Scientific paper

Synthesis and Characterization of a Novel Iminooxime Schiff Base Ligand and Its Complexation with Copper(II), Nickel(II), Zinc(II), Cadmium(II), and Cobalt(II)

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Abstract

In this study, a novel iminooxime ligand having dimetoxide groups as well as its complexes with copper(II), nickel(II), zinc(II), cadmium(II), and cobalt(II) were synthesized. We have used 3,4-dimetoxyacetophenone as starting material, and synthesized isonitroso-3,4-dimetoxyacetophenone by reaction of 3,4-dimetoxyacetophenone with n-butyl nitrite in presence of sodium ethoxide. 3-hydroxyphenylimino-isonitroso-3,4-dimetoxyacetophenone(**3**) was obtained from reaction of such nitroso compound with 3-aminophenol and its complexes were prepared by treatment of iminooxime with metal salts as Cu(II), Ni(II), Zn(II), Cd(II), and Co(II) in methanol, respectively. All of the structures were characterized by using spectroscopic techniques.

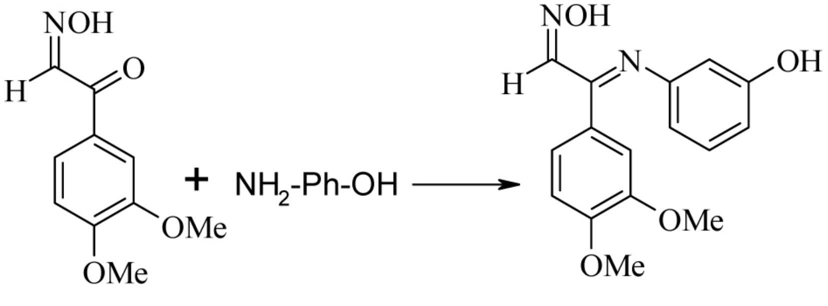
Keywords: Iminooxime, metal salts, schiff base, NMR spectroscopy

1. Introduction

Generally, the chelating ligands are polyfunctional molecules which can encage heavy metals in an organic sphere. Many types of Schiff base ligands are known and the properties of their metal chelates have been investigated.[1,2] Acyclic ligands containing nitrogen, oxygen and sulphur donor atoms in their structures can act as effective chelating agents for transition and non-transition metal ions.[3] The importance of the coordination compounds in biological structures, the increasing proportion of the application and utilization of these compounds as agents has given rise to an intensification into the investigations of the complexes, especially "vic-dioxime compounds". In technique, owing to resemble of the vic-dioxime compounds to vitamin B_{12} and chlorophyll as a color material of the plants, the importance on the illuminate of the biological structures[4,5] have increased. New synthetic methods need to be combined with new techniques in terms to "enabling technologies for organic synthesis" to achieve rapid incorporation into industrial processes.[6] Typical enabling technologies are microwave assistance, 3-new solvent systems,[7] continuous flow reactors[8] and immobilization of chemically active species such as reagents and homogeneous catalysts[9] which have recently seen widespread applications in research laboratories. Various successful examples of combining two or more of these techniques in order to achieve faster synthesis or improved work-up have recently appeared in the literature, particularly in the field of catalysis. Oximes, an important class of chelating agents,[10] have found numerous applications as highly selective reagents for the separation and determination of a number of metal ions.[10] In this study, iminooxime ligand and its metal complexes were synthesized according to the studies of the Ponzio.[11,12]

2. Experimental

All reagents were obtained either from Merck or Fluka, and used without further purification. Isonitroso-2,3-dimetoxyacetophenone and novel ligand, 3-hydroxyphenylimino-isonitroso-3,4-dimetoxyacetophenone, and its complexes were synthesized according to procedures described in literature. Mass spectrum, ^{13}C and ^{1}H NMR data were carried out at TÜBİTAK Research Laboratories (Turkish Research Council). IR Spectra were recorded on Jasco, FT/IR-300E. Electronic spectra were measured on



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3

Scheme 1. The illustration of the synthesis of the ligand (3).

Shimadzu UV-160A. Conductivities were measured in DMF using a LF 330 / SET conductivity meter at 24 °C. Magnetic moments were measured by the Gouy method, using Hg[Co(SCN)4] as calibrant.

