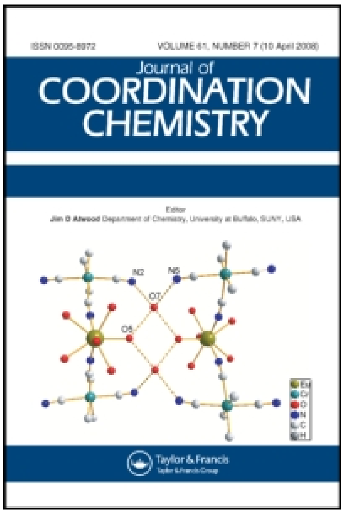


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and spectroscopic studies of new Cu(II), Ni(II), VO(IV) and Zn(II) complexes with *N*, *N*′-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis-(*o*-aminophenoxy)ethane

Hamdİ Temel[a]
[a] Dicle University, Faculty of Education, Chemistry Department, 21010 Diyarbakr, Turkey

To cite this Article Temel, Hamdİ(2004) 'Synthesis and spectroscopic studies of new Cu(II), Ni(II), VO(IV) and Zn(II) complexes with *N*, *N*′-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis-(*o*-aminophenoxy)ethane', Journal of Coordination Chemistry, 57: 9, 723 — 729

To link to this Article: DOI: 10.1080/00958970410001721024

URL: http://dx.doi.org/10.1080/00958970410001721024

J. Coord. Chem., Vol. 57, No. 9, 15 June 2004, pp. 723–729

SYNTHESIS AND SPECTROSCOPIC STUDIES OF NEW Cu(II), Ni(II), VO(IV) AND Zn(II) COMPLEXES WITH *N*, *N′*-BIS(2-HYDROXYNAPHTHALIN-1-CARBALDEHYDENE)-1,2-BIS-(*O*-AMINOPHENOXY)ETHANE

HAMDİ TEMEL*

Dicle University, Faculty of Education, Chemistry Department, 21010 Diyarbakır, Turkey

(Received 13 November 2003; In final form 24 April 2004)

A novel tetradentate, N_2O_2-type Schiff base, synthesized from 1,2-bis-(*o*-aminophenoxy)ethane and 2-hydroxynaphthalin-1-carbaldehyde, forms stable complexes with transition metal ions such as Cu(II), Ni(II), VO(IV) and Zn(II) in DMF. Microanalytical data, elemental analyses, magnetic measurements, ^{1}H NMR, UV, visible and IR-spectra as well as conductance measurements were used to confirm the structures.

Keywords: Schiff base; Cu(II), Ni(II), VO(IV), Zn(II) complexes

INTRODUCTION

Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most metal cations [1–6]. Transition metal complexes of tetradentate Schiff-base ligands find applications as models of certain metal enzymes and in catalysis and materials chemistry [7]. In the field of coordination chemistry, *ortho*-hydroxylated Schiff bases have received considerable attention [8,9]. Research on liquid crystals has discovered that the introduction of lateral polar hydroxy groups will enhance the molecular polarizability as well as stabilizing the liquid crystalline compounds [10]. A typical example is the effect of lateral hydroxyl groups on mesomorphism of azobenzene derivatives [11]. In addition, Schiff-base complexes are known to show antifungal activity, which is increased by the presence of hydroxy groups in the ligand [12].

In the present paper Cu(II), Ni(II), VO(IV) and Zn(II) complexes with the Schiff base derived from 1, 2-bis-(*o*-aminophenoxy)ethane and 2-hydroxynaphthalin-1-carbaldehyde are reported. These have been characterized by analysis of the solid

---

*Author for correspondence. E-mail: htemel@dicle.edu.tr

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001721024

complexes, elemental analysis, magnetic measurements, ^1H NMR, UV, visible and IR spectra as well as conductance studies. As far as we know, this is the first report on this ligand.

