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Synthesis of (2-Hydroxo-5-Chlorophenylaminoisonitrosoacetyl)phenyl Ligands and Their Complexes: Spectral, Thermal and Solvent-Extraction Studies[1]

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Abstract—Four different types of new ligands Ar[COC(NOH)R]$_n$ (Ar=biphenyl, $n = 1$ H_2L^1; Ar=biphenyl, $n = 2$ H_4L^2; Ar=diphenylmethane, $n = 1$ H_2L^3; Ar=diphenylmethane, $n = 2$ H_4L^4; R=2-amino-4-chlorophenol in all ligands) have been obtained from 1 equivalent of chloroketooximes Ar[COC(NOH)Cl]$_n$ (HL^1–H_2L^4) and 1 equivalent of 2-amino-4-chlorophenol (for H_2L^1 and H_2L^3) or 2 equivalent of 2-amino-4-chlorophenol (for H_4L^2 and H_4L^4). (Mononuclear or binuclear cobalt(II), nickel(II), copper(II) and zinc(II) complexes were synthesized with these ligands.) These compounds have been characterized by elemental analyses, AAS, infra-red spectra and magnetic susceptibility measurements. The ligands have been further characterized by ^{1}H NMR. The results suggest that the dinuclear complexes of H_2L^1 and H_2L^3 have a metal:ligand ratio of 1:2; the mononuclear complexes of H_4L^2 and H_4L^4 have a metal:ligand ratio of 1:1 and dinuclear complexes H_4L^2 and H_4L^4 have a metal:ligand ratio of 2:1. The binding properties of the ligands towards selected transition metal ions (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Pb^{II}, Cd^{II}, Hg^{II}) have been established by extraction experiments. The ligands show strong binding ability towards mercury(II) ion. In addition, the thermal decomposition of some complexes is studied in nitrogen atmosphere.

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INTRODUCTION

The chemistry of transition metal complexes with α-dioxime ligands has been well studied and is the subject of a lot of paper [1–7]. Yet little was known about the coordination chemistry of ketooxime ligands until last years, reports on these keto oxime ligands are rather few [8–12]. Our interest in this area evolved from previous studies of terdentate ligands and a desire to prepare mono and binuclear complexes.

In recent years, the design and synthesis of binuclear or polynuclear transition metal complexes has gained sustained interest. Several types of ligand system, which can bind two metal ions in close proximity have been used as biomimetic studies of binuclear metalloenzyme and metalloproteins due to their interesting catalytic properties, their ability to stabilize unusual oxidation states and possibilities for magnetic interaction between two metal ions [13–16]. These complexes have found many applications as catalysts for specific purposes, as mimics for metallobiomolecules, and in investigations concerning the mutual influence of two or more metal centers on the electronic, magnetic and electrochemical properties of such closely spaced metal centers [17–20].

The new extractants with high selectivity for metal ions are of interest for analytical purposes as well as for the removal, separation and concentration of metallic species, broadening its applications in the recycling of resources in the field of metallurgy and waste water treatment as demand increases for the development of new approaches to resolve the various problems presented. Some metals such as Cr^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, Ag^{I}, Hg^{II}, Pb^{II}, are recognized as highly toxic for many biological systems [21, 22]. Thus, the determination of trace amounts of these metals is becoming increasingly important because of the increased interest in environmental pollution. They are not degradable, such metals can accumulate in the environment and produce toxic effects in plants and animals even at very low concentrations. Therefore, separation of these trace metals is vital due to the potential health and ecological hazard. There are many processes, such as solvent extraction, ion exchange, adsorption and complexing that can be used for the removal of metals from wastewaters. For this purpose, many oxime derivatives have been synthesized and their extraction properties investigated by solvent extraction [23–27].

In the previous studies, substituted 4,4'-bis(alkylaminoisonitrosoacetyl)diphenylmethanes [9] and 4-(alkylaminoisonitrosoacetyl)biphenyls and metal chelates has been isolated [12]. These ligands have a tendency to form a dimeric or polymeric complexes. But the thermal characterization of the metal com-

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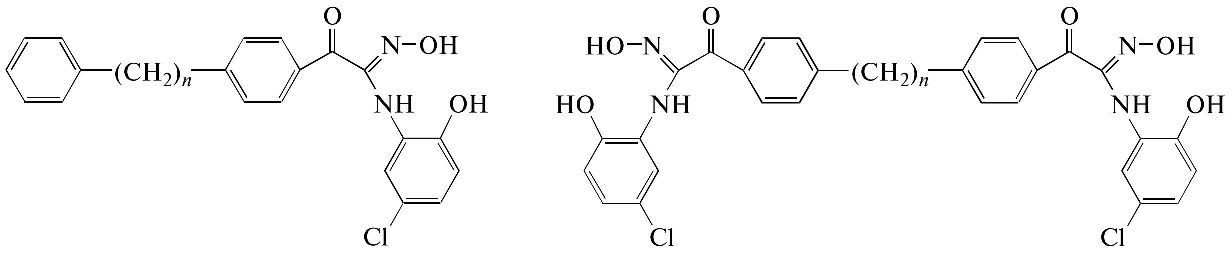

H_2L^1 ($n = 0$), H_2L^3 ($n = 1$) H_4L^2 ($n = 0$), H_4L^4 ($n = 1$)

Fig. 1. Structure of the ligands (H_2L^1–H_4L^4).

plexes and solvent-extraction studies of these kind of ligands, have not been reported earlier. In this study, as part of a systematic study, we describe the synthesis, spectroscopic properties, solvent-extraction studies and thermal decompositions of four new (alkylaminoisonitrosoacetyl)phenyl ligands using same amine (2-amino-4-chlorophenol) (Fig. 1) and their the mononuclear and binuclear Co(II), Ni(II), Cu(II) and Zn(II) complexes.

