicates that the compound undergoes *cis–trans* isomerization [6,18,23] (Table II). The isomer ratio was found to be 51% *cis* and 49% *trans* from the ^{1}H-NMR and ^{13}C-NMR data.

The characterization of the ligand LH_2 was carried out by elemental analyses, IR, ^{1}H- and ^{13}C-NMR and TGA. In the IR spectrum of LH_2, characteristic peaks appear at 3364 cm^{-1} υ(N–H), 3391–3259 cm^{-1} υ(O–H), 1639 cm^{-1} υ(C=N), 1090 cm^{-1} δ(C–O–C), and 977 cm^{-1} υ(N–O) as expected for a substituted vic-dioxime [24]. In the ^{1}H-NMR spectrum, since the OH protons of the oxime are equivalent in the (*E*,*E*) form, two peaks were observed for the protons [6,24]. In the LH_2 chemical shifts of =N–OH protons were observed at 9.89 and 9.41 ppm as singlets. Also, chemical shifts of N–H protons were observed at 6.40 and 5.90 ppm. These bands are easily identified by deuterium exchange.

The C–H protons adjacent to the oxime groups were observed at about 7.73 ppm. This value is in agreement with that reported [5,25]. In the ^{13}C-NMR, carbon resonances of dioxime groups (C_{13} and C_{14}) were observed at 150.70 and 145.30 ppm as expected for (*E*,*E*) dioxime [6,26]. The most characteristic signal for C_5(ipso), is at 109.60 ppm.

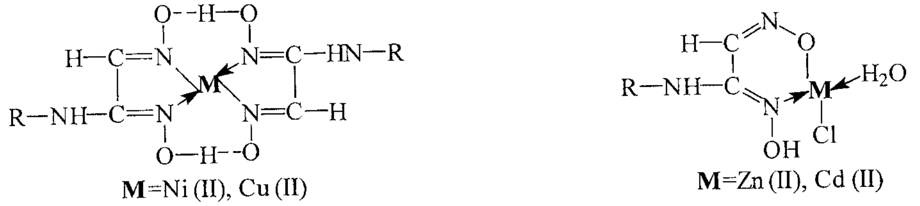


FIGURE 1 Suggested structure of the square-planar and tetrahedral complexes of the ligand LH_2.

The ligand LH_2 has been synthesized by the reaction of compound (**2**) and anti-chloroglyoxime. Excess sodium bicarbonate was used to neutralize the HCl liberated in the reaction.

The red color for the Ni(II) complex of the LH_2 indicates that the ligand is in the (*E*,*E*) form [27], the antiform of the ligand.

The mononuclear complexes of LH_2 with Ni(II) and Cu(II) have a metal : ligand ratio of 1 : 2. The infrared band observed near $1639\,cm^{-1}$, assigned to the υ(C=N) frequency in the free ligand, is shifted to lower frequencies after complexation (1610–$1604\,cm^{-1}$) due to *N*,*N*-metal coordination [3,13,28]. Also the band observed at $977\,cm^{-1}$ in the free ligand assigned to the υ(N–O), is shifted to lower frequency after complexation (Table I). On the other hand, a band not seen in the free ligand which is assigned to (O···H–O) [28,29] is observed at $1736\,cm^{-1}$ for Ni(II), $1729\,cm^{-1}$ for Cu(II). The absorptions indicate that the oxime group takes part in complexation.

In the ^{1}H-NMR spectrum of the Ni(II) complex, there are no OH peaks as expected for the formula in Fig. 1, but there is peak at 14.80 ppm for Ni(II) which is assigned to the (O···H–O) [25,28]. The Ni(II) complex is diamagnetic as expected for a square planar d^8 electronic configuration. Whereas the Cu(II) complex is paramagnetic and its magnetic susceptibility value is 1.65 B.M. For these complexes, additional analytical data are given in Table I–IV. These results indicate a square-planar geometry for the Ni(II) and Cu(II) complexes. The suggested structures of the complexes are shown in Fig. 1.

The Zn(II) and Cd(II) complexes have a 1 : 1 metal : ligand ratio according to the elemental analyses and the ligand is coordinated only by the N, O atoms of the vic-dioxime [30]. Therefore in the IR spectrum of the Zn(II) and Cd(II) complexes, the stretching band of υ(C=N) appearing at $1639\,cm^{-1}$ in H_2L is shifted to $1630\,cm^{-1}$ for Zn(II) and $1625\,cm^{-1}$ for Cd(II). At the same time, the υ(N–O) band at $977\,cm^{-1}$ in the free ligand was moved to higher frequency (according to H_2L) of *ca.* 10–$15\,cm^{-1}$ after complexation [31,32] (Table I). These suggest that the ligand is coordinated to metal through the nitrogen and oxygen donors. A chloride ion and a water molecule are also coordinated to metal ions. A broad band at 3430–$3440\,cm^{-1}$ was observed in the spectra of the complexes, due to a coordinated water molecule in the complexes.

In the ^{1}H-NMR spectrum, the Zn(II) and Cd(II) complexes show the presence of a coordinated water molecule at 3.33 ppm [5,30] and there are no (O···H–O) peaks as expected for the complexes but there is a resonance at 9.45–9.93 ppm which is assigned to (–OH). The suggested structures of the complexes are shown in Fig. 1. The Zn(II) and Cd(II) complexes were characterized by IR, NMR, TGA, and elemental analyses indicating the geometry of complexes to be tetrahedral [3,31].