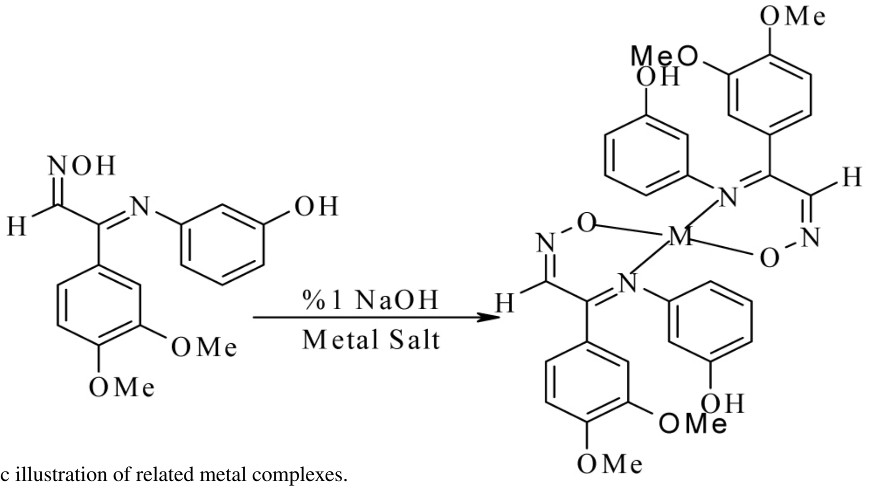
Synthesis of isonitroso-3,4-dimetoxyacetophenone (2): Isonitroso-3,4-dimetoxyacetophenone was synthesized by reaction of the 3,4-dimetoxyacetophenone with n-butyl nitrite in presence of sodium ethoxide.[11–13] The product was soluble in some solvents such as methanol, isopropyl alcohol, methylene chloride and chloroform, but was insoluble in hexane and carbon tetrachloride (isolated yield: 5.2 g (25%), m.p.: 123–124 °C).

Synthesis of 3-hydroxyphenylimino-isonitroso-3,4-dimetoxyacetophenone (3): The ligand was synthesized as follows. A mixture of solutions of isonitroso-3,4-dimetoxyacetophenone (0.002 mmol) in 20 mL methanol and 3-aminophenol (0.002 mmol) in 10 mL methanol was stirred on a magnetic stirrer for 4.5 h with heating. On cooling, the precipitates formed were filtered off and recrystallized in methanol.[11,12] Product was soluble in methanol, isopropyl alcohol, and chloroform, but insoluble in hexane and acetone (isolated yield: 0.298 g (47%), m.p.: 135–137 °C with decomposition).

Preparation of complexes: All of the complexes were prepared by the reaction of the Schiff base ligand 3 (0.004 mmol) in 20 mL methanol with the corresponding metal salts (0.004 mmol) in 10 mL methanol at 50 °C over 4 h. The resulting precipitate was filtered off and washed several times with methanol and dried over calcium chloride under vacuum.

3. Results and Discussion

In this paper, we describe the synthesis of novel iminooxime Schiff base ligand **3** by the reaction of isonitroso-3,4-dimetoxyacetophenone (**2**) with 3-aminophenol as mentioned. Our motive behind the synthesis of this type of ligands was to examine their possible applications in cation recognition processes, as homo or heteronuclear complexes which can be synthesized from alkaline and transition metal cations and may also serve as models of relevance to bioinorganic chemistry such as metalloenzymes. Even though an enormous number of Schiff base macrocycles and their complexes have already been described, many more interesting systems of this type await to be discovered. These structures are found to be powerful tools used to define interesting features related to general chemistry and application. Composition and proper-



Scheme 2. The schematic illustration of related metal complexes.

Table 1. Spectral Data of Newly Prepared Compounds.