EXPERIMENTAL

Materials and Methods

All solvents, 2-amino-4-chlorophenol and metal salts [$Co(AcO)_2 \cdot 4H_2O$, $Ni(AcO)_2 \cdot 4H_2O$, $Cu(AcO)_2 \cdot H_2O$, $Zn(AcO)_2 \cdot 2H_2O$] used for the synthesis and physical measurements were of reagent grade and used as received. The starting materials (chloroketones) were prepared by the Friedel-Crafts acylation reaction of biphenyl and diphenylmethane with chloroacetyl chloride in 1 : 1 and 1 : 2 molar ratio according to literature procedures [28–30]. Chloroketooximes [30, 31] were also prepared by following the literature methods.

Elemental analyses of the ligands and their complexes were obtained on a LECO 932 CHNS analyzer. ^{1}H NMR spectra of the ligands were obtained by the Laboratories of the Scientific and Technical Research Council of Turkey (TUBITAK) using TMS as the internal reference in $CDCl_3$ or deuterated DMSO. ^{1}H NMR spectra of the complexes could not be determined, since these compounds are not totally soluble in organic solvents. Infrared spectra were recorded as KBr pellet on a Shimadzu IRPrestige-21 FT-IR Spectrophotometer in the range 4000–400 cm^{-1}. Atomic absorption spectrophotometer used to determine metal ion concentration in the aqueous phase was Perkin Elmer 800 AAS. The spectrophotometric measurements were carried out with a Perkin Elmer λ 20 U.v.-vis. Spectrometer. Magnetic properties were determined by means of a Sherwood Scientific MX1 Model Gouy Magnetic Susceptibility Balance. The thermogravimetric analysis (TG and DTG) was carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) with a heating rate of 10°C min^{-1} using a Perkin Elmer Pyris 1 TGA thermal analyzer in the Central Laboratory at METU (Ankara-Turkey). Melting points were measured on a IA 9100 Electrothermal apparatus.

Preparation of the Ligands

All ligands were prepared by a similar methods. First, chloroketooximes (10 mmol, 2.60 g HL^1, 3.65 g H_2L^2, 2.74 g HL^3, 3.79 g H_2L^4) were dissolved in EtOH (40 cm^3) and the mixture was cooled—5°C. Then 2-amino-4-chlorophenol (11 mmol, 1.58 g for HL^1 and HL^3; 22 mmol, 3.16 g for H_2L^2 and H_2L^4) and Et_3N (10 mmol, 1.38 cm^3 for HL^1 and HL^3; 20 mmol, 2.77 cm^3 for H_2L^2 and H_2L^4) and in MeOH (20 cm^3) were added dropwise to solutions of chloroketooximes over 15 min with cooling. Precipitation and colour change were observed in the reaction medium immediately. After that period, the reaction mixture was stirred 2 h at the same temperature. Then it was allowed to stir at ambient temperature for 2 h. The powder (resulted) from the reaction is insoluble in ethanol and this was filtered off, washed aqueous sodium bicarbonate (1%), distilled water, ethanol and dried on P_2O_5.

Preparation of Metal Complexes

All complexes were prepared by similar methods. A solution of equivalent amount of metal salt in ethanol (20 cm^3) was added to a hot solution of ligand (H_2L^1–H_4L^4) [1 mmol, 0.367 g H_2L^1, 0.579 g H_4L^2, 0.381 g H_2L^3, 0.593 g H_4L^4] in ethanol (50 cm^3) and was continuously stirred. A distinct change in colour and decrease in pH (pH = 3.0–3.5) was observed, an equivalent amount of ethanolic solution of KOH (0.1 M) was added dropwise to adjust a pH value of about 5–6, solid product precipitated. The complex precipitated, was kept on a water bath at 80°C for one hour in order to complete the precipitation. The mixture was cooled to ambient temperature and the solid product was filtered off. Then it was washed hot water, ethanol and dried on P_2O_5.

The colours, yield, melting points, elemental analyses and IR data of complexes and ligands are given in Table 1 and 3. ^{1}H NMR data of ligands are given in Table 2.

Solvent Extraction

The extraction properties of the Schiff base ligands (H_2L^1, H_4L^2, H_2L^3 and H_4L^4) were investigated under liquid–liquid phase and neutral conditions using selected metal picrates (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Pb^{II}, Cd^{II}, Hg^{II}) as substrates and measuring by U.v.-vis. measurements the amounts of metal picrate in the aqueous phase before and after treatment with the compounds. About 10 cm^3 of 2×10^{-5} M aqueous picrate solution and 10 cm^3 of 1×10^{-3} M solution of ligand in $CHCl_3$ were vigorously agitated in a stoppered plastic tube with a mechanical shaker for 2 min, then magnetically stirred at 25°C for 1 h, and finally left standing for an additional 30 min. The concentration of the picrate ion remaining in the aqueous phase was then determined spectrophotometrically. Blank experiments showed that no picrate extraction occurred in the absence of ligand. Metal picrates were prepared by successive addition of a 1×10^{-2} M metal nitrate solution to 2×10^{-5} M aqueous picric acid solution and shaken at 25°C for 1 h. These metal picrates (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Pb^{II}, Cd^{II}, Hg^{II}) were measured by U.v.-vis. using maximum wavelength 352 nm. For each combination of host and metal picrate, the picrate extraction was conducted on three different samples and the average value of percent picrate extracted, was calculated. In the absence of host, a blank experiment, no metal ion picrate extraction was detected. The extractability was calculated by using the equation below:

Extractability(%) = $[(A_0 - A) / A_0] \times 100$ where A_0 is the absorbance in the absence of ligand. A denotes the absorbance in the aqueous phase after extraction.