TGA data of LH_2 and its metal complexes of Ni(II), Cu(II), Zn(II), and Cd(II) are given in Table III. The decomposition temperature and the weight losses of the complexes were calculated from the TGA data. The ligand LH_2 is stable up to 98°C and its decomposition starts at 98°C and is completed at 700°C. As can be seen in the TGA data, all the complexes and the ligand decompose in two steps at different temperature ranges. All these complexes undergo complete decomposition to the corresponding metal oxides, NiO, CuO, ZnO, CdO [33,34].

Acknowledgments

We gratefully acknowledge the financial support of Firat University Research Fund (Project No:FÜNAF-280).

References

[1] A. Chakravorty (1974). *Coord. Chem. Rev.*, **13**, 1.
[2] M.E.B. Jones, D.A. Thornton and R.F. Webb (1961). *Macromol. Chem.*, **49**, 62.
[3] A. Gül and Ö. Bekaroğlu (1983). *J. Chem. Soc. Dalton Trans.*, 2537.
[4] C. Grundmann, V. Mini, J.M. Dean and H.D. Frommeld (1965). *Liebigs Ann. Chem.*, **687**, 191.
[5] G. İrez and Ö. Bekaroğlu (1983). *Synth. React. Inorg. Met.-Org. Chem.*, **13**, 781.
[6] H.İ. Uçan and R. Mirzaoğlu (1990). *Synth. React. Inorg. Met.-Org. Chem.*, **20**, 437.
[7] İ. Karataş, G. İrez, M. Sezgin, H.İ. Uçan and A.D. Bedük (1991). *Synth. React. Inorg. Met.-Org. Chem.*, **21**, 1031.
[8] H.İ. Uçan and İ. Karataş (1991). *Synth. React. Inorg. Met.-Org. Chem.*, **21**, 1083.
[9] A.N. Nesmeyanow and N.A. Nesmeyanow (1981). *Fundamentals of Organic Chemistry*, 2nd Ed., **111**, 167. English Translation, Mir Publishers, Moscow.
[10] O. Piloty and H. Steinbock (1902). *Chem. Ber.*, **35**, 3113.
[11] J.V. Burokovich, A.M. Lore and G.P. Vollp (1971). *J. Coord. Chem.*, **36**, 1.
[12] S. Serin and Ö. Bekaroğlu (1983). *Z. Anog. Allgem. Chem.*, **496**, 192.
[13] E. Özcan and R. Mirzaoğlu (1988). *Synth. React. Inorg. Met.-Org. Chem.*, **18**, 559.
[14] Y. Gök and H. Kantekin (1990). *Chem. Ber.*, **123**, 1479.
[15] Y. Gök, S.Z. Yıldız and M. Tüfekçi (1993). *J. Coord. Chem.*, **28**, 237.
[16] A.S. Abusaimleh, P.J. Chimiclewski, P.R. Warburton, L. Morales, N.A. Stephenson and D.H. Busch (1991). *J. Coord. Chem.*, **23**, 91.
[17] Y. Gök, H. Kantekin and İ. Değirmencioğlu (1993). *Polyhedron*, **12**, 2097.
[18] E. Taş, A. Çukurovali and M. Kaya (1999). *J. Coord. Chem.*, **48**, 411.
[19] A. Çukurovalı, E. Taş and M. Kaya (1998). *Synth. React. Inorg. Met.-Org. Chem.*, **28**(3), 463.
[20] İ. Gürol, V. Ahsen and Ö. Bekaroğlu (1992). *J. Chem. Soc. Dalton Trans.*, 2283.
[21] G. Ponzio and F. Baldrocco (1930). *Gazz. Chim. Ital.*, **60**, 415.
[22] A. Earnshaw (1968). *Introduction to Magnetochemistry*, p. 4. Academic Press, London.
[23] J.C. Soutif, L. Ouchatar, D. Courret and J.C. Brosse (1986). *Macromol. Chem.*, **187**, 561.
[24] H. Kamogawa, Y. Haramoto, T. Nakazawa, H. Sugiura and M. Nanasawa (1981). *Bull. Chem. Soc. Jpn.*, **54**, 1577.
[25] V. Ahsen, F. Gökçeli and Ö. Bekaroğlu (1987). *J. Chem. Soc. Dalton Trans.*, 1827.
[26] E. Taş, A. Çukurovalı and M. Kaya (1999). *J. Coord. Chem.*, **46**, 479.
[27] S.B. Pedersen and E. Larsen (1973). *Acta Chemica Scandinavica*, **27**, 3291.
[28] A. Nakamura, A. Konushi and S. Otsuka (1979). *J. Chem. Soc. Dalton Trans.*, 488.
[29] H.C. Sevindir, R. Mirzaoğlu, E. Özcan, S. Kurtul and E. Güler (1994). *Synth. React. Inorg. Met.- Org. Chem.*, **24**, 613.
[30] B. Mercimek, G. İrez, M.A. Deveci, A.D. Bedük, N. Sarıkavaklı and H.İ. Uçan (1995). *Macromolecular Reports*, **A 32**, 1199.
[31] B. Mercimek, M.A. Özler, G. İrez and Ö. Bekaroğlu (1999). *Synth. React. Inorg. Met.-Org. Chem.*, **29**(3), 513.
[32] C. Bank and Ö. Bekaroğlu (1983). *Synth. React. Inorg. Met.-Org. Chem.*, **13**(8), 1047.
[33] E. Dubler and G. Hanggi (1994). *Thermochim. Acta*, **124**, 981.
[34] M.L. Dahar and O. Singh (1991). *Thermochim. Acta*, **191**, 285.