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Synthesis and Characterization of New Ketooximes and Their Complexes¹

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Abstract—The starting point of the research was the reaction of chloroacetyl chloride with biphenyl in the presence of aluminum chloride. 4-Biphenylhydroximoyl chloride (HL) was obtained by reacting synthesized 4-(chloroacetyl)biphenyl with alkyl nitride. Four new substituted 4-(alkylaminoisonitrosoacetyl)biphenyles (ketooximes) were prepared by reacting 4-biphenylhydroximoyl chloride with corresponding amines in EtOH. The following amines were used for ligands: *p*-toluidine, *p*-chloroaniline, pyrrolidine, and 4-aminoacetophenone. Mononuclear complexes with a metal-ligand ratio of 1 : 2 were prepared using cadmium(II), cobalt(II), copper(II), nickel(II), lead(II), and zinc(II) salts. These compounds have been characterized by elemental analyses, AAS, infrared spectra and magnetic susceptibility measurements. The ligands have been further characterized by ¹H NMR. The results suggest that the ketooximes act as bidentate ligands which bond metal ions through the oxime and carbonyl oxygen.

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INTRODUCTION

The chemistry of transition metal complexes with α -dioxime ligands has been well studied and is the subject of several reviews and many papers [1-5]. However, little information concerning the ketooxime metal complexes is available [6, 7]. Several similar compounds were synthesized by Karipcin et al. [8, 9]. Karipcin et al. have synthesized the ketooxime of 4,4'-bis(chloroacetyl)biphenylmethane and some of their amine derivatives and complexes [8]. In the present study, cadmium(II), cobalt(II), copper(II), nickel(II), lead(II), and zinc(II) complexes with four new ketooxime-derived 4-biphenylhydroximoyl chlorides and corresponding amines were synthesized. In the studies mentioned above, similar complexation characteristics were observed as the ligand with same amine derivatives formed mononuclear complexes with metal-ligand ratio of 1 : 2.

EXPERIMENTAL

4-(Chloroacetyl)biphenyl [10] and 4-biphenylhydroximoyl chloride [10] were synthesized as previously described. All solvents, amines and metal salts $(Co(NO_3)_2 \cdot 6H_2O, Ni(AcO)_2 \cdot 4H_2O, Cu(AcO)_2 \cdot H_2O,$ $Zn(AcO)_2 \cdot 2H_2O, Cd(NO_3)_2 \cdot 4H_2O, Pb(AcO)_2 \cdot 3H_2O)$ used for the synthesis and physical measurements were commercially purchased and were used without further purification.

IR spectra (4000–400 cm⁻¹) were recorded on a Perkin Elmer BX FT-IR spectrophotometer as KBr pellets. ¹H NMR spectra of the ligands were recorded from DMSO solutions with TMS as an internal standard at the Laboratories of the Scientific and Technical Research Council of Turkey (TUBITAK). ¹H NMR spectra of the complexes could not be determined, since these compounds are not totally soluble in organic solvents. C, H, and N contents were determined microanalytically on a LECO 932 CHNS analyzer, and metal contents were estimated spectrophotometrically on a Perkin Elmer 800 AA spectrometer. Room temperature magnetic susceptibility measurements were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MX1). Melting points were measured on an IA 9100 Electrothermal apparatus and are uncorrected.

Preparation of the Ligands

All ligands were prepared by a similar method. A solution of amines (16.5 mmol *p*-toluidine, *p*-chloroaniline, pyrrolidine, and 4-aminoacetophenone) in absolute ethanol (20 cm³) was added dropwise with continuous stirring to a solution of 4-biphenylhydroximoyl chloride (3.893 g, 15 mmol) in ethanol (50 cm³) in the presence of Et₃N (15 mmol) for 30 min. at 0°C. Precipitation and color change were observed in the reaction medium immediately. After that period, the reaction

¹The text was submitted by the authors in English.

mixture was stirred for 2 h more at the same temperature. Then it was allowed to stir at ambient temperature for 2 h. The powder resulting from the reaction is insoluble in ethanol and this was filtered off; washed with aqueous sodium bicarbonate (1%), distilled water, and ethanol; and dried in air.

Preparation of the Complex

A solution of an equivalent amount of metal salt in ethanol (20 cm³) was added to a hot solution of ligand (HL¹–HL⁴) [1 mmol, 0.284 g HL¹, 0.346 g HL², 0.331 g HL³, 0.358 g HL⁴] in ethanol (50 cm³) and was continuously stirred. A distinct change in color 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 to a pH value of about 5–6, and the solid product was 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 with hot water and ethanol and dried in air.