RESULTS AND DISCUSSION

Chloro ketones (1) were prepared from chloroacetyl chloride with biphenyl and diphenylmethane in presence of aluminium chloride according to Friedel-Crafts acylation [28–30]. Chloro ketooximes (2) were obtained from the reaction of (1) with alkyl nitrite in presence of dry HCl gase [30, 31]. 4 and 4,4'-(2-hydroxo-5-chlorophenylaminoisonitrosoacetyl)phenyl ligands (H_2L^1–H_4L^4) were prepared by a condensation reaction of (2) with 2-amino-4-chlorophenol (Scheme 1). 4-(2-hydroxo-5-chlorophenylaminoisonitrosoacetyl)biphenyl [H_2L^1], 4,4'-(2-hydroxo-5-chlorophenylaminoisonitrosoacetyl)biphenyl [H_4L^2], 4-(2-hydroxo-5-chlorophenylaminoisonitrosoacetyl)diphenylmethane [H_2L^3], and 4,4'-(2-hydroxo-5-chlorophenylaminoisonitrosoacetyl)diphenylmethane [H_4L^4] were prepared. Analytical and spectroscopic data of the ligands (H_2L^1–H_4L^4) clearly confirmed the success of the condensation reaction.

$$\mathrm{Ar[COC(NOH)Cl]}_n + x\mathrm{RNH_2} \longrightarrow \mathrm{Ar[COC(NOH)NHR]}_n + x\mathrm{HCl}$$

Ar = biphenyl, $n = 1, x = 1$ H_2L^1 Ar = biphenyl, $n = 2, x = 2$ H_4L^2

Ar = diphenylmethane, $n = 1, x = 1$ H_2L^3 Ar = diphenylmethane, $n = 2, x = 2$ H_4L^4

RNH_2 = 2-amino-4-chlorophenol

Scheme. Synthesis of (alkylaminophenylisonitrosoacetyl)phenyles (H_2L^1–H_4L^4).

The mononuclear or binuclear metal complexes formed between these ligands and metal salts. The structural formula of the ketooxime ligands and their complexes was verified by elemental analyses, ^{1}H NMR, IR spectral data and elemental analyses data. Analytical results of the ligands and their complexes are listed in Table 1. All compounds were found to be nonhygroscopic and stable in air.

^{1}HNMR Spectra

The ^{1}H NMR shifts are listed and assigned in Table 2. The ^{1}H NMR spectra of chloroketooximes exhibit a singlet peak for the OH protons of oxime group at 9.85–13.69 ppm range. In all ligands, a singlet peak in 9.74–11.09 ppm range is also attributed to the OH proton of the oxime group. The lower shift of the OH protons of the oxime group is typical of condensation reaction with 4-biphenylhydroximoyl chloride and corresponding amines. The chemical shifts belonging to –NH– protons at δ= 7.85–8.13 ppm, appeared after the condensation reaction. The aromatic C–H protons of the ligands measured at 6.77–7.78 ppm, aliphatic C–H protons at 3.70–4.20 ppm, OH protons phenol groups 6.61–6.81 ppm, respectively. These values are in accord with the previously reported oxime derivatives [4–9, 32, 33].

FT-IR Spectra

The FT-IR spectra of chloroketooximes, the ligands and their complexes provide an insight into the mode of bonding of the ligand to the metal ions. Assignments were made based on typical group frequencies. The most important IR spectral bands of the ligands and their complexes are listed in Table 3. In the IR spectrum of these compounds, the difference between the spectra of chloroketooximes (HL^1–H_2L^4) and the ligands (H_2L^1–H_4L^4) is clear by the presence of characteristic vibrations, at 3420–3319 cm^{-1}

Table 1. Analytical and physical data for the ligands and their complexes

Compound	μ_{eff} (B.M.) per M(II)	Colour	Mp (°C)	Yield (%)	Calcd. (Found) %			
					C	H	N	Metal
HL^1	–	Light yellow	169	54	64.75	3.88	5.39	–
($C_{14}H_{10}NO_2Cl$)					(64.72)	(4.05)	(4.96)	
H_2L^1	–	Light brown	162	65	65.49	4.12	7.64	–
($C_{20}H_{15}N_2O_3Cl$)					(65.39)	(3.97)	(7.58)	
$[Co_2(L^1)_2(H_2O)_2] \cdot 2H_2O$	2.73	Brown	284	77	52.25	3.73	6.09	12.82
($C_{40}H_{34}N_4O_{10}Cl_2Co_2$)					(52.07)	(3.64)	(5.86)	(12.60)
$[Ni_2(L^1)_2(H_2O)_2] \cdot 2H_2O$	3.17	Dark brown	>300	83	52.28	3.73	6.10	12.77
($C_{40}H_{34}N_4O_{10}Cl_2Ni_2$)					(51.94)	(3.88)	(5.67)	(12.54)
$[Cu_2(L^1)_2(H_2O)_2] \cdot 2H_2O$	1.22	Dark brown	240	43	51.73	3.69	6.03	13.68
($C_{40}H_{34}N_4O_{10}Cl_2Cu_2$)					(51.54)	(3.46)	(5.82)	(13.27)
$[Zn_2(L^1)_2(H_2O)_4] \cdot H_2O$	Dia.	Brown	255	63	50.55	3.82	5.89	13.76
($C_{40}H_{36}N_4O_{11}Cl_2Zn_2$)					(51.01)	(3.42)	(5.78)	(13.47)
H_2L^2	–	Yellow	169	35	52.63	2.76	7.67	–
($C_{16}H_{10}N_2O_4Cl_2$)					(52.12)	(4.74)	(6.61)	
H_4L^2	–	Light brown	205*	56	58.04	3.48	9.67	–
($C_{28}H_{20}N_4O_6Cl_2$)					(58.12)	(3.91)	(9.87)	
$[Co(H_2L^2)] \cdot 2H_2O$	3.76	Dark brown	>300	79	43.94	3.16	7.32	15.40
($C_{28}H_{24}N_4O_{10}Cl_2Co_2$)					(43.61)	(3.48)	(7.67)	(15.61)
$[Ni_2(L^2)(H_2O)_2] \cdot 2H_2O$	3.35	Dark green	235	90	43.97	3.16	7.33	15.35
($C_{28}H_{24}N_4O_{10}Cl_2Ni_2$)					(43.74)	(3.52)	(7.16)	(15.46)
$[Cu(H_2L^2)] \cdot H_2O$	1.43	Dark brown	222	75	51.04	3.06	8.50	9.64
($C_{28}H_{20}N_4O_7Cl_2Cu$)					(51.12)	(3.41)	(8.29)	(9.59)
$[Zn_2(L^2)(H_2O)_2] \cdot 2H_2O$	Dia.	Brown	>300	69	41.41	3.23	6.90	16.10
($C_{28}H_{26}N_4O_{12}Cl_2Zn_2$)					(41.69)	(3.61)	(6.86)	(19.21)
HL^3	–	Yellow	108	79	65.82	4.42	5.12	–
[$C_{15}H_{12}NO_2Cl$]					(65.34)	(4.18)	(4.99)	
H_2L^3	–	Light brown	165	75	66.23	4.50	7.36	–
($C_{21}H_{17}N_2O_3Cl$)					(66.08)	(4.36)	(7.19)	
$[Co_2(L^3)_2(H_2O)_2] \cdot 2H_2O$	2.78	Dark brown	>300	70	53.24	4.04	5.91	12.44
($C_{42}H_{38}N_4O_{10}Cl_2Co_2$)					(52.05)	(3.83)	(5.67)	(12.69)
$[Ni_2(L^3)_2(H_2O)_2] \cdot 2H_2O$	3.12	Dark brown	282	46	53.26	4.04	5.92	12.39
($C_{42}H_{38}N_4O_{10}Cl_2Ni_2$)					(52.95)	(3.93)	(5.72)	(12.65)
$[Cu_2(L^3)_2(H_2O)_2] \cdot 2H_2O$	1.24	Dark green	215	97	52.72	4.00	5.86	13.28
($C_{42}H_{38}N_4O_{10}Cl_2Cu_2$)					(52.58)	(3.66)	(5.63)	(13.63)
$[Zn_2(L^3)_2(H_2O)_2] \cdot 2H_2O$	Dia.	Brown	255	65	52.52	3.99	5.83	13.62
($C_{42}H_{38}N_4O_{10}Cl_2Zn_2$)					(52.27)	(3.73)	(5.75)	(13.32)
H_2L^4	–	Cream	171–172	76	53.85	3.19	7.39	–
($C_{17}H_{12}N_2O_4Cl_2$)					(54.20)	(3.30)	(7.00)	
H_4L^4	–	Light brown	205	94	58.70	3.74	9.44	–
($C_{29}H_{22}N_4O_6Cl_2$)					(58.81)	(4.21)	(9.86)	
$[Co(H_2L^4)] \cdot 2H_2O$	3.52	Brown	230	78	50.75	3.52	8.16	8.59
($C_{29}H_{24}N_4O_8Cl_2Co$)					(50.40)	(3.83)	(8.24)	(8.16)
$[Ni_2(L^4)(H_2O)_2] \cdot 2H_2O$	2.82	Green	187	65	44.72	3.36	7.19	15.07
($C_{29}H_{26}N_4O_{10}Cl_2Ni_2$)					(44.45)	(3.88)	(7.47)	(15.31)
$[Cu(H_2L^4)] \cdot 2H_2O$	1.47	Green	279	83	50.41	3.50	8.11	9.20
($C_{29}H_{24}N_4O_8Cl_2Cu$)					(50.75)	(3.69)	(8.03)	(9.06)
$[Zn_2(L^4)(H_2O)_2] \cdot 2H_2O$	Dia.	Yellow	250	42	43.97	3.31	7.07	16.51
($C_{29}H_{26}N_4O_{10}Cl_2Zn_2$)					(43.61)	(3.78)	(7.34)	(16.80)

