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Synthesis of Iminooxime Derivatives and Investigation of Their Complexes[1]

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Abstract—Three novel ligands, a-pycolyliminoisonitrosoacetophenone ($L^1H \cdot HCl$), α-pycolylimino-*p*-methylisonitrosoacetophenone ($L^2H \cdot HCl$), and a-pycolylimino-p-chloroisonitrosoacetophenone L^3H, were synthesized. Their metal complexes with Co(II), Cu(II), and Ni(II) were prepared. The mononuclear complexes of these ligands with Co^{2+}, Cu^{2+}, and Ni^{2+} ions were obtained in ethanol. The structures of the ligands and their complexes were characterized by 1H NMR, IR spectroscopy, elemental analyses, and magnetic susceptibility.

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The early studies reported on derivatives of monoglyoximes, diaminoglyoximes, heterocyclic *vic*-dioximes, tetraoximes, and their some transition metal complexes [1–4]. In addition to cobaltoximes, which are regarded as vitamin B_{12} model compounds [5, 6], the Schiff base complexes of cobalt and a number of tetranitrogen macrocycles also serve as good models [7–9]. The Co(III) complexes (cobaltoximes) readily undergo reduction with $NaBH_4$ to give blue Co(I) compounds, which are capable of binding various alkyl or aryl groups [10, 11]. The coordination chemistry of *vic*-dioximes is interesting, and numerous transition metal complexes of these ligands have been investigated [8]. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure stabilized by hydrogen bonding.

Recently, several complexes of *vic*-dioximes and their derivatives are known to exhibit an anti-tumor activity for cancer researches. Another property of the *vic*-dioximes is the liquid crystalline character. Therefore, the aim of this study is to synthesize three new ligands, $L^1H \cdot HCl$, $L^2H \cdot HCl$, and L^3H, by the reactions of 2-(aminomethyl)pyridine with isonitrosoacetophenone, *p*-methylisonitrosoacetophenone, and *p*-chloroisonitrosoacetophenone and to prepare their complexes with Ni^{2+}, Co^{2+}, and Cu^{2+} ions.

EXPERIMENTAL

Elemental analyses were determined and ^1H NMR spectra were recorded on a Bruker GmbH Dpx–400 MHz high-performance digital FT-NMR spectrometer at the TUBITAK Laboratory (Center of Science and Technology Research of Turkey). IR spectra were recorded on a Perkin Elmer 1600 series spectrometer as KBr pellets, 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.

Isonitrosoacetophenone, *p*-methylisonitrosoacetophenone, and p-chloroisonitrosoacetophenone were prepared according to published procedures [12, 13].

Synthesis of α-picolyliminoisonitrosoacetophenone ($L^1H \cdot HCl$). Isonitrosoacetophenone (5.0 mmol, 0.745 g) was dissolved in 40 ml of diethyl ether, and then α-picolylamine (5.0 mmol, 0.54 g) was added dropwise with stirring at room temperature. The color of the solution was light yellow at first and turned dark within 30 min by stirring. Then it was stirred 1 h more, and absolute HCl gas was passed through this solution in cold. The light yellow crystals formed were filtered off, washed with diethyl ether, and dried in vacuum. The final product was soluble in ethyl alcohol, DMSO, and DMF. The yield was 0.97 g (70%).

IR (ν, cm^{-1}): 3478 ν(OHN), 3044 $\nu(CH_{ar})$, 2878 $\nu(CH_{alif})$, 1633 ν(CN), 1467 ν(CC), 989 ν(NO).

^1H NMR (δ, ppm): 12.60 s. (OH), 8.90 s. (HCN), 7.50–7.60 m. (CH_{ar}), 8.00–8.50 m. (CH_{Py}), 4.30 s. $(=NCH_2)$.

Synthesis α-picolylimino-*p*-methylisonitrosoacetophenone ($L^2H \cdot HCl$). *p*-Methylisonitrosoacetophenone (5.0 mmol, 0.815 g) was dissolved in 40 ml of diethyl ether, and then α-picolylamine (5.0 mmol, 0.54 g) was added dropwise with stirring at room temperature. The color of the solution was light yellow at first and turned dark within 30 min. Then it was stirred

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[†] Deceased.

[1] The text was submitted by the authrs in English.