EXPERIMENTAL

All chemicals, such as the metal salts [$Cu(OAc)_2{\cdot}H_2O$, $Ni(OAc)_2{\cdot}4H_2O$, $Zn(OAc)_2{\cdot}H_2O$ and $VOSO_4{\cdot}2H_2O$] and solvents, were from Merck and used without purification. Conductivities of 10^{-3} M solutions of the complexes were measured in DMF at 25°C using a hand-held conductivity meter LF 330. The electronic spectra of the complexes in the UV-vis region were recorded in DMF solutions using a Shimatzu Model 160 UV-visible spectrophotometer. The IR spectra of the complexes were recorded with a Midac 1700 instrument in KBr pellets. ^1H NMR (400 MHz) spectra were recorded on a Bruker DPX-400 high performance digital FT-NMR spectrometer. Magnetic moments were determined on a Sherwood Scientific magnetic moment balance (Model No: MK1) at room temperature (23°C) using $Hg[Co(SCN)_2]$ as a calibrant: diamagnetic corrections were calculated from Pascal's constants [13]. The elemental analyses were conducted on a Carlo Erba instrument.

Synthesis of (*N*,*N′*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis-(*o*-aminophenoxy)ethane)

A solution of 2-hydroxynaphthalin-1-carbaldehyde (20.00 mmol, 2.72 g) in 50 cm^3 absolute ethanol was added dropwise over 2 h to a stirred solution of 1,2-bis(*o*-aminophenoxy)ethane (10.00 mmol, 2.44 g) dissolved in 50 cm^3 warm absolute ethanol. A solid mass separated on cooling, and the solution was kept in a refrigerator for better crystallization. It was then filtered, washed with ethanol and ether and subsequently dried over anhydrous $CaCl_2$ in a desiccator. This ligand is insoluble in all common organic solvents, acetone, alcohol, benzene, etc., and soluble in polar organic solvents such as DMF and DMSO. The yellow imines were purified by recrystallization from dimethyl formamide, m.p. 260°C; yield: 4.68 g (85%).

Spectral Characterization of the Ligand

Characteristic IR bands (KBr cm^{-1}): 3443 (phenolic, OH), 3069 (arom., C–H), 2959 (aliph., C–H), 1618 (–C=N), 1287 (phen., C–O). Characteristic ^1H NMR bands (DMSO-d_6, TMS, δ ppm): 13.00 (OH, s, 2H), 8.69 (HC=N, s, 2H), 7.00–7.89 (arom., CH, m, 20H), 4.35 (O–CH_2, s, 4H).

Synthesis of Cu(II), Zn(II) and Ni(II) Complexes

A solution of metal acetate (20 mmol) in DMF was mixed with the Schiff-base ligand (20 mmol) in DMF. The contents were refluxed in 150 cm^3 of DMF on an oil bath for 2–3 h. The refluxed solution was then poured into ice-cold water and a colored solid separated. The product was isolated by filtration, washed with ether, recrystallized from a mixture of dimethyl sulfoxide and dimethyl formamide and dried over anhydrous $CaCl_2$ in vacuum at room temperature. The yield was 55–60% for all complexes with respect to the ligand. The complexes decompose at 275–290°C and are almost insoluble in common organic solvents such as ethanol, methanol, benzene, acetone, nitrobenzene, dichloromethane and chloroform. However, they are slightly to fairly soluble in polar organic solvents (DMSO and DMF).