* Decomposition point

Table 2. The ^{1}H NMR data (as p.p.m.) for chloroketooximes and the ligands

Compound	O–H$_a$	O–H$_b$	C–H$_{(arom.)}$	C–H$_{(aliph.)}$	N–H
HL^1 [9]	13.69 (s,1H)	–	7.31–8.08 (m, 9H)	–	–
H$_2$L^1	11.09 (s, 1H)	6.68 (s, 1H)	7.01–7.78(m, 12H)	–	8.06 (s, 1H)
H$_2$L^2	11.55 (s, 2H)	–	6.90–7.75 (m, 8H)	–	–
H$_4$L^2	10.13 (s, 2H)	6.81(s, 2H)	7.20–7.69(m, 14H)	–	7.85(s, 2H)
HL^3	9.85 (s, 1H)	–	8.10–7.10 (m, 9H)	4.20 (s, 2H)	–
H$_2$L^3	9.74 (s, 1H)	6.74 (s, 1H)	6.82–7.54(m, 12H)	4.06 (s, 2H)	8.13 (s, 1H)
H$_2$L^4 [5]	13.20 (s, 2H)	–	6.90–7.40 (d, 8H)	3.70 (s, 2H)	–
H$_4$L^4	10.40 (s, 2H)	6.61 (s, 2H)	6.77–7.59 (m, 14H)	3.89 (s, 1H)	7.89 (s, 2H)

s – singlet, d – dublet, t – triplet, m – multiplet: a – oxime, b – phenol.

belonging to the NH groups. The ligands exhibit two OH stretching frequencies (oxime, 3311–3271 cm^{-1} and phenolic OH, 3524–3493 cm^{-1}) and NO (1011–990 cm^{-1}) as for substituted aminooximes.

The IR spectra of all the metal complexes resemble each other. The spectra of the complexes, hydroxyl frequencies of phenol and oxime groups are shifted to higher or lower frequencies, which indicates the separation of OH protons of both phenol and oxime groups. The free OH vibration of phenol appears at 3524–3493 cm^{-1} range in the ligands and disappears completely in the binuclear and mononuclear metal complexes. This result indicates coordination through the O-atoms of the phenolates in mononuclear metal complexes of H$_4$L^2 and H$_4$L^4 [9].

Because ν_{OH} stretching vibrations of the complexes appeared in the range of 3502–3435 cm^{-1} are belonging to crystal water molecules of the complexes. The coordinated water appears at frequencies lower than those of the crystal water [34, 35]. Therefore, OH stretching vibrations of oxime groups in mononuclear complexes of H$_4$L^2 and H$_4$L^4 and coordine H$_2$O in the complexes also are probably shown same range with NH stretching vibrations [12]. In the complexes, N–H stretching vibrations are shifted to higher or lower frequencies in the 3397–3361 cm^{-1} range, and this confirms that the nitrogen atom of the amine group is coordinated to the metal ions. The coordination of the amine nitrogen to the metal ion can be inferred from the shift of $\nu_{C=N}$ from 1607–1606 to about 1605–1576 cm^{-1}. Strong absorption bands in the range of 1674–1640 cm^{-1} characterize the C=O group of the ligands in the complexes. Metal complexes show the characteristic bands at 998–923 cm^{-1} belong to N–O stretching vibrations. FT-IR data of the ligands and their complexes are in good agreement with those of known oximes [4–9, 36].