Table 1. Elemental analyses data and some physical properties of iminooximes derivatives and their complexes

Compound	Empirical formula	Color	μ_{eff}, μ_B	M.p. (decomp.), °C	Yield, %	Contents (calcd/found), %				
						C	H	N	M	Cl
$L^1H \cdot HCl$	$C_{14}H_{14}N_3OCl$	Light yellow		(210)	70	60.98/60.66	5.12/4.78	15.24/15.45		12.86/12.56
$L^2H \cdot HCl$	$C_{15}H_{16}N_3OCl$	Light yellow		(215)	76.8	62.18/61.86	5.53/5.82	14.58/14.88		12.26/12.10
L^3H	$C_{14}H_{12}N_3OCl$	Yellow		(220)	71.4	61.42/61.40	4.39/4.15	15.36/15.20		12.98/12.76
L^1Cu	$C_{14}H_{12}N_3OClCu$	Brown	1.74	135	45	49.85/49.50	3.56/3.48	12.46/12.24	8.84/18.46	10.53/10.23
$(L^1H)_2Ni$	$C_{29}H_{27}N_6O_2Ni$	Light brown	3.28	140	40	55.29/55.68	5.28/5.87	13.82/13.42	9.66/9.25	11.68/11.37
$(L^1H)_2Co$	$C_{29}H_{27}N_6O_2Co$	Deep brown	3.15	160	45	55.26/55.43	4.27/4.67	13.82/13.72	9.70/9.38	11.68/11.45
L^2Cu	$C_{15}H_{14}N_3OClCu$	Green	1.71	102	52	51.28/41.36	3.99/3.76	11.96/12.41	18.09/18.00	10.11/9.95
L^2Ni	$C_{15}H_{14}N_3OClNi$	Light brown		104	36	52.00/53.74	4.04/4.28	12.13/13.72	16.95/16.55	10.25/10.53
$(L^2H)_2Co$	$C_{31}H_{30}N_6O_2Co$	Brown	3.80	170	48	56.60/57.05	4.72/4.42	13.21/13.48	9.28/9.68	11.16/11.50
L^3Cu	$C_{14}H_{11}N_3OCl_2Cu$	Green	1.78	164	60	45.22/45.42	3.96/4.08	11.30/11.54	17.09/17.28	19.11/19.46
L^3Ni	$C_{14}H_{11}N_3OCl_2Ni$	Green	2.73	215	50	45.81/45.44	3.00/3.48	11.45/11.48	16.00/16.22	19.36/19.05
L^3Co	$C_{14}H_{11}N_3OCl_2Co$	Light brown	1.98	210	65	45.77/45.27	3.00/2.68	11.44/11.22	16.08/16.53	19.35/20.05

Table 2. Data of the ^1H NMR spectra of the ligands in DMSO-d^6 (δ, ppm)

Ligand	O–H	H–C=N	C–H_{ar} (C–H_{Py})	=N–CH_2	CH_3
$L^1H \cdot HCl$	12.60 s.	8.90 s.	7.50–7.60 m. (8.00–8.50) m.	4.30 s.	
L^3H	12.90 s.	8.85 s.	7.50–7.70 m. (8.00–8.60) m.	4.25 s.	
$L^2H \cdot HCl$	12.65 s.	8.85 s.	7.60–7.85 m. (8.10–8.70) m.	4.30 s.	2.50 s.

1 h more, and absolute HCl gas was passed into this solution in a cold medium. The light yellow crystals formed were filtered off, washed with diethyl ether, and dried in vacuum. The final product was soluble in DMSO, DMF, ethyl alcohol, and water. The yield was 1.12 g (76.8%).

IR (ν, cm^{-1}): 3456 ν(OHN), 3047 ν(CH_{ar}), 2826 ν(CH_{alif}), 1638 ν(CN), 1475 ν(CC), 992 ν(NO).

^1H NMR (δ, ppm): 12.65 s. (OH), 8.85 s. (HCN), 7.60–7.85 m. (CH_{ar}), 8.10–8.70 m. (CH_{Py}), 4.30 s. (=NCH_2), 2.50 s. (CH_3).

Synthesis α-picolylimino-*p*-chloroisonitrosoacetophenone (L^3H). *p*-Chloroisonitrosoacetophenone (5 mmol, 0.920 g) was dissolved in 40 ml of absolute ethanol and then 5 mmol (0.54 g) α-picolylamine was added dropwise with stirring at room temperature. After 15 min yellowish crystals started to form. Stirring was continued further for 1 h. The crystals formed were filtered off, washed with ethanol, and dried in vacuum. The final product was soluble in DMSO, DMF, and $CHCl_3$. The yield was 0.98 g (71.4%).

