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Tetradentate Schiff base ligands of 3,4-diaminobenzophenone: Synthesis, characterization and thermodynamics of complex formation with Ni(II), Cu(II) and Zn(II) metal ions

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Abstract: Some new symmetrical diimino tetradentate Schiff base ligands were synthesized by the reaction of 3,4-diaminobenzophenone with salicylaldehyde derivatives, such as [3,4-bis(((2-hydroxy-4-methoxyphenyl)methylene)amino)-phenyl]phenylmethanone (L^1), [3,4-bis(((2-hydroxy-5-methoxyphenyl)methylene)amino)phenyl]phenylmethanone (L^2), [3,4-bis(((5-bromo-2-hydroxyphenyl)methylene)amino)phenyl]phenylmethanone (L^3) and [3,4-bis(((2-hydroxy-5-nitrophenyl)methylene)amino)phenyl]phenylmethanone (L^4). Additionally, a tetradentate Schiff base ligand [3,4-bis(((2-hydroxy-3-methoxyphenyl)methylene)amino)phenyl]phenylmethanone (L^5) was synthesized. All the Schiff bases and their Ni(II), Cu(II) and Zn(II) complexes were characterized using elemental analysis and infrared, electronic, mass and ^{1}H-NMR spectroscopy. The formation constants of the complexes were measured using UV–Vis spectroscopic titration at constant ionic strength 0.10 M ($NaClO_4$), at 25 °C in dimethylformamide (DMF) as solvent.

Keywords: synthesis; tetradentate Schiff base; metal complex; diaminobenzophenone; formation constant.

INTRODUCTION

Tetradentate Schiff base ligands were synthesized by the reaction of diamines with the corresponding salicylaldehyde derivative. These reactions are important due to the great number of molecules that can be generated and the well-known ability of these tetradentate ligands to form stable complexes with different metal cations.[1]

The literature clearly shows that the study of Schiff base ligand systems is linked with many of the key advances made in inorganic chemistry.[2–4] They played a seminal role in the development of modern coordination chemistry.[5] Se-

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veral metal chelates of the ONNO donor class of Schiff bases were studied as oxygen carrier and they were found to be useful models for bioinorganic processes.[6,7] Schiff bases are effective inhibitors and could be adsorbed on the surface of metals.[8] Symmetric tetradentate Schiff base complexes have been extensively used as macrocycle models.[9] These compounds have received considerable attention because of their potential use as catalysts,[10–14] and their antibacterial,[5,15,16] antifungal,[17] antitumour[18,19] and herbicidal activities.[20]

The main goals of this study were the synthesis and characterization of some new tetradentate Schiff bases and their complexation with Ni(II), Cu(II) and Zn(II) metals. These compounds were characterized by elemental analysis, and FT–IR, ^{1}H-NMR, mass and UV–Vis techniques. In addition, the formation constants, K_f, were determined spectrophotometrically and the free energy changes, $\Delta G^{\ominus}$, at 25 °C, were calculated for the complexes. The effects of the electronic and steric nature of substituents on the Schiff base type ligands on the formation constants and free energy changes resulting from complex formation were studied.

EXPERIMENTAL

Materials and instruments

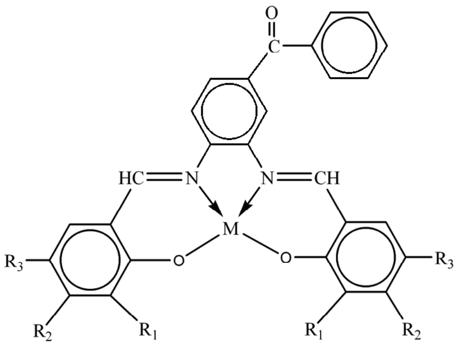
The materials, 3,4-diaminobenzophenone, 3-methoxysalicylaldehyde, 4-methoxysalicylaldehyde, 5-methoxysalicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, dimethylformamide, methanol, chloroform, nickel acetate tetrahydrate, zinc acetate dihydrate and copper acetate monohydrate were purchased from Merck and Fluka, Germany. Spectrograde solvents were used for the spectral measurements.