Compound	Spectral data
2	IR ($\tilde{\nu}$, cm^{-1}): 3430 cm^{-1} (OH), 3100 cm^{-1} (C–H aryl), 1700 cm^{-1} (C=O), 1660 cm^{-1} (C=N oxime), 1450–1600 cm^{-1} (C=C aryl), 1220 cm^{-1} (Ar–O), 1006 cm^{-1} (N–O); ^{1}H NMR (300 MHz, CDCl$_3$) δ(ppm): 3.9–4.1 (s, 6H, (OCH$_3$)$_2$), 6.9–7.0 (d, 1H, C–H$_{arom.}$), 7.6–7.7(s, 1H, C–H$_{arom.}$), 7.8 (d, 1H, C–H$_{arom.}$), 8.0–8.1 (s, 1H, HC(=N)), 8.3(s, 1H, N–OH); ^{13}C NMR (75 MHz, CDCl$_3$) δ(ppm): 55.1–58.5 (CH$_3$), 113.8 (C$_{ar}$H), 115.1 (C$_{ar}$H), 123.6 (C$_{ar}$H), 130.7 (C$_{ar}$–C=O), 147.4 (C=N), 151.3 (C$_{ar}$–OCH$_3$), 155.6(C$_{ar}$–OCH$_3$), 183.8 (C=O); Mass spectra (FAB), m/z: 210.01 (MH$^+$), 181 (M$^+$–C$_2$H$_4$, 100%), 150 (M$^+$–C$_2$H$_4$NOH, 8%), 137 (M$^+$–C$_3$H$_5$NOH, 60%), 122 (M$^+$–C$_4$H$_8$NOH, 10%).
3	IR ($\tilde{\nu}$, cm^{-1}): 3420 cm^{-1} (OH), 3050 cm^{-1} (C–H aryl), 1610 cm^{-1} (C=N oxime), 1650 cm^{-1} (C=N imin), 1450–1500 cm^{-1} (C=C aryl), 1220 cm^{-1} (Ar–O), 1110 cm^{-1} (C–N), 1010 cm^{-1} (N–O); ^{1}H NMR (300 MHz, CDCl$_3$) δ(ppm): 3.7–4.2 (s, 6H, (OCH$_3$)$_2$), 5.7 (s, 1H, OH), 6.6–6.8 (s, 1H, C–H$_{arom}$), 6.9–7.0 (s, 1H, C–H$_{arom.}$), 7.5–7.7 (dd, 5H, C–H$_{arom.}$), 8.0–8.1 (s, 1H, (HC(=N)), 8.2 (s, 1H, N–OH); ^{13}C NMR (75 MHz, CDCl$_3$) δ(ppm): 53.5–56.2 (CH$_3$), 107.8 (C$_{ar}$H), 113.6 (C$_{ar}$H), 117.2 (C$_{ar}$H), 119.3 (C$_{ar}$H), 123.8 (C$_{ar}$H), 127.1 (C$_{ar}$H), 134.4 (C$_{ar}$–C=N), 139.7 (C$_{ar}$H), 144.8 (C$_{ar}$–OCH$_3$), 147.4 (C=NOH), 151.1 (C$_{ar}$–OCH$_3$), 155.7 (C$_{ar}$–N), 158.6(C$_{ar}$–OH), 162.8 (C=N); Mass spectra (FAB), m/z: 301.07 (MH$^+$), 300 (M$^+$–H, 95%), 283 (M$^+$–OH$_2$, 40%), 258 (M$^+$–CHNOH, 75%), 150 (M$^+$–C$_7$H$_7$N$_2$O$_2$, 60%), 138 (M$^+$–C$_8$H$_7$N$_2$O$_2$, 100%).

Table 2. Illustration of IR data of newly prepared compounds and complexes (cm^{-1}).

Compoud	N–OH	C=O	C=N$_{oxim}$	C=N$_{imin}$	C=C$_{Ar}$	N–O	C–N	C–H$_{Ar}$	Ar–O	M–N	M–O
2	3433	1700	1660	–	1450 1600	1600	–	3100	1220	–	–
3	3420	–	1610	1650	1450 1500	1010	1110	3050	1220	–	–
Ni–(3)	3420	–	1620	1670	1450 1520	1010	1110	3050	1210	420	560
Cu–(3)	3420	–	1610	1660	1460 1560	1010	1110	3100	1220	480	540
Co–(3)	3200 3450	–	1620	1660	1450 1600	1010	1110	3050	1210	410	520
Zn–(3)	3400	–	1620	1650	1450 1520	1010	1110	3050	1220	440	580
Cd–(3)	3400	–	1610	1640	1400 1500	1010	1110	3050	1210	480	560

Table 3. Some analytical data and physical properties of newly prepared compounds and complexes