In order to prepare complexes, we used a standard procedure through the reaction of ligands with metal salts. A mixture of ligand, metal salts and an equivalent amount of KOH (0.1 M) in ethanol gave the desired complexes in 42–97% yields. The room temperature magnetic moment measurements show that all Zn(II) complexes are diamagnetic. The nickel(II) complexes are paramagnetic with magnetic susceptibility values of 2.82–3.35, which fit the d^8 metal ion in an octahedral or square pyramidal structure, the two-spin value, 2.83 B.M. [37]. The copper(II) and cobalt(II) complexes are paramagnetic with magnetic susceptibilities 1.22–1.47 and 2.73–3.76, respectively. The Cu^{II} complexes fits the a spin value 1.73 B.M. and Co^{II} complexes fits tri-spin value 3.87 B.M., which are consistent with a weak field octahedral or square pyramidal geometry as expected. The magnetic moments of the dinuclear copper(II) complexes lie in the 1.22 and 1.24 B.M., which is well below the spin-only value of 1.73 B.M., indicating spin-exchange interaction between copper(II) ions. The magnetic moments of the dinuclear cobalt(II) complexes is 2.78 and 2.73 B.M., which is also below the three spin value of 3.87 B.M. And magnetic moments of the dinuclear Ni^{II} complexes are below the two spin value of 2.83 B.M. Reported some bridged Ni^{II} and Co^{II} complexes, exhibit moderate to weak antiferromagnetic interactions [6, 12, 38, 39].

Extraction Ability of the Ligands

The extraction efficiencies of the ligands toward metal ions (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Pb^{II}, Cd^{II}, Hg^{II}) were determined by the picrate extraction method developed by Pedersen [40]. Solvent extraction of aqueous metal cation into water saturated organic hosts' solutions, were performed at 25°C. An aqueous solution containing metal picrate was extracted with the host solution (CHCl$_3$), and the data are expressed as percentages of the cation extracted (E%) by the ligand, as given in the Table 4 and represented in Fig. 5.

Table 3. IR spectral data for the ligands and their metal complexes (cm^{-1})

Compound	N–H	ν(OH)	C=O	ν(C=N)	ν(NO)
HL^1	–	3256 b	1655 s	1602 s	1029 s
H_2L^1	3420 m	3493 s 3275 b	1691 m	1607 m	990 m
$[Co_2(L^1)_2(H_2O)_2] \cdot 2H_2O$	3382 b	3458 b	1653 m	1602 s	931 m
$[Ni_2(L^1)_2(H_2O)_2] \cdot 2H_2O$	3391 b	3461 b	1667 m	1598 s	923 m
$[Cu_2(L^1)_2(H_2O)_2] \cdot 2H_2O$	3371 b	3447 b	1640 m	1576 s	948 m
$[Zn_2(L^1)_2(H_2O)_4] \cdot H_2O$	3377 b	3469 b	1661 m	1582 m	931 m
H_2L^2	–	3283 b	1657 s	1607 m	1036 s
H_4L^2	3381 b	3524 s 3311 b	1667 s	1607 s	1011 m
$[Co(H_2L^2)] \cdot 2H_2O$	3393 b	3448 b	1652 s	1603 s	945 m
$[Ni_2(L^2)(H_2O)_2] \cdot 2H_2O$	3392 b	3495 b	1652 s	1602 s	938 m
$[Cu(H_2L^2)] \cdot H_2O$	3397 b	3487 b	1663 s	1601 m	998 m
$[Zn_2(L^2)(H_2O)_2] \cdot 2H_2O$	3361 b	3502 b	1674 s	1602 s	944 m
HL^3	–	3229 b	1655 s	1598 s	1027 s
H_2L^3	3319 m	3496 s 3294 b	1682 m	1607 m	990 m
$[Co_2(L^3)_2(H_2O)_2] \cdot 2H_2O$	3368 b	3436 b	1646 m	1602 s	932 m
$[Ni_2(L^3)_2(H_2O)_2] \cdot 2H_2O$	3372 b	3435 b	1653 m	1600 s	926 m
$[Cu_2(L^3)_2(H_2O)_2] \cdot 2H_2O$	3364 b	3435 b	1647 m	1583 s	948 m
$[Zn_2(L^3)_2(H_2O)_2] \cdot 2H_2O$	3369 b	3487 b	1654 m	1603 m	930 m
H_2L^4	3326 w	3270 b	1670 s	1602 s	1017 w
H_4L^4	3319 b	3518 s 3271 b	1654 s	1606 s	1010 m
$[Co(H_2L^4)] \cdot 2H_2O$	3363 b	3439	1652 s	1605 s	943 m
$[Ni_2(L^4)(H_2O)_2] \cdot 2H_2O$	3364 b	3469 b	1661 s	1602 m	943 m
$[Cu(H_2L^4)] \cdot 2H_2O$	3375 b	3439 b	1663 s	1605 s	953 m
$[Zn_2(L^4)(H_2O)_2] \cdot 2H_2O$	3364 b	3496 b	1652 s	1604 m	943 m

s: strong, m: medium, w: weak, b: broad.