C, H, N analysis data were obtained using a Thermo Finningan Flash EA-1112 elemental analysis instrument. Melting points were measured in capillary tubes using a Buchi 535 melting point apparatus. The infrared spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer using the KBr pellet technique. The UV–Vis spectra were obtained in DMF on a Perkin Elmer Lambda 2-UV/Vis spectrophotometer. The ^{1}H-NMR spectra were recorded on a Bruker Avance DPX-250 MHz spectrometer with TMS as internal standard and the mass spectra were obtained on a Perkin-Elmer R MU-6E instrument.

Synthesis of the Schiff base ligands and their complexes

All the new tetradentate Schiff base ligands (L^1–L^4) were prepared by condensation of a derivative of salicylaldehyde (2 mmol) with 3,4-diaminobenzophenone (1 mmol) by refluxing in MeOH (30 cm^3) for 2 h. The final products were analytically pure solids after recrystallization from 1:1 chloroform/methanol mixed solvent for L^1, L^2 and L^3, and dimethylformamide/methanol mixture (1:1) for L^4. The products were dried at 50 °C under vacuum for 24 h. The L^5 Schiff base ligand was prepared according to a previously published method.[21]

Ni(II), Cu(II) and Zn(II) complexes of L^1, L^2 and L^3 were prepared by the addition of 1.5 mmol of the appropriate metal acetate hydrates dissolved in 10 cm^3 of methanol to a hot mixture of methanol (20 cm^3) and chloroform (15 cm^3) containing 1 mmol of the required Schiff base ligand. The mixture was then refluxed for 3 h for L^1, L^2 and L^3. The precipitated solids were recrystallized from methanol and dried under vacuum. The Ni(II), Cu(II) and Zn(II) complexes of L^4 were prepared in a similar way but the Schiff base ligand was dissolved in a hot mixture of methanol (15 cm^3) and DMF (20 cm^3). The same metal complexes of L^5 were also prepared by a similar method but dissolved in methanol at room temperature (Scheme 1).



M = Ni^{2+}, Cu^{2+}, Zn^{2+}
L^1: $R_1 = R_3 = H$, $R_2 = OMe$
L^2: $R_1 = R_2 = H$, $R_3 = OMe$
L^3: $R_1 = R_2 = H$, $R_3 = Br$
L^4: $R_1 = R_2 = H$, $R_3 = NO_2$
L^5: $R_2 = R_3 = H$, $R_1 = OMe$

Scheme 1. A structural representation of the Schiff base complexes.

Thermodynamic studies

The formation constants, K_f, were determined by UV–Vis absorption spectroscopy through titration of a fixed concentration (3×10^{-5} M) of the ligands with various concentrations of the metal ions (10^{-4}–10^{-5} M) at constant ionic strength (0.1 M $NaClO_4$) and at 25 °C. The interaction of $NaClO_4$ with the ligands in dimethylformamide was negligible. The absorption measurements were performed at various wavelengths, where the difference in the absorption was the maximum after equilibrium. The formed product exhibited different absorptions from those of the free ligand, while the metal ion solution showed no absorption at these wavelengths.

RESULTS AND DISCUSSION

The elemental analyses and some physical properties of the synthesized ligands and their complexes are collected in Table I.

TABLE I. The analytical and the physical data of the ligands and their complexes

Compound	Empirical formula	Formula weight	Yield %	Colour	M.p. °C	Found (Calcd.), % C	H	N
L^1	$C_{29}H_{24}N_2O_5$	480.62	78	Yellow	127	72.71 (72.49)	5.17 (5.03)	5.75 (5.83)
L^2	$C_{29}H_{24}N_2O_5$	480.62	70	Yellow	152	72.79 (72.49)	5.18 (5.03)	5.62 (5.83)
L^3	$C_{27}H_{18}N_2Br_2O_3$	578.36	80	Yellow	169	55.74 (56.08)	3.16 (3.14)	4.99 (4.84)
L^4	$C_{27}H_{18}N_4O_7$	510.63	83	Yellow	237	63.60 (63.53)	3.73 (3.55)	11.03 (10.98)
CuL^1	$C_{29}H_{22}N_2O_5Cu$	542.15	70	Brown	>250	64.35 (64.26)	4.12 (4.09)	5.15 (5.17)