Synthesis of the VOL (IV) Complex

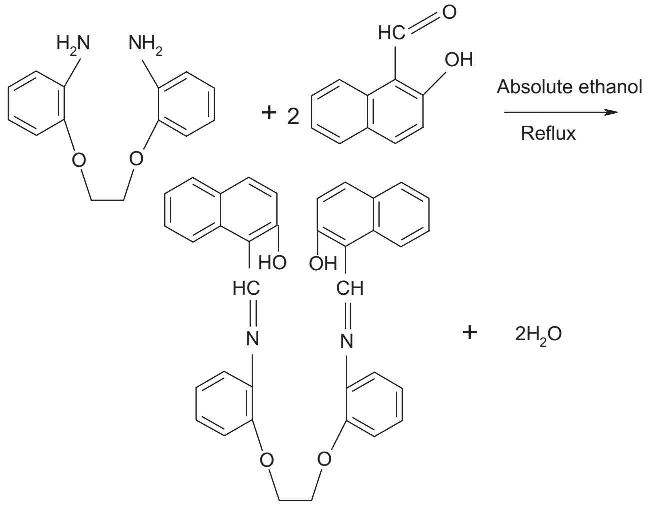
The salt $[VOSO_4 \cdot 2H_2O]$ (20 mmol) was dissolved in hot methanol (50 cm^3) and a mixture of NEt_3 (40 mmol) and the ligand (20 mmol) in DMF (50 cm^3) was added with stirring over about 10 min. The mixture was kept hot (60–64°C) and stirred for about 2–3 h. The solid complexes that separated after 24 h were filtered and washed with diethyl ether, hot water and ethyl alcohol. The resulting solid was recrystallized in 50 cm^3 DMSO/50 cm^3 DMF and dried over anhydrous $CaCl_2$ in vacuum at room temperature. The yield was 55%. This complex decomposes at 280–281°C and is almost insoluble in water but partially soluble in polar organic solvents (DMSO and DMF).

Spectral Characterization of Complexes

Characteristic IR bands for Ni(II) complex (KBr, cm^{-1}): 3444 (H_2O), 3053 (arom., C–H), 2937 (aliph., C–H), 1608 (–C=N), 1258 (phen., C–O), 522 (M–N) and 453 (M–O). Characteristic IR bands for Cu(II) complex (KBr, cm^{-1}): 3056 (arom., C–H), 2932 (aliph., C–H), 1603 (–C=N), 1245 (phen., C–O), 530 (M–N) and 455 (M–O). Characteristic IR bands for VO(IV) (KBr, cm^{-1}): 3430 (H_2O), 3064 (arom., C–H), 2958 (aliph., C–H), 1615 (–C=N), 1250 (phen., C–O), 964 (V=O) 550 (M–N) and 460 (M–O). Characteristic IR bands for Zn(II) (KBr, cm^{-1}): 3026 (arom., C–H), 2958 (aliph., C–H), 1623 (–C=N), 1258 (phen., C–O), 514 (M–N) and 460 (M–O). Characteristic ^1H NMR bands of the Zn(II) complex (DMSO-d_6, TMS, δ ppm): 8.76 (HC=N, s, 2H), 7.00–7.91 (arom., CH, m, 20H) and 4.30 (O–CH_2, s, 4H). Characteristic ^1H NMR bands of the Ni(II) complex (DMSO-d_6, TMS, δ ppm): 8.75 (HC=N, s, 2H), 7.00–7.80 (arom., CH, m, 20H), 4.30 (O–CH_2, s, 4H), 3.0 (H_2O, br, 2H).

RESULTS AND DISCUSSION

The new Schiff base *N*,*N*′-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis-(o-aminophenoxy)ethane (H_2L) was synthesized by condensation of 1,2-bis-(*o*-aminophenoxy)ethane [14] and 2-hydroxynaphthalin-1-carbaldehyde. The preparation of the Schiff base is described in Scheme 1.



SCHEME 1 Synthesis of the ligand (H_2L): *N*,*N*′-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis-(*o*-aminophenoxy)ethane.