Host-guest interactions between macrocyclic ligand and metal cation are interesting for analytical processes. The cation binding properties of the ligands depend upon different factors such as macrocyclic effect, cavity size, the hard and soft acids and bases (HSAB) principles and the type and number of donor atoms. The extraction ability of the ligands in this study varies as $Hg^{II} > Pb^{II} \gg Cu^{II} > Ni^{II} > Zn^{II} = Co^{II} > Cd^{II} > Mn^{II}$. However ionic radius of these metal ions varied as $Pb^{II} > Hg^{II} > Cd^{II} > Mn^{II} > Cu^{II} > Zn^{II} > Co^{II} > Ni^{II}$ [41]. These results suggest that the match between the cation and the ligands cavity dimensions is not an evident factor in selectivity. The type of donor atoms in all ligands of this study is same. But the type of aromatic group bonding carboyl group and the number of donor atoms in the ligands are changing. The type of aromatic group in the ligand is not an important factor in selectivity. The number of donor atoms in the ligands from H_2L^1 and H_2L^3 to H_4L^2 and H_4L^4 increases. This increase is effective in the extraction levels of some metal ions such as Pb^{II} and Cu^{II}, but it is not effective for all metal ions (especially Hg^{II} and Zn^{II} ions). Our ligands contain soft donor nitrogen atoms [24–26]. Therefore they show a very clear preference for Hg^{II}. While the extraction levels for the soft Lewis acid, Hg^{II} (82.34–87.36%) are very superior to ours, for Pb^{II} (58.13–79.52%) are second, and mainly for Cu^{II} (36.85–41.49%) are inferior. It is clear from these data that the complexation ability of the ligands toward Hg^{II} is much higher and all ligands are excellent extractants for Hg^{II} ion. Also the presence of oxime groups (–C=ON–OH) indicate that the oxime groups play an important role in the extraction process [42]. It is difficult to comment whether or not the increase in extraction capability is the result of oxime groups or the increase in the number of donor atoms,

Table 4. Extraction of metal picrates with ligands[a]

Ligand	Percent of metal picrate extracted (%)[b]							
	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	Hg^{2+}
H_2L^1	4.47	14.22	19.71	38.14	16.34	70.14	6.63	87.36
H_4L^2	7.51	15.76	23.42	41.49	15.96	79.52	9.12	85.60
H_2L^3	3.26	11.26	16.24	36.85	17.82	58.13	6.29	82.34
H_4L^4	6.61	15.84	20.13	39.94	13.48	62.89	8.81	84.57

[a] $H_2O/CHCl_3$ = 10/10 (v/v): [picric acid] = 2×10^{-5} M, [ligand] = 1×10^{-3} M, [metal nitrate] = 1×10^{-2} M, 298 K, 1 h contact time.
[b] Average for three independent measurements.

but, according to these data, we can conclude that, the hard and soft acids and bases principles and the number of donor atoms are much more effective than the other factors [43, 44].

Thermal Analyses

The TG for the some metal complexes of these ligands was carried out within the temperature range from room temperature up to 1000°C. Thermal data of the complexes are given in Table 5. The correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in terms of the proposed formulae of the complexes.

The Co^{II} complex with the general formula $[Co_2(L^1)_2(H_2O)_2] \cdot 2H_2O$ is thermally decomposed in six successive decomposition steps. First step occurs within the temperature range 30–130°C with an estimated mass loss 3.60% (calculated mass loss = 3.92%) are reasonably accounted for the liberation of the two H_2O molecules. The second estimated mass loss of 11.30% within the temperature range 130–305°C may be attributed to the loss of two H_2O and 2 Cl molecules (calculated mass loss = 11.63%). The third, forth and fifth steps occur within the same temperature range 305–580°C with an estimated mass loss 38.90% (calculated mass loss = 39.41%), which is reasonably accounted for the loss of two biphenyls and two CO groups. The remaining step of decompositions occur within the temperature range 580–1000°C with an estimated mass loss of 29.50% (calculated mass loss = 28.74%) which corresponds to the decomposition of the compound completely leaving CoO residue.

The Ni^{II} complex, $[Ni_2(L^1)_2(H_2O)_2] \cdot 2H_2O$, is thermally decomposed in five successive decomposition steps within the temperature range 40–1000°C. In the first step, estimated mass loss of 8.10% (calculated mass loss = 7.84%) within the temperature range 40–190°C can be attributed to the liberation of two moles of coordinated water and two moles of crystallization water. Other three decomposition steps of estimated mass loss 46.80% which is responsibly accounted for loss of two biphenyl two Cl and two CO groups (calculated mass loss = 47.15%) within the temperature range 190–650°C. Decomposition is going on in 1000°C, therefore we did not determine metallic residue.

The Cu^{II} complex with the general formula $[Cu_2(L^1)_2(H_2O)_2] \cdot 2H_2O$ was thermally decomposed in five successive decomposition steps. In the first step, estimated mass loss of 8.00% (calculated mass loss = 7.76%) within the temperature range 50–240°C can be attributed to the liberation of four H_2O molecule. The second decomposition step occurs within the temperature range 240–295°C with an estimated mass loss

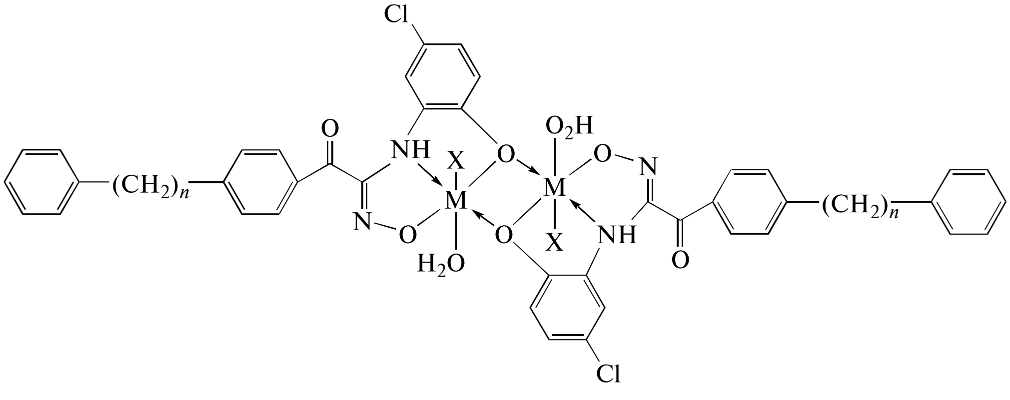

Fig. 2. Dinuclear metal complexes of H_2L^1 and H_2L^3 (M = Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}; X: H_2O or O).