TABLE I. Continued

Compound	Empirical formula	Formula weight	Yield %	Colour	M.p. °C	Found (Calcd.), %		
						C	H	N
CuL[2]	$C_{29}H_{22}N_2O_5Cu$	542.15	70	Brownish red	>250	64.21	3.95	5.12
						(64.26)	(4.09)	(5.17)
CuL[3]	$C_{27}H_{16}N_2Br_2O_3Cu$	639.88	54	Brown	>250	50.58	2.53	4.32
						(50.69)	(2.52)	(4.38)
CuL[4]	$C_{27}H_{16}N_4O_7Cu$	572.15	45	Green	>250	56.65	2.84	9.85
						(56.70)	(2.82)	(9.80)
CuL[5]	$C_{29}H_{22}N_2O_5Cu$	542.15	53	Brown	>250	64.10	4.14	5.20
						(64.26)	(4.09	(5.17)
NiL[1]	$C_{29}H_{22}N_2O_5Ni$	537.30	45	Brownish red	>250	64.71	4.18	5.04
						(64.84)	(4.13)	(5.21)
NiL[2]	$C_{29}H_{22}N_2O_5Ni$	537.30	71	Brownish red	>250	64.53	4.02	4.90
						(64.84)	(4.13)	(5.21)
NiL[3]	$C_{27}H_{16}N_2Br_2O_3Ni$	635.03	50	Brownish red	>250	50.80	2.45	4.44
						(51.07)	(2.54)	(4.41)
NiL[4]	$C_{27}H_{16}N_4O_7Ni$	567.30	55	Brownish red	>250	57.25	2.72	9.62
						(57.18)	(2.84)	(9.76)
NiL[5]	$C_{29}H_{22}N_2O_5Ni$	537.30	58	Brownish red	>250	64.62	4.23	5.11
						(64.84)	(4.13)	(5.21)
ZnL[1]	$C_{29}H_{22}N_2O_5Zn$	543.99	37	Yellow	>250	64.12	4.06	5.24
						(64.04)	(4.08)	(5.15)
ZnL[2]	$C_{29}H_{22}N_2O_5Zn$	543.99	70	Red	>250	64.14	4.10	4.29
						(64.04)	(4.08)	(5.15)
ZnL[3]	$C_{27}H_{16}N_2Br_2O_3Zn$	641.72	45	Orange	>250	56.42	2.46	4.29
						(56.51)	(2.51)	(4.37)
ZnL[4]	$C_{27}H_{16}N_4O_7Zn$	573.99	72	Yellow	>250	62.15	2.78	9.62
						(62.19)	(2.81)	(9.76)
ZnL[5]	$C_{29}H_{22}N_2O_5Zn$	543.99	40	Red	245	64.15	4.02	4.95
						(64.04)	(4.08)	(5.15)

Spectral characterization

^{1}H-NMR spectra. The ^{1}H-NMR spectra of the compounds were obtained in DMSO-d_6 and $CDCl_3$ at room temperature using TMS as the internal standard. The ^{1}H-NMR assignments of the compounds are presented in Table II. The chemical shift observed for the OH protons in the ligands (12.27–13.88 ppm) were not observed in any of the complexes. This confirms the bonding of the oxygen atoms to the metal ions (C–O–M).The presence of a sharp singlet for the –C(H)=N proton in the Schiff bases (7.99–9.15 ppm) clearly indicates that the magnetic environments for all such protons were similar, suggesting the presence of a planar ligand in these complexes.[22] The multiplets of the aromatic protons appeared within the range 6.15–8.63 ppm. In ligands L^1, L^2, L^5 and their complexes, the protons peak of O–CH_3 appeared in 3.69–3.86 ppm region.

TABLE II. ^{1}H-NMR data of the Schiff bases and their complexes (δ / ppm)

Compounds	OH	H–C=N	Ar–H	OMe
L^{1a}	12.27	8.63	6.45–7.77	3.81
L^{2a}	13.37	7.99	6.96–7.77	3.79
L^{3a}	12.75	8.61	6.92–7.76	–
L^{4b}	13.88	9.01	6.82–8.25	–
NiL^{1b}	–	8.14	6.31–7.80	3.80
NiL^{2b}	–	8.95	6.82–8.50	3.71
NiL^{3b}	–	8.46	6.77–8.10	–
NiL^{4b}	–	9.15	6.53–8.52	–
NiL^{5a}	–	9.15	6.53–8.50	3.75
ZnL^{1b}	–	8.91	6.15–8.16	3.73
ZnL^{2b}	–	9.08	6.63–8.25	3.69
ZnL^{3b}	–	8.25	6.63–7.97	–
ZnL^{4b}	–	8.96	6.73–8.63	–
ZnL^{5b}	–	9.04	6.40–8.21	3.73