The colors, yield, melting points, elemental analyses, and IR data of the complexes and ligands are given in Tables 1 and 2. ¹H NMR data of ligands are given in Table 3.

RESULTS AND DISCUSSION

The reaction steps for the synthesis of 4-(alkylaminoisonitrosoacetyl)biphenyl ligands (HL¹–HL⁴) are given in Scheme 1. 4-(Chloroacetyl)biphenyl was prepared from chloroacetyl chloride and biphenyl in the presence of aluminum chloride according to Friedel-Crafts acylation [10]. 4-Biphenylhydroximoyl chloride (HL) was obtained by reacting 4-(chloroacetyl)biphenyl with alkyl nitride in the presence of dry HCl gas [10]. 4-(alkylaminoisonitrosoacetyl)biphenyls (HL^1-HL^4) were prepared by reaction of HL with *p*-toluidine, p-chloroaniline, pyrrolidine, and 4-aminoacetophenone, respectively. 4-(4-methylphenylaminoisonitrosoacetyl)biphenyl(HL¹), 4-(4-chlorophenylaminoisonitrosoacetyl)biphenyl(HL²), 4-[pyrrolidylisonitrosoacetyl]biphenyl (HL3) and 4-(4-acetylphenylaminoisonitrosoacetyl)biphenyl (HL⁴) were prepared. The structural formula (Fig. 1) of ketooxime ligands were verified by elemental analyses, ¹H NMR, and IR spectral data, presented in Tables 1–3.

On interaction with cadmium(II), cobalt(II), copper(II), nickel(II), lead(II), and zinc(II) salts, ketooxime ligands yielded complexes corresponding to the general formula $[M(L^x)_2(H_2O)_2]$. For the structural characterization of metal complexes, elemental analyses, AAS, FT-IR and magnetic susceptibility measurements were used and spectral-analytical data for all these complexes are presented in Tables 1 and 2. The metal-to-ligand ratio of the all complexes was found to be 1 : 2 and they have two additional coordinated H₂O molecules.

The ¹H NMR spectrum of 4-biphenylhydroximoyl chloride exhibits a singlet peak for the OH protons of oxime group at 13.69 ppm. In all ligands, a singlet peak in the 11.15–11.78 ppm. range is also attributed to the OH proton of the oxime group. The higher shift of the OH protons of the oxime group is typical of condensation reaction with 4-biphenylhydroximoyl chloride and corresponding amines. The other singlet peak observed



Scheme 1. Synthesis of 4-(Alkylaminoisonitrosoacetyl)biphenyls (HL¹–HL⁴).