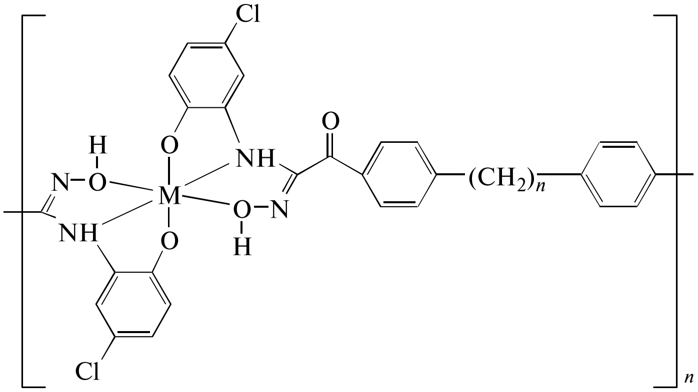

Fig. 3. Mononuclear Co^{II} and Cu^{II} complexes of H_4L^2 and H_4L^4.

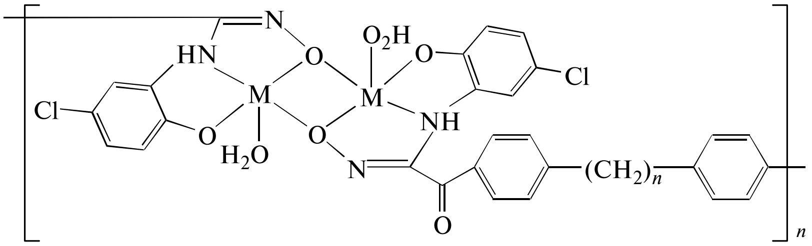

Fig. 4. Dinuclear Ni^{II} and Zn^{II} complexes of H_4L^2 and H_4L^4.

7.20% (calculated mass loss = 7.64%), which is reasonably accounted for the loss of two Cl atoms. Decomposition was going on in 1000°C, therefore we did not determine metallic residue.

The Zn^{II} complex, with the general formula $[Zn_2(L^1)_2(H_2O)_4] \cdot H_2O$, shows decomposition pattern of six stages. The first step with estimated mass loss of 1.95%, found within the temperature range 50–105°C. Corresponding to loss of one H_2O molecule (calculated mass loss = 1.90%). The second step with an estimated mass loss 7.45% which is due to loss of four H_2O molecules within the temperature range 105–275°C

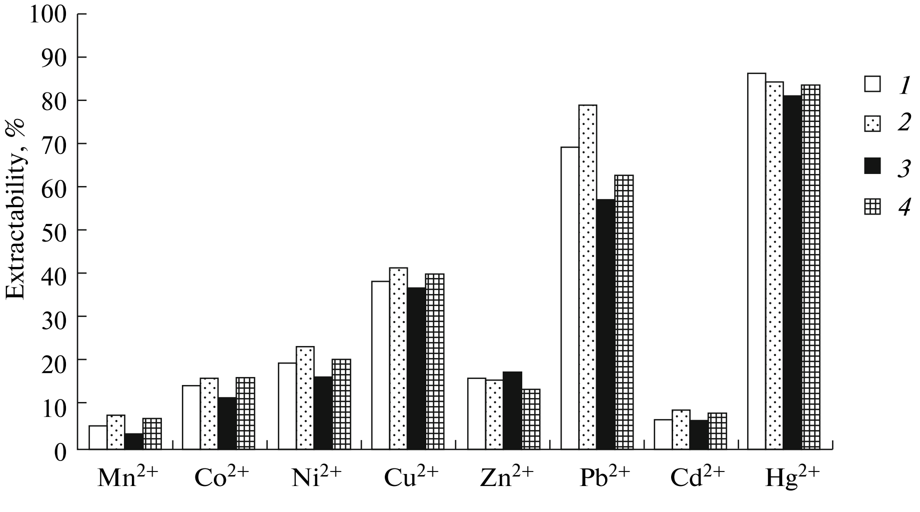

Fig. 5. Extraction percentage of the metal picrates with ligands. Ligands: *1* = H_2L^1, *2* = H_4L^2, *3* = H_2L^3 , *4* = H_4L^4 $H_2O/CHCl_3$ = 10/10 (v/v): [picric acid] = 2×10^{-5} M, [ligand] = 1×10^{-3} M, [metal nitrate] = 1×10^{-2} M, 298 K, 1 h contact time.

Table 5. Thermoanalytical results (TG, DTG) of metal complexes

Complex	TG range (°C)	DTGmax (°C)	Estimated (%, calculated)		Assignment	Metallicresidue
			Mass loss	Total mass loss		
$[Co_2(L^1)_2(H_2O)_2] \cdot 2H_2O$	30–130	70	3.60 (3.92)		Loss of two H_2O molecules	
	130–305	290	11.30 (11.63)		Loss of two H_2O and 2 Cl molecules	
	305–580	365, 445, 525	38.90 (39.41)		Loss of 2 biphenyl and 2 CO groups	
	580–1000	710	29.50 (28.74)	83.30 (83.70)	Decomposition of the compound completely	2 CoO
$[Ni_2(L^1)_2(H_2O)_2] \cdot 2H_2O$	40–190	75	8.10 (7.84)		Loss of four H_2O molecules	
	190–650	335, 430, 575	46.80 (47.15)		Loss of 2 biphenyl 2 Cl and 2 CO groups	
	650–1000	730	–		Decomposition is going on	?
$[Cu_2(L^1)_2(H_2O)_2] \cdot 2H_2O$	50–240	230	8.00 (7.76)		Loss of four H_2O molecules	
	240–295	255	7.20 (7.64)		Loss of two Cl atoms	
	295–1000	340, 710, 755			Decomposition is going on	?
$[Zn_2(L^1)_2(H_2O)_4] \cdot H_2O$	50–105	80	1.95 (1.90)		Loss of one H_2O molecule	
	105–275	245	7.45 (7.58)		Loss of four H_2O molecules	
	275–330	305	7.30 (7.46)		Loss of two Cl atoms	
	330–515	430	38.40 (38.13)		Loss of 2 biphenyl and 2 CO groups	
	515–725	575, 630	27.35 (27.80)	82.45 (82.87)	Decomposition of the compound completely	2 ZnO
$[Ni_2(L^2)(H_2O)_2] \cdot 2H_2O$	30–190	87	9.80 (9.42)		Loss of four H_2O molecule	
	190–487	230, 434	36.40 (36.50)		Loss of biphenyl 2 Cl and 2 CO groups	
	487–740	637	34.70(34.55)	80.90 (80.47)	Decomposition of the compound completely	2 NiO
$[Cu(H_2L^2)] \cdot H_2O$	40–150	95	3.10 (2.73)		Loss of one H_2O molecule	
	150–245	215	42.45 (42.36)		Loss of biphenyl 2 Cl and 2 CO groups	
	580–980	765, 855	45.10 (45.27)	90.65 (90.36)	Decomposition of the compound completely	Cu
$[Co(H_2L^4)] \cdot 2H_2O$	30–105	65	5.50 (5.26)		Loss of two H_2O molecules	
	105–490	220, 445	45.50 (45.21)		Loss of diphenylmethane 2 Cl and 2 CO groups	
	490–920	570, 900	38.50 (38.58)	89.50 (89.05)	Decomposition of the compound completely	CoO
$[Ni_2(L^4)(H_2O)_2] \cdot 2H_2O$	30–110	75	5.10 (4.63)		Loss of two H_2O molecules	
	110–200	180	4.70 (4.63)		Loss of other two H_2O molecules	
	200–460	425	37.40 (37.64)		Loss of diphenylmethane 2 Cl and 2 CO groups	
	460–625	550	38.30 (38.60)	85.50 (84.93)	Decomposition of the compound completely	2 Ni