^{a}CDCl$_3$; ^{b}DMSO-d_6

IR spectra. The IR spectra provided valuable information regarding the nature of the functional groups attached to the metal atom. The main infrared bands and their assignments are listed in Table III. The strong broad band in the IR spectra of the ligands in the range 3375–3463 cm^{-1} is assigned to O–H stretching vibrations, which is affected by the intramolecular hydrogen bond to the azomethine group (O–H···N=C). These bands disappeared through complexation with the metal ions.[23] The weak bands at 2823–3062 cm^{-1} are related to (C–H) vibrations. The band in the region 1643–1666 cm^{-1} is attributed to ($\nu_{C=O}$). The spectra of the ligands showed two different (–C=N) bands in the region 1527–1620 cm^{-1}, which were shifted to lower frequencies in the spectra of all the complexes, indicating the involvement of the –C=N nitrogen in the coordination to the metal ions. [24] The ring skeletal vibrations (C=C) were observed in the region 1427–1546 cm^{-1}. The phenolic C–O stretching vibrations appeared in the region 1188–1292 cm^{-1}. The assignment of the proposed coordination sites was further supported by the appearance of bands at 489–574 cm^{-1} and 412–493 cm^{-1}, which could be attributed to $\nu_{N–M}$ and $\nu_{O–M}$, respectively. All the IR data suggest that the metal was bonded to the Schiff bases through the phenolic oxygen and the imino nitrogen.[25]

Electronic spectra. The electronic spectra of the free ligands L$^{1–3}$ and L^5 show a weak band, as a shoulder in the region of 415–485 nm, which is assigned to n→π* transition involving molecular orbitals of the C=N chromophore and the benzene ring.[26–29] L^4 shows a sharp peak at 428 nm. The band in the range of 320–404 nm for L$^{1–3}$ and L^5 is assigned to π→π* type transition, which involves molecular orbitals essentially localized on the C=N group and the benzene ring; thus, the transition involves the azomethine group. This type of transition in L^4 is a sharp peak at 375 nm. These differences in shape and position of the band in L^4 are probably due to the presence of the NO_2 chromophore in the ligand (See Table IV).

TABLE III. The IR bands of the ligands and their complexes, cm^{-1} (*s* – strong, *m* – medium, *w* – weak)