SYNTHESIS AND CHARACTERIZATION OF NEW KETOOXIMES

Compound	Colour	Mp, °C	Yield, %	Calcd. (Found), %				
				С	Н	N	Metal	
HL	Light yellow	169	54	64.79 (64.72)	3.88 (4.05)	5.39 (4.96)	_	
HL^1	Yellow	144	85	76.40 (76.31)	5.49 (5.70)	8.48 (8.29)	-	
$[Cd(L^1)_2(H_2O)_2]$	Light brown	240	76	62.52 (62.57)	5.25 (4.96)	6.94 (6.73)	13.94 (13.60)	
$[\mathrm{Co}(\mathrm{L}^1)_2(\mathrm{H}_2\mathrm{O})_2]$	Dark brown	240	73	63.54 (66.98)	5.62 (5.72)	7.44 (7.81)	7.82 (8.27)	
$[\mathrm{Cu}(\mathrm{L}^1)_2(\mathrm{H}_2\mathrm{O})_2]$	Dark brown	220	96	66.55 (66.15)	5.59 (5.10)	7.39 (7.48)	8.38 (8.54)	
$[\mathrm{Ni}(\mathrm{L}^1)_2(\mathrm{H}_2\mathrm{O})_2]$	Brown	270*	69	66.98 (66.68)	5.62 (5.32)	7.44 (7.91)	7.79 (7.81)	
$[Pb(L^1)_2(H_2O)_2]$	Yellow	200	67	55.95 (56.30)	4.69 (4.74)	6.21 (6.61)	22.97 (23.14)	
$[Zn(L^1)_2(H_2O)_2]$	Light brown	205*	56	66.39 (66.54)	5.57 (5.91)	7.37 (7.67)	8.60 (8.82)	
HL ²	Yellow	168	85	68.50 (68.31)	4.31 (4.31)	7.99 (7.59)	_	
$[Cd(L^2)_2(H_2O)_2]$	Orange	285*	95	56.68 (56.74)	4.28 (4.19)	6.61 (6.28)	13.27 (13.42)	
$[Co(L^2)_2(H_2O)_2]$	Dark brown	270*	89	60.49 (60.12)	4.57 (5.02)	7.06 (6.79)	7.43 (7.56)	
$[\mathrm{Cu}(\mathrm{L}^2)_2(\mathrm{H}_2\mathrm{O})_2]$	Brown	208	74	60.15 (59.72)	4.54 (4.06)	7.01 (6.86)	7.95 (8.21)	
$[Ni(L^2)_2(H_2O)_2]$	Light brown	>300	62	60.51 (60.57)	4.57 (4.75)	7.06 (7.84)	7.39 (7.06)	
$[Pb(L^2)_2(H_2O)_2]$	Yellow	205	55	50.98 (50.99)	3.85 (3.94)	5.95 (5.96)	21.98 (22.33)	
$[Zn(L^2)_2(H_2O)_2]$	Light brown	241	58	60.01 (59.85)	4.53 (4.87)	6.99 (6.46)	8.18 (8.49)	
HL ³	Yellow	131	61	73.49 (73.48)	6.17 (6.31)	9.52 (9.74)	_	
$[Cd(L^3)_2(H_2O)_2]$	Yellow	297*	84	58.85 (58.69)	5.76 (6.16)	7.63 (7.19)	15.30 (15.73)	
$[Co(L^3)_2(H_2O)_2]$	Dark brown	184.5	73	63.47 (63.32)	6.21 (6.19)	8.22 (8.29)	8.65 (9.02)	
$[\mathrm{Cu}(\mathrm{L}^3)_2(\mathrm{H}_2\mathrm{O})_2]$	Green	190	69	63.04 (62.99)	6.17 (6.48)	8.17 (7.91)	9.26 (9.20)	
$[Ni(L^3)_2(H_2O)_2]$	Dark brown	>300	50	63.49 (63.81)	6.22 (6.25)	8.23 (7.88)	8.61 (8.40)	
$[Pb(L^3)_2(H_2O)_2]$	Yellow	185	63	52.12 (52.41)	5.10 (4.73)	6.75 (6.46)	24.98 (25.16)	
$[Zn(L^3)_2(H_2O)_2]$	Yellow	>300	70	62.87 (62.76)	6.16 (6.08)	8.15 (7.97)	9.51 (9.81)	
HL^4	Cream	144	68	73.77 (73.91)	5.07 (5.48)	7.82 (7.56)	_	
$[Cd(L^4)_2(H_2O)_2]$	Orange	240	75	61.25 (61.21)	4.91 (5.08)	6.49 (6.04)	13.03 (13.40)	
$[Co(L^4)_2(H_2O)_2]$	Brown	230*	72	65.29 (65.67)	5.23 (4.95)	6.92 (7.29)	7.28 (7.39)	
$[\mathrm{Cu}(\mathrm{L}^4)_2(\mathrm{H}_2\mathrm{O})_2]$	Dark brown	244*	62	64.92 (65.02)	5.20 (4.76)	6.88 (7.21)	7.80 (8.12)	
$[Ni(L^4)_2(H_2O)_2]$	Light brown	270*	58	65.31 (65.09)	5.23 (4.96)	6.92 (6.82)	7.26 (7.06)	
$[Pb(L^4)_2(H_2O)_2]$	Yellow	250	69	55.19 (55.38)	4.42 (3.97)	5.85 (5.47)	21.64 (21.85)	
$[Zn(L^4)_2(H_2O)_2]$	Yellow	>300	74	64.78 (64.75)	5.19 (5.54)	6.87 (7.08)	8.01 (8.29)	

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

* Decomposition point.