Compound	Empirical Formula	Formula wt.	Color	M. p. (°C)	Yield (%)	Found (calcd) %		
						C	H	N
2	$C_{10}H_{11}NO_4$	209	White	123–124	25	57.31 (57.39)	5.38 (5.30)	6.55 (6.67)
3	$C_{16}H_{16}N_2O_4$	300	White	135–137	47	62.78 (63.96)	5.43 (5.37)	9.23 (9.32)
Cu–(3)	$C_{32}H_{30}N_4O_8Cu$	661.5	Dark Green	300^d>	49	58.21 (58.06)	4.49 (4.60)	8.37 (8.42)
Ni–(3)	$C_{32}H_{30}N_4O_8Ni$	656.7	Dark Green	300^d>	31	58.50 (58.44)	4.52 (4.60)	8.47 (8.55)
Zn–(3)	$C_{32}H_{30}N_4O_8Zn$	663.4	Yellow	300^d>	30	57.71 (57.83)	4.63 (4.50)	8.57 (8.46)
Cd–(3)	$C_{32}H_{30}N_4O_8Cd$	710.4	Yellow	300^d>	26	53.97 (54.03)	4.07 (4.21)	7.89 (7.83)
Co–(3)	$C_{32}H_{34}N_4O_{10}Co$	656.9	Dark Brown	300^d>	38	55.50 (55.41)	4.78 (4.90)	8.11 (8.03)

d: Decomposition points of the corresponding molecule ties of these compounds and metal complexes are summarized in Tables 1–3.

The composition of the complexes is $[M–(3)_2] \cdot nH_2O$ for all complexes (n = 0 or 2). The metal complexes were prepared by treatment of ligand with appropriate metal Cu(II), Ni(II), Zn(II), Cd(II), and Co(II) acetates or chlorides, respectively. The molecular structure of novel ligand and its complexes were characterized by MS, FT-IR, UV-vis, ^{13}C, ^{1}H NMR spectra and magnetic susceptibility measurements. The main IR bands and their assignment are listed in Table 2. Significant frequencies were selected by comparing the IR spectra of the free ligand and its metal complexes. The absence of the O–H stretching and bonding vibrations from the spectra of the complexes indicates deprotonation of the O–H groups located at oxime groups (N–OH). A strong band, typical of $C=N_{oxime}$ and $C=N_{imin}$ stretching, is found in the 1610–1620 cm^{-1}, and 1640–1670 cm^{-1} range in the spectra of the complexes and free ligand, respectively. The both observed shifts in the C=N stretch region and deprotonation of the O–H groups located at oxime groups after complexation confirms the formation of coordinate bonds from the imine nitrogen and oxygen atom of oxime group to metal ion. When the spectra of the complexes are compared with that of the uncomplexed Schiff base ligand, the υ(C=N) band is shifted to a lower region.[14,15] This situation indicates that the imine nitrogen must be coordinated to the metal ion. Additionally, the characteristic carbonyl peak is not seen around 1700 cm^{-1} in the IR spectra of the free ligand. This data support the proposed structures of the complexes and free ligand. In the IR spectra of the free ligand and its complexes, the bands at 1110 cm^{-1} and 1210–1220 cm^{-1} can be attributed to C–N and C–O bonds, respectively. The occurrence of new bands in the 410–580 cm^{-1} region in the IR spectra of the metal complexes confirms the presence of metal-nitrogen and metal-oxygen bonds, respectively. Furthermore, the presence of broad absorption band centered at 3100 cm^{-1} in the IR spectra of the Co(II) complex indicate the presence of water molecules in metal complexes. This was also confirmed by elemental analyses. Electronic absorption spectral data showed π–π* transitions related to benzene ring at 220–260 nm and imine π–π* transition at 332–343 nm. Comparing the free ligand and its complexes, it can be seen that the imine π–π* transitions are shifted to some extent, because the imine nitrogen is involved in coordination with metal ion. For complexes, the ratios of the ligand to metal (L/M = 2:1) are founded by means of both UV spectra (Fig. 1 and 2) and elemental analyses. The magnetic measurements of the complexes are measured at room temperature. Nickel(II), cobalt(II, and copper(II) complexes are paramagnetic and their magnetic susceptibilities are 2.90, 4.10 and 1.82 B.M. respectively. Zinc(II) and cadmium(II) complexes are diamagnetic. ^{1}H NMR spectrum of the free ligand **3** and compound **2** clearly demonstrates the presence of a C=N–OH environment at 8.2 and 8.3 ppm, and the azomethine (CH=N) protons at 8.0 and 8.1 ppm, respectively. Comparing the chemical shifts values for the compounds **2** and **3**, it can be seen that there is no any great difference between them. The appearance of a new signal at 5.7 ppm may be assigned to the existence of –OH group of the ligand **3**, and aromatic C–H protons are observed at 6.6–7.8 ppm. The molar conductance values of the synthesized 3-hydroxyphenylimino-isonitroso-3,4-dimetoxyacetophenone and its Cu(II), Ni(II), Zn(II), Cd(II) and Co(II) complexes are in range from 2.5 to 33.5 Ω^{-1} cm^{2} mol^{-1} in DMF solutions, indicating the non-electrolite nature of these compounds. These values provide some indication to support our proposed structural conformation for complexes and the mass spectrum of the related compounds **2** and **3** exhibits the highest m/z peaks which are in agreement with the calculated values for compounds.