Compounds	$\nu_{\text{O–H}}$	$\nu_{\text{C–H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=C}}$	$\nu_{\text{C–O}}$	$\nu_{\text{N–M}}$	$\nu_{\text{O–M}}$
L^1	3444	3047(*w*) 2927(*w*)	1647(*s*)	1612(*s*) 1584(*s*)	1546(*s*) 1508(*s*)	1234(*m*)	–	–
L^2	3463	3209(*w*) 2823(*w*)	1647(*s*)	1604(*s*) 1577(*s*)	1488(*s*) 1461(*s*)	1269(*m*)	–	–
L^3	3402	3047(*w*) 2927(*w*)	1643(*s*)	1620(*s*) 1554(*s*)	1469(*s*) 1446(*s*)	1276(*m*)	–	–
L^4	3382	3055(*w*) 2850(*w*)	1647(*s*)	1620(*s*) 1589(*s*)	1533(*s*) 1481(*s*)	1292(*m*)	–	–
CuL^1	–	2935(*w*) 2835(*w*)	1647(*s*)	1612(*s*) 1573(*s*)	1515(*s*) 1461(*s*)	1199(*m*)	516(*w*)	439(*w*)
CuL^2	–	2931(*w*) 2835(*w*)	1654(*s*)	1600(*s*) 1581(*s*)	1523(*s*) 1465(*s*)	1215(*m*)	505(*w*)	451(*w*)
CuL^3	–	3047(*w*) 2912(*w*)	1643(*s*)	1608(*s*) 1577(*s*)	1504(*s*) 1454(*s*)	1242(*m*)	516(*w*)	443(*w*)
CuL^4	–	2912(*w*) 3058(*w*)	1666(*s*)	1608(*s*) 1581(*s*)	1542(*s*) 1492(*s*)	1272(*m*)	524(*w*)	443(*w*)
CuL^5	–	2927(*w*) 2835(*w*)	1658(*s*)	1620(*s*) 1600(*s*)	1537(*s*) 1475(*s*)	1238(*m*)	520(*w*)	443(*w*)
NiL^1	–	2935(*w*) 2835(*w*)	1647(*s*)	1612(*s*) 1573(*s*)	1504(*s*) 1431(*s*)	1207(*m*)	528(*w*)	435(*w*)
NiL^2	–	2835(*w*) 2827(*w*)	1654(*s*)	1577(*s*) 1527(*s*)	1461(*s*) 1427(*s*)	1215(*m*)	509(*w*)	451(*w*)
NiL^3	–	3058(*w*) 2908(*w*)	1654(*s*)	1608(*s*) 1577(*s*)	1512(*s*) 1446(*s*)	1245(*m*)	516(*w*)	412(*w*)
NiL^4	–	3062(*w*) 2923(*w*)	1658(*s*)	1604(*s*) 1581(*s*)	1542(*s*) 1504(*s*)	1276(*m*)	516(*w*)	455(*w*)
NiL^5	–	3000(*w*) 2920(*w*)	1647(*s*)	1608(*s*) 1581(*s*)	1539(*s*) 1461(*s*)	1242(*m*)	574(*w*)	493(*w*)
ZnL^1	–	2923(*w*) 2854(*w*)	1647(*s*)	1608(*s*) 1577(*s*)	1519(*s*) 1427(*s*)	1188(*m*)	509(*w*)	466(*w*)
ZnL^2	–	2890(*w*) 2831(*w*)	1649(*s*)	1604(*s*) 1581(*s*)	1527(*s*) 1469(*s*)	1211(*m*)	489(*w*)	443(*w*)
ZnL^3	–	3047(*w*) 2908(*w*)	1651(*s*)	1612(*s*) 1581(*s*)	1515(*s*) 1461(*s*)	1245(*m*)	547(*w*)	497(*w*)
ZnL^4	–	2997(*w*) 2923(*w*)	1654(*s*)	1612(*s*) 1585(*s*)	1546(*s*) 1485(*s*)	1272(*m*)	505(*w*)	439(*w*)
ZnL^5	–	2997(*w*) 2920(*w*)	1647(*s*)	1608(*s*) 1577(*s*)	1539(*s*) 1465(*s*)	1230(*m*)	501(*w*)	439(*w*)

Shifts were observed in the visible spectra of the metal complexes when compared with those of the corresponding free ligands. The formation of the metal–nitrogen bond stabilizes the electron pair on the nitrogen atom, *i.e.*, the energy of the non-bonding orbital is lowered and the transition occurs at a lower wavelength. This band is obscured by a strong band which can be assigned to $\pi\rightarrow\pi^*$ type transitions involving the metal–ligand bonds.[30,31] The d–d band was not observed, as it was masked by the metal to ligand charge transfer (MLCT) band.

TABLE IV. The electronic spectral data of the Schiff bases and their complexes (nm) in DMF

Compounds	π–π^*	n–π^*	Charge transfer transition
L^1	393	450(*sh*)	–
L^2	338	485(*sh*)	–
L^3	344	477(*sh*)	–
L^4	375	428	–
L^5	331	415(*sh*)	–
NiL^1	390	–	452
NiL^2	390	–	478
NiL^3	386	–	484
NiL^4	323	–	392
NiL^5	395	–	467
ZnL^1	395	–	454
ZnL^2	382	–	481
ZnL^3	330	–	420
ZnL^4	330	–	390
ZnL^5	330	–	431
CuL^1	404	–	462
CuL^2	380	–	494
CuL^3	320	–	427
CuL^4	325	–	390
CuL^5	371	–	475

In the compounds, bands of the ligands were observed in the 331–393 nm and 415–485 nm ranges, as shoulders. In their complexes, the bands were shifted to lower energy. The spectral changes were observed in DMF solution when up to 3.5 equivalents of $Ni(OAc)_2$ were added relative to L^2. In the absence of the metal ion, the L^2 solution showed absorption bands at 338 and 485 nm as shoulders. As the metal ion solution was added, the signals of L^2 decreased and those of the new complex, NiL^2, at 390 and 478 nm increased in intensity with isosbestic points at 370 and 700 nm. After the addition of 3.5 equivalents of the metal ion, the solution showed only the signals for NiL^2. The same was valid for the other systems.