Compound	$ \begin{array}{c} \mu_{eff}\left(\mu_{B}\right) \\ per \ M(II) \end{array} $	N–H	v(OH)	v(CH) _{aliph}	C=O	v(C=N)	v(NO)
HL	_	_	3256 b	2824 w	1655 s	1602 s	1029 s
HL^1	-	3379 m	3233 b	2919 w	1671 s	1600 s	946 s
$[Cd(L^1)_2(H_2O)_2]$	Dia.	3395 m	_	2922 w	1671 w	1600 s	985 m
$[Co(L^1)_2(H_2O)_2]$	3.90	3392 b	_	2920 w	1668 w	1601 s	1006 m
$[\operatorname{Cu}(\operatorname{L}^1)_2(\operatorname{H}_2\operatorname{O})_2]$	2.09	3391 b	_	2920 w	1674 w	1601 s	1006 m
$[Ni(L^1)_2(H_2O)_2]$	3.56	3391 b	_	2920 w	1670 w	1600 s	1005 m
$[Pb(L^1)_2(H_2O)_2]$	Dia.	3401 b	_	2924 w	1654 w	1600 s	967 m
$[Zn(L^1)_2(H_2O)_2]$	Dia.	3392 b	_	2922 w	_	1576 s	991 m
HL^2	-	3428 s	3368 s	2915 w	1650 s	1599 s	963 s
$[Cd(L^2)_2(H_2O)_2]$	Dia.	3427 b	_	2925 w	1654 w	1599 s	984 m
$[Co(L^2)_2(H_2O)_2]$	3.95	3448 b	_	2921 w	1669 w	1600 s	1007 m
$[Cu(L^2)_2(H_2O)_2]$	1.51	3415 b	_	2926 w	1671 s	1600 s	1007 m
$[Ni(L^2)_2(H_2O)_2]$	3.76	3416 b	_	2928 w	1669 w	1599 s	1007 m
$[Pb(L^2)_2(H_2O)_2]$	Dia.	3425 b	_	2915 w	1654 w	1599 s	973 m
$[Zn(L^2)_2(H_2O)_2]$	Dia.	3414 b	_	2931 w	1660 s	1599 s	1006 m
HL ³	-	_	3413 m	2918 m	1675 m	1602 s	1006 m
$[Cd(L^3)_2(H_2O)_2]$	Dia.	_	3469 b	2923 w	_	1601 m	1006 m
$[Co(L^3)_2(H_2O)_2]$	2.12	_	3400 b	2969 w	_	1600 s	1007 m
$[Cu(L^3)_2(H_2O)_2]$	2.39	_	3385 b	2971 w	_	1600 s	1006 m
$[Ni(L^3)_2(H_2O)_2]$	3.57	_	3401 b	2971 w	_	1599 s	1007 m
$[Pb(L^3)_2(H_2O)_2]$	Dia.	_	3415 b	2969 w	_	1600 m	1007 m
$[Zn(L^3)_2(H_2O)_2]$	Dia.	_	3400 b	2920 m	_	1575 s	1021 m
HL^4	-	3429 s	3357 s	2920 w	1672 s	1601 s	963 s
$[Cd(L^4)_2(H_2O)_2]$	Dia.	3430 b	_	2922 w	1668 s	1599 s	987 m
$[Co(L^4)_2(H_2O)_2]$	4.70	3432 b	_	2922 w	1673 s	1599 s	1006 m
$[\mathrm{Cu}(\mathrm{L}^4)_2(\mathrm{H}_2\mathrm{O})_2]$	2.50	3447 b	_	2925 w	1674 s	1599 s	1006 m
$[Ni(L^4)_2(H_2O)_2]$	3.64	3452 b	_	2926 w	1669 m	1599 s	999 m
$[Pb(L^4)_2(H_2O)_2]$	Dia.	3436 b	_	2926 w	1671 m	1598 s	1006 m
$[Zn(L^4)_2(H_2O)_2]$	Dia.	3401 b	_	2929 w	1673 s	1574 s	1021 m

Table 2. Magnetic measurements and IR spectral data for the ligands and their metal complexes (cm^{-1})

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

Compound	O–H	N–H	C–H _{arom}	C–H _{aliph}	C–H _{ring}
HL	13.69 (s, 1H)	_	7.31-8.08 (m, 9H)	-	-
HL^{1}	11.15 (s, 1H)	8.57 (s, 1H)	6.70-8.08(m, 13H)	3.44 (s, 3H)	-
HL^2	11.45 (s, 1H)	8.85 (s, 1H)	6.80-8.09 (m, 13H)	-	-
HL^3	-	_	6.60–8.14(m, 9H)	-	3.13–4.11(m, 8H)
HL^4	11.78 (s, 1H)	9.238 (s, 1H)	7.42-8.07(m, 13H)	2.46 (s, 1H)	_

Note: s-singlet, d-dublet, t-triplet, m-multiplet.



4-(4-metylphenylaminoisonitrosoacetil)biphenyl, C₂₁H₁₈N₂O₂



4-(4-clorophenylaminoisonitrosoacetil)biphenyl, C₂₀H₁₅N₂O₂Cl



4-(pyrrolidilisonitrosoacetil)biphenyl, C18H18N2O2



4-(4-acetophenylaminoisonitrosoacetil)biphenyl, C₂₂H₁₈N₂O₃

Fig. 1. The Structure of 4-(Alkylaminoisonitrosoacetyl)biphenyls.

in the $\delta = 8.57-9.24$ ppm. range can be assigned to the NH signal; it appeared after the condensation reaction. The aromatic C–H protons of the ligands measured 6.60–8.14 ppm., aliphatic C–H protons 2.46–4.11 ppm. The spectral data of a DMSO solution of the ligands support the proposed structure and indicate the formation of 4-(alkylaminoisonitrosoacetyl)biphenyl ligands. These values are also in good agreement with those of known oximes [11, 12].