(calculated mass loss = 7.58%). The third estimated mass loss of 7.30% (calculated mass loss = 7.46%) within the temperature range 275–330°C can be attributed to the liberation of two Cl atoms. The forth step occurs within the temperature range 330–515°C and fifth and sixth steps occur within the temperature range 515–725°C with an estimated total mass loss 82.45% (calculated total mass loss = 82.87%), which is reasonably accounted for decomposition of the compound completely leaving ZnO as residue.

The Ni^{II} complex with the general formula $[Ni_2(L^2)(H_2O)_2] \cdot 2H_2O$ was thermally decomposed in four successive decomposition steps. The first estimated mass loss of 9.80% within the temperature range 30–190°C may be attributed to the liberation of four H_2O molecule (calculated mass loss = 9.42%). The remaining steps of decomposition occur within the temperature range 190–487°C (loss of biphenyl, two Cl and two CO groups) and 487–740 with an estimated total mass loss of 80.90% (calculated mass loss = 80.47%) which corresponds to decomposition of the compound completely leaving NiO residue.

The Cu^{II} complex with the formula $[Cu(H_2L^2)] \cdot H_2O$ was thermally decomposed in four successive decomposition steps. The first estimated mass loss of 3.10% (calculated mass loss = 2.73%) within the temperature range 40–150°C can be attributed to the liberation of one H_2O molecule. The second step occurs within the temperature range 150–245°C with an estimated mass loss 42.45% (calculated mass loss = 42.36%), which is reasonably accounted for the loss of biphenyl, two Cl and two CO groups, and last steps is decomposition of the compound completely leaving Cu as residue with total estimated mass loss 90.65% (total calculated mass loss = 90.36%).

The Co^{II} complex, with the general formula $[Co(H_2L^4)] \cdot 2H_2O$, shows decomposition pattern of five stages. The first step with estimated mass loss of 5.50%, found within the temperature range 30–105°C. Corresponding to loss of two H_2O molecules (calculated mass loss = 5.26%). The second and third steps with estimated mass loss of 45.50%, found within the temperature range 105–490°C. Corresponding to loss of diphenylmethane, two Cl and two CO (calculated mass loss = 45.21%). The remaining two decomposition steps with an estimated mass loss 38.50% which is due to decomposition of the compound completely leaving CoO residue occurring within the temperature range 490–920°C (calculated mass loss = 38.58%). The total estimated mass loss is 89.50% (total calculated mass loss = 89.05%).

The Ni^{II} complex, with the general formula $[Ni_2(L^4)(H_2O)_2] \cdot 2H_2O$, shows decomposition pattern of four stages. The first step with estimated mass loss of 5.10%, found within the temperature range 30–110°C. Corresponding to loss of two H_2O molecules (calculated mass loss = 4.63%). The second step with an estimated mass loss 4.70% which is due to loss of other two H_2O molecules within the temperature range 110–200°C (calculated mass loss = 4.63%). The third estimated mass loss of 37.40% (calculated mass loss = 37.64%) within the temperature range 200–460°C can be attributed to the liberation of diphenylmethane, two Cl and two CO groups. The last step occurs within the temperature range 460–625°C with an estimated total mass loss 38.30% (calculated total mass loss = 38.60%), which is reasonably accounted for decomposition of the compound completely leaving Ni as residue.

CONCLUSIONS

(2-Hydroxo-5-chlorophenylaminoisonitrosoacetyl)phenyl ligands (H_2L^1–H_4L^4) and their mono- and dinuclear cobalt(II), nickel(II), copper(II) and zinc(II) complexes were synthesized and characterized by elemental analyses, magnetic susceptibility measurements, IR and ^1H NMR. It was found that, the dinuclear complexes of H_2L^1 and H_2L^3 have a metal : ligand ratio of 1 : 2 (Fig. 2); the mononuclear complexes of H_4L^2 and H_4L^4 have a metal : ligand ratio of 1 : 1 (Fig. 3) and dinuclear complexes H_4L^2 and H_4L^4 have a metal : ligand ratio of 2 : 1 (Fig. 4). All complexes of these ligands have square pyramidal or octahedral structure. The results of elemental analyses and ICP-OES the complexes are in good agreement with the proposed formula. The IR data support the proposed structure for the ligands and their complexes. The thermal analyses data of these chelates shows that some of the complexes have one or two mole crystallization water molecules. The complexes were generally thermally decomposed in 4–6 successive decomposition steps. The final decomposition products are found to be the corresponding metal or metal oxides. But in the some complexes, decomposition of the compound did not finish completely at 1000°C. Therefore, we did not find last decomposition product. Furthermore liquid–liquid extraction of some transition metal ions (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Pb^{II}, Cd^{II}, Hg^{II}) with the ligands have been examined. All ligands behave as good extractants and complexing agents for mercury(II) and can be used for mercury recovery.

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