TABLE I Some properties of the ligand and its complexes

Compound	*Color*	*F.Wt* (g/mol)	*M.p.* (°C)	*Yield* (%)	*Elemental analyses calculated (found), (%)*			μ_{eff} *(BM)*	Λ^a
					C	*H*	*N*		
Ligand (H_2L)	Yellow	552.00	260.0	60.0	78.26	5.07	5.07	–	–
$C_{36}H_{28}N_2O_4$					(78.39)	(5.35)	(5.29)		
CuL	Brown	613.5	290.0	55.0	70.42	4.24	4.56	1.61	5.0
$C_{36}H_{26}N_2O_4Cu$					(70.50)	(4.27)	(4.55)		
[NiL]H_2O	Green	626.7	284.0	60.0	68.93	4.47	4.47	Dia	3.7
$C_{36}H_{28}N_2O_5Ni$					(68.80)	(4.45)	(4.40)		
[VO(IV)L]H_2O	Dark yellow	634.9	275.0	55.0	68.04	4.41	4.41	1.74	2.1
$C_{36}H_{28}N_2O_6V$					(68.30)	(4.25)	(4.20)		
ZnL	Light yellow	615.4	288.0	52.0	70.20	4.22	4.55	Dia	3.2
$C_{36}H_{26}N_2O_4Zn$					(69.95)	(4.20)	(4.65)		

[a] $\Omega^{-1}\,\mathrm{mol}^{-1}\,\mathrm{cm}^2$ (measured in 10^{-3} M solution in DMF).

Microanalytical, molar conductance and magnetic susceptibility data of the ligand and its complexes are given in Table I. The stoichiometries of the ligand and its complexes were confirmed by their elemental analyses. The molar conductances measured in DMF of 10^{-3} M solutions of these complexes fall in the range 2.1–5.0 $\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$, indicative of non-electrolytic behavior [1–6].

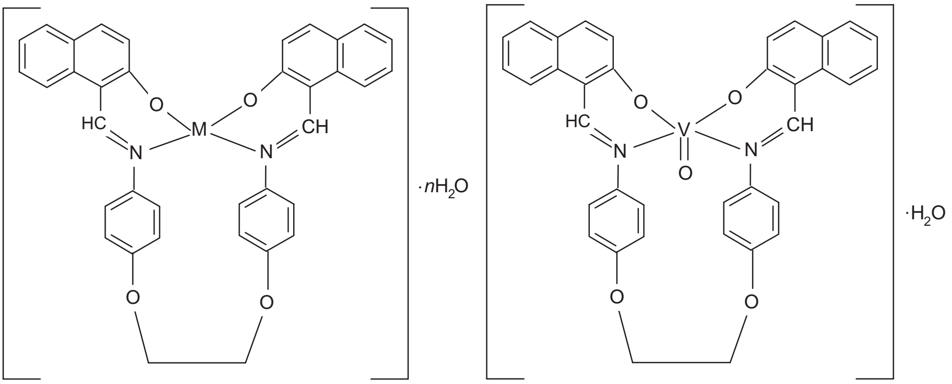
The reactions of the transition metal salts with the Schiff base are indicated by the following equations.

$$H_2L + Ni(OAc)_2{\cdot}4H_2O \rightarrow [NiL]{\cdot}H_2O + 2AcOH + 3H_2O$$

$$H_2L + Cu(OAc)_2{\cdot}H_2O \rightarrow CuL + 2AcOH + H_2O$$

$$H_2L + Zn(OAc)_2{\cdot}2H_2O \rightarrow ZnL + 2AcOH + 2H_2O$$

$$H_2L + VOSO_4{\cdot}2H_2O \rightarrow [VO(IV)L]{\cdot}H_2O + H_2SO4 + H_2O$$



M = Cu(II), Zn(II); $n = 0$. M = Ni(II); $n = 1$.

FIGURE 1 Suggested structures of the tetrahedral Zn(II) and square-planar Cu(II) and Ni(II) and square-pyramidal VO(IV)L complexes of H_2L.

The metal-to-ligand ratio of the Cu(II), Ni(II), VO(IV) and Zn(II) complexes was found to be 1:1 and in addition Ni(II) and VO(IV) complexes have one additional molecule of water of crystallization (Fig. 1). The observed magnetic moment of the Cu(II) complex' 1.61 BM, suggested square-planar stereochemistry. The VO(IV) complex has a magnetic moment of 1.74 BM suggesting square-pyramidal geometry. The Ni(II) and Zn(II) complexes are found to be diamagnetic as expected. These results are consistent with a square-planar geometry for the Ni(II) and tetrahedral geometry for the Zn(II) complex.