In the FT-IR spectra of keto oxime ligands (as KBr pellets), bands at 3379-3429, 3233-3413, 1650-1675, 1599–1602, and 946–1006 cm⁻¹ were assigned to NH, OH, C=O, C=N, and N=O stretching vibrations, respectively. Stretching C=N vibrations appearing at about 1600 cm⁻¹ in the ligands appeared at the same place in the metal complexes of these ligands, indicating coordination through the O atom of oxime groups. Stretching $\vartheta_{C=0}$ vibrations are affected upon complexation and became weaker or dissappeared completely. This indicated coordination through the C=O group. The OH vibrations of oxime appearing at 3233–3413 cm⁻¹ in the spectra of ligands dissappeared completely in the spectra of metal complexes. Howewer, the OH vibration of the coordinated H₂O appeared in the ketooxime-pyrrolidyne (HL₃) ligand and its complexes. Furthermore, the OH stretching vibrations of coordinated H₂O in the complexes are probably shown in same range as NH stretching vibrations. In the IR spectra of metal complexes, bands at 3448–3401, 1675–1654, 1601–1574, and 1007–967 cm⁻¹ belong to N–H, C=O, C=N and N–O stretching vibrations, respectively. These absorption data are in agreement with those previously reported for substituted ketooximes [13, 14].

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 50–96% yields. According to the IR data, elemental analyses and magnetic susceptibility measurements, the mononuclear complexes have a metal : ligand ratio of 1 : 2 and an octahedral structure (Fig. 2). The room temperature magnetic moment measurements show that all Zn(II), Cd(II), and Pb(II) complexes are diamagnetic. The nickel(II) complexes are paramagnetic with magnetic susceptibility values of 3.56–3.76 μ_B , which fits the two-spin value, 2.83 μ_B . The results of the Ni(II) complexes fit the d^8 metal ion in an octahedral structure [15, 16]. The copper(II) and cobalt(II) complexes are paramagnetic with magnetic susceptibilities 1.51–2.50 and 2.12–4.70 μ_B , respectively. The Cu(II) complexes fit spin values $1.73 \,\mu_B$ and the Co(II) complexes fit tri-spin values, $3.36 \mu_B$.



M: Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II)



Fig. 2. The Structure of metal complexes of 4-(Alkylaminoisonitrosoacetyl)biphenyls.

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REFERENCES

- 1. L. Tschugaeff, Ber. 40, 3498 (1907).
- J. V. Burakevich, A. M. Lore, and G. P. Volpp, J. Org. Chem. 36, 1 (1971).
- I. Karatas and H. I. Ucan, Synth. React. Inorg. Met.-Org. Chem. 28, 383 (1998).
- F. Karipcin and I. Karatas, Synth. React. Inorg. Met.-Org. Chem. **31**, 1817 (2001).
- 5. A. Coskun and I. Karatas, Turk. J. Chem. 28, 173 (2004).
- 6. A. Chakravorty, Coord. Chem. Rev. 13, 3 (1974).

- P. S. Reddy and K. H. Reddy, Polyhedron 19, 1687 (2000).
- F. Karipcin, H. I. Ucan, and I. Karatas, Trans. Met. Chem. 27, 813 (2002).
- F. Karipcin, I. Karatas, and H. I. Ucan, Turk. J. Chem. 27, 453 (2003).
- 10. N. Levin and W. H. Hartung, J. Org. Chem. 7, 408 (1942).
- 11. H. E. Ungnade, B. Fritz, and L. W. Kissinger, Tetrahedron **19**, 235 (1963).
- 12. H. E. Ungnade, L. W. Kissinger, A. Narath, and D. C. Barham, J. Org. Chem. **28**, 134 (1963).
- 13. J. E. Caton and C. V. Banks, Inorg. Chem. 6, 1670 (1967).
- A. Nakamura, A. Konishi, and S. Otsuka, J. Chem. Soc., Dalton Trans., 488 (1979).
- 15. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Wiley, New York, 1988).
- M. A. Deveci and G. Irez, Synth. React. Inorg. Met.-Org. Chem. 26, 871 (1996).