IR (ν, cm^{-1}): 3430 ν(OHN), 3030 ν(CH_{ar}), 2882 ν(CH_{alif}), 1635 ν(CN), 1481 ν(CC), 995 ν(NO).

^1H NMR (δ, ppm): 12.90 s. (OH), 8.85 s. (HCN), 7.50–7.70 m. (CH_{ar}), 8.00–8.60 m. (CH_{Py}), 4.25 s. (=NCH_2).

Synthesis of Ni(II), Co(II), and Cu(II) complexes of L^1H, L^2H, and L^3H. A solution of $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, or $CuCl_2 \cdot 2H_2O$ (5 mmol) dissolved in 20 ml of distilled water and added dropwise with stirring to a solution of ligand (5.0 mmol; 1.20 g of L^1H, 1.27 g of L^2H, or 1.37 g of L^3H), which was dissolved

Table 3. IR spectrum (ν, cm^{-1}) data of iminooximes derivatives and their complexes*

Compound	O–H···N	$C–H_{ar}$	$C–H_{aliph}$	C=N	C=C	N–O
L^1H	3478	3044	2878	1633	1467	989
L^3H	3430	3030	2882	1635	1481	995
L^2H	3456	3047	2826	1638	1475	992
L^2Ni		3036	2860	1606	1425	967
$(L^2H)_2Co$	3415	3072	2848	1606	1445	900
L^2Cu		3045	2890	1608	1463	974
$(L^1H)_2Ni$	3412	3060	2860	1642	1454	989
$(L^1H)_2Co$	3414	3061	2848	1648	1453	990
L^1Cu		3035	2855	1635	1475	976
L^3Ni		3071	2853	1645	1445	896
L^3Co		3071	2853	1592	1441	906
L^3Cu		3067	2853	1589	1476	890

* KBr pellets.

in 50 ml of ethyl alcohol. The pH of the reaction mixture was adjusted from 3.0–3.5 to 5.0–5.5 with a 1% NaOH solution. The formed complexes were stirred in a water bath at 70°C for 30 min, then filtered off, washed with water and alcohol, and dried in vacuum. The obtained complexes were soluble in DMSO and DMF.

The elemental analyses data and some physical properties of the ligands and their complexes are given in Table 1.

Their ^1H NMR and IR spectral data are presented in Tables 2 and 3, respectively.

RESULTS AND DISCUSSION

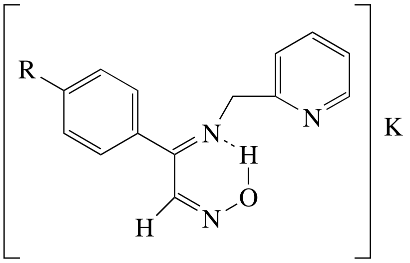
In the present work, the ligands have been synthesized by two ways. L^3H was synthesized by the reaction of α-picolylamine with *p*-chloroisonitrosoacetophenone in absolute alcohol at room temparature. The other compounds, $L^1H \cdot HCl$ and $L^2H \cdot HCl$, were synthesized by the reaction of α-picolylamine with isonitrosoacetophenone or p-methylisonitrosoacetophenone in dry ether at room temperature. Moreover, these compounds were obtained in the form of their hydrochloride salts, because no precipitates were formed in their solutions in cold. The complexes of each ligand with Ni^{2+}, Co^{2+}, and Cu^{2+} ions were isolated. The structures of the ligands and their complexes were characterized by elemental analyses, ^1H NMR, and IR spectroscopy.

^1H NMR spectra of the ligands and their complexes. All the ^1H NMR spectra of the iminooxime derivatives were taken in DMSO-d_6 (Table 2). The N–OH protons gave a low-field shift as a singlet in a region of 12.65–12.90 ppm due to the intramolecular hydrogen bonding [14–16]. The disappearance of this peak by the addition of D_2O to the solution evidenced that this chemical shift belongs to the N–OH proton.

The protons (C–H) adjacent to the oxime groups lie at 8.85 ppm [16–18]. The chemical shift values of the aromatic protons of the benzene and pyridine rings were observed at 8.70–7.50 ppm [14, 16]. The protons of the $=N–CH_2–$ and $–CH_3$ groups were observed at 4.25 and 2.50 ppm as singlets, respectively. The $–CH_2$ protons adjacent to nitrogen exhibit low-field shifts compared with their normal chemical shift values [19–22].