The complexes give fine powders and we were unable to prepare single crystals to obtain an X-ray structure.

Electronic Spectra

The electronic spectra of all the complexes were recorded in 10^{-3} M DMF at room temperature. The absorption spectra of the Schiff base are characterized by two absorption bands in the region 275–400 nm. In the spectra of the Schiff-base ligand, the aromatic bands at 221–297 nm ($\varepsilon = 2500\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}$) are attributed to a benzene $\pi \rightarrow \pi^*$ transition. The band at 475 nm ($\varepsilon = 505\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}$) is assigned to the imino $\pi \rightarrow \pi^*$ transition. The longer wavelength band is assigned to intramolecular charge transfer while the shorter wavelength is due to $\pi \rightarrow \pi^*$ transitions within the C=N bands influenced by CT interaction [15–17].

IR Spectra

Tentative assignments of the important bands of the Schiff base and corresponding metal complexes are recorded in Table II. The important features for the Schiff base and its complexes may be summarized as follows.

The ligand exhibits a weak absorption of ν(O–H) near $3443\,\text{cm}^{-1}$ due to hydrogen bonds associated with (O–H...O–H). The disappearance of this band in all the complexes suggests coordination of phenolic oxygen after deprotonation [18–20]. The

TABLE II Some IR frequencies (cm^{-1}) of the Schiff base and its complexes

Ligand (H_2L)	*CuL*	*NiL*	*VO(IV)L*	*ZnL*	*Assignment*
–	3440	–	3430	–	H_2O
3443w	–	–	–	–	Phenolic –OH (O–H···O)
1618s	1603	1608s	1615	1623s	Central C=N stretching
1287	1245	1258	1250	1258	Phenolic C–O stretching
–	530w	522w	550w	514w	ν(M–N)
–	455w	453w	460w	460w	ν(M–O)
–	–	–	964	–	V=O stretching

band at 1287 cm^{-1} in the IR spectrum of the ligand is ascribed to the phenolic C–O stretching vibration according to the assignment made by Kovacic [21] for salicylidene-anilines. This band is found in the region 1284–1245 cm^{-1} in the IR spectra of the complexes. These changes suggest that the *o*-OH group of this Schiff-base moiety has taken part in complex formation. The solid state IR spectra of the complexes compared with those of the ligand indicate that the C=N band at 1618 cm^{-1} is shifted to lower values for complexes of Cu(II), Ni(II) and VO(IV) and to higher value for the Zn(II) complex [1–6]. Conclusive evidence of the bonding is shown by the observation that new bands in the spectra of the metal complexes appear at 453–460 cm^{-1} and 514–550 cm^{-1} assigned to (M–O) and (M–N) stretching vibrations that are not observed in the spectra of the ligand [19–22]. Ni(II) and VO(IV) complexes show a broad band in the 3430–3440 cm^{-1} region indicating the presence of water molecules [1–6,22]. In addition, the vanadyl complex displays a band at 964 cm^{-1} assignable to V=O modes [23].

Magnetic Properties

The VO(IV) and Cu(II) complexes are paramagnetic and their magnetic moments are 1.74 and 1.61 BM, respectively. Since the VO(IV)and Cu(II) complexes are paramagnetic [1–6], their ^1H NMR spectra could not be obtained. The Ni(II) and Zn(II) complexes are diamagnetic and ^1H NMR spectra were obtained.

Conductivity

The complexes are non-electrolytes as shown by their molar conductivity (Λ_M) measurements in DMF, which are in the range 2.1–5.0 $\Omega^{-1} cm^2 mol^{-1}$ [1–6,17,19].