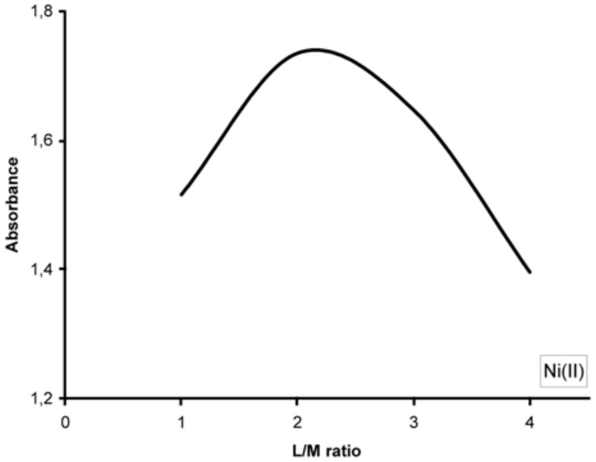


Fig. 1. Determination of ligand to metal ratio for Ni(II) by using of absorbance values.

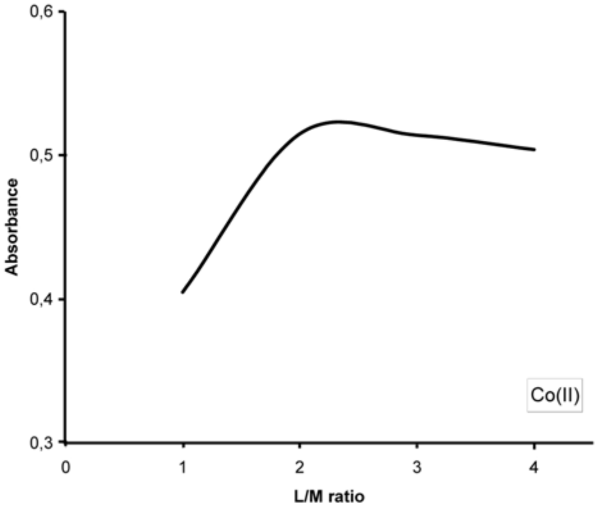


Fig. 2. Determination of ligand to metal ratio for Co(II) by using of absorbance values.

4. Conclusions

In this study, we reported the preparation of a novel iminooxime Schiff base ligand containing substitute groups and its complexes with the appropriate transition metal ions such as Cu, Ni, Zn, Cd and Co in methanol solution. The addition of some additional groups at the coordination system may enlarge the possibility of specific hetero-nuclear complexation with the consequent formation of ordered polynuclear complexes. These complexes may serve as models of relevance to bioinorganic chemistry such as metalloenzymes.

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6. References

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Povzetek

V prispevku je podana priprava novih iminooksimskih ligandov z dvema metoksidnima skupinama in njihovih kompleksov z bakrom(II), nikljem(II), cinkom(II), kadmijem(II) in kobaltom(II). Kot izhodno spojino smo vzeli 3,4-dimetoksiacetofenon iz katerega smo pripravili izonitrozo-3,4-dimetoksiacetofenon pri reakciji z n-butil nitritom v prisotnosti natrijevega etoksida. Z reakcijo ustrezne nitrozo spojine in 3-aminofenola smo pripravili 3-hidroksifenilimino-izonitrozo-3,4-dimetoksiacetofenon (**3**). Njegovi kompleksi s kovinskimi solmi, kot so Cu(II), Ni(II), Zn(II), Cd(II) in Co(II), so bili pripravljeni z obdelavo iminoksimov v metanolu kot topilu. Vsi komleksi so bili okarakterizirani s pomočjo spektroskopskih tehnik.