IR spectra of the ligands and their complexes. IR spectroscopy results for the ligands and their metal complexes are presented in Table 3. The IR spectrum of the –OH group of oxime shows stretching vibration at 3450 and 2300 cm^{-1} instead of a band at 3300 cm^{-1} because of an intramolecular hydrogen bonding (N····H–O–) [16]. The stretching band of the imine group (C=N) of these compounds was observed at 1638–1630 cm^{-1}. A band belonging to the N–O group was observed at 990 cm^{-1}. These values are in agreement with literature [16, 23–25].

According to the results of IR spectroscopy, elemental analyses data, and melting points (~220°C decomposition), the structures of the ligands may be written in the following form:



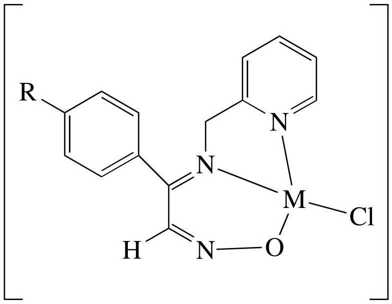
R = H, K = HCl;
R = CH_3, K = HCl;
R = Cl.

By examining the IR spectra of the complexes, we observed that the OH bands of the hydroxylimine group (3450 and 2350 cm^{-1}) of the ligands show a hydrogen band bridge, which was present no more in the IR spectra of L^1Cu, L^2Cu, L^3Ni, L^3Cu, and L^3Co complexes. Because of the absence of the OH band at 3200 cm^{-1} in the IR spectra of the complexes, the central atom of the complexes is bonded directly with oxygen of the oxime group.

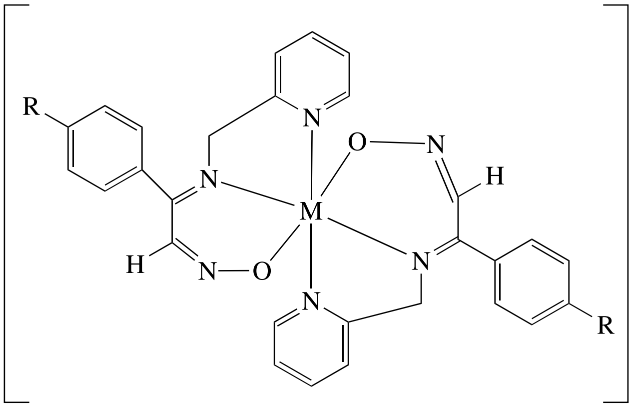
Moreover, the analyses for chlorine by the Mohr method were performed for the ligands and complexes. There are two chlorine ions bonded to the $(L^1H)_2Ni$, $(L^1H)_2Co$, $(L^2H)_2Ni$, and $(L^2H)_2Co$ complexes, and only one chlorine ion is bonded with the coordination sphere of the L^1Co, L^2Cu, L^3Ni, L^3Co, and L^3Cu complexes. This has been supported by the elemental analyses data given in Table 1.

Magnetic data of the complexes. The magnetic susceptibility of the complexes has been examined. The complex L^2Ni has got four coordination of d^8 configuration, and the diamagnetic nature of the compound shows that it acquires a square-planar structure. The paramagnetic measured data for the Ni(II) complexes has been found as 2.73 and 3.28 μ_B. According to these data, the value 3.28 μ_B shows that the complexes can be of tetragonal structure and sp^3d^2 hybridization. However, the value 2.73 μ_B indicates that the complexes can be of tetrahedral structure. In addition, this structure has been supported by the microanalyses. The complexes of Co(II) and Cu(II) have got paramagnetic properties. From them, the magnetic susceptibility of the complexes having d^7 configuration was measured and found as 1.98 for CoL_1, 3.15 for L_2Co, and 3.30 μ_B for L^3Co. These data and those obtained from the microanalyses show that the complex L^1Co can be square-planar and the complexes L^2Co and L^3Co can have tetragonal structures. The Cu(II) complexes having d^9 configuration were also examined and were found to exist in four coordination modes and their magnetic susceptibility is equal to 1.70 μ_B. These data are in agreement with literature [16, 22–24].

According to elemental analyses data and magnttic and IR spectrum data suggested structure of tetrahedral (**A**) and octahedral (**B**) complexes are shown below:



(A)



(B)

For A: R = H, L^1M, M = Cu(II);
R = CH_3, L^2M, M = Cu(II);
R = Cl, L^3M, M = Ni(II), Cu(II), and Co(II).
For B: R = H, $(L^1H)_2M$, M = Co(II), Ni(II);
R = CH_3, $(L^2H)_2M$, M = Co(II).

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