References

[1] H. Temel, Ü. Çakır, H.İ. Uğraş, M. Sekerci, *J. Coord. Chem.*, **56**, 943 (2003).

[2] H. Temel and M. Şekerci, *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 849 (2001).

[3] H. Temel, MBCAC III "3rd Mediterranean Basin Conference on Analytical Chemistry", Antalya, Turkey, PII 36 (2000).

[4] H. Temel, S. Ilhan, M. Şekerci and R. Ziyadanoğulları, *Spectrosc. Lett.*, **35**, 219 (2002).

[5] H. Temel and H. Hoşgören, *Transition Met. Chem.*, **27**, 609 (2002).

[6] H. Temel, S. Ilhan and M. Şekerci, *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 1627 (2002).

[7] A. Garoufis, S. Kasselouri, C.A. Mitsopoulou, J. Sletten, C. Papadimitriou and N. Hadjiliadis, *Polyhedron,* **18**, 39 (1999).

[8] G.Y. Yeap, S.T. Ha, N. Ishizawa, K. Suda, P.L. Boey and W.A.K. Mahmood, *J. Mol. Struct.*, **658**, 87 (2003).

[9] G.Y. Yeap, S.G. Teoh, S.B. Teo, S.C. Loh and H.K. Fun, *Polyhedron*, **15**, 3941 (1996).

[10] N.V.S. Rao, D. Singha, M. Das and M.K. Paul, *Mol. Cryst. Liq. Cryst.*, **373**, 105, (2002).

[11] A.K. Prajapati, R.A. Vora and H.M. Pandya, *Mol. Cryst. Liq. Cryst.*, **369**, 37, (2001).
[12] L. Chang-Hsien, *Synth. React. Inorg. Met.-Org. Chem.*, **23**, 1097 (1993).
[13] A. Earnshaw, *Introduction to Magnetochemistry*. (Academic Press, London, 1968), p. 4.
[14] (a) P.A. Tasker and E.B. Fleischer, *J. Am. Chem. Soc.*, **92**, 7072 (1970); (b) R. Jaunin and R. Holl, *Helv. Chim. Acta*, **192**, 1783 (1958); (c) J.F. Biernat and E. Luboch, *Tetrahedron*, **40**, 1927 (1984); (d) C. Cope, *J. Am. Chem. Soc.*, **57**, 572 (1935); (e) V. Baliah and K. Aparajıthan, *J. Ind. Chem. Soc.*, **69**, 255 (1992); (f) J.S. Bradshaw, H. Koyama, N.K. Dalley and R.M. Izatt, *J. Heterocyclic Chem.*, **24**, 1077 (1987); (g) J.F. Biernat, E. Jerecsek and A. Bujewski, *Pol. J. Chem.*, **53**, 2351 (1979); (h) A.P. King and C.G. Krespan, *J. Org. Chem.*, **39**, 1315 (1974).
[15] W. Guangbin, *Spectrosc. Lett.*, **32**, 679 (1999).
[16] N.T. Madhu and P.K. Radhakrishnan, *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 315 (2001).
[17] H. Temel, Ü. Çakır, B. Otludil and H.I. Uğraş, *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 1323 (2001).
[18] P.K. Sharma, A.K. Sen, K. Singh and S.N. Dubey, *J. Ind. Chem. Soc.*, **74**, 446 (1997).
[19] H. Temel, U. Çakır and H.İ. Uğraş, *Russ. J. Inorg. Chem.*, **46**(12), 1846 (2001).
[20] R.C. Maurya and P. Patel, *Spectroscop. Lett.*, **32**, 213–236 (1999).
[21] J.E. Kovacic, *Spectrochim. Acta,* **23A**, 183 (1967).
[22] K. Nakamato, *Infrared and Raman Spectra of Inorganic Compounds*. (J. Wiley & Sons, New York, 1978).
[23] A. Syamal, *Coord. Chem. Rev.*, **16**, 309 (1975).