The electronic spectra of the complexes formed during the titration were the same as those of the separately synthesized complexes. The UV–Vis spectra of

L^2, NiL^2 from the titration and the synthesized NiL^2 product are shown in Fig. 1. The data show that the synthesized complex and the product of the titration are same. The results were same for the other systems.

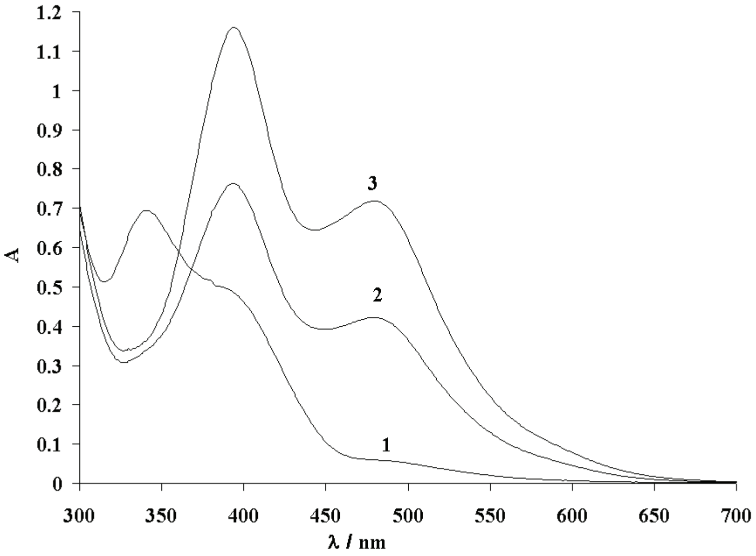


Fig. 1. UV–Vis spectra of the ligand L^2 (1), the end point of the titration of the ligand with Ni^{2+} (2), and the synthesized NiL^2 (3) in DMF.

Mass spectra. The mass spectra of the ligands and complexes show intense molecular ion peaks *m*/*z* $M^+/(M+H)^+$. In addition to these peaks, they show some peaks due to elimination of phenyl or benzyl derivative species from the molecular ion. The mass spectra of the compounds also show some prominent peaks corresponding to *m*/*z* $(M–Ar)^+$, $(M–Ar–CH)^+$, $(Ar)^+$, $(Ar–CH)^+$ and $(PhCO)^+$ (Table V). The fragmentation of the mass spectrum of the L^2 ligand is: 480 (M+, 9.9), 344 ($C_6H_5COC_6H_3N=CHC_6H_3OHOMeN$, 70.6), 239 ($C_6H_3N=CHC_6H_3OHOMeN$, 4.6), 221 ($C_6H_5COC_6H_3N=CHN$, 5.0), 180 ($C_6H_5COC_6H_3$, 3.2), 123 ($C_6H_3OHOMe$, 11.5), 105 ($C_6H_5CO$, 95.0), 77($C_6H_5$, 100.0) (Table V).

The formation constants

Complexes were obtained from the reaction of the metals with the Schiff base donors according to Eq. (1):

$$H_2L^x + M(OAc)_2 \rightleftarrows [ML^x] + 2HOAc \qquad (1)$$

The formation constants were determined by UV–Vis absorption spectroscopy through titration of the ligands with various concentrations of the metal ions at a constant ionic strength 0.1 M ($NaClO_4$) at 25 °C. The complex formation constants, K_f, were calculated using the SQUAD computer program,[32] designed to calculate the best values for formation constants by employing a non-linear, least squares approach. The free energy change $\Delta G^{\ominus}$ of the formed complexes were calculated from $\Delta G^{\ominus} = -RT \ln K_f$ at 25 °C, where K_f is the complex formation constant, R the gas constant and T the thermodynamic temperature (Table VI).

TABLE V. The mass spectra of the ligands and their complexes

Compound	*m*/*z*								
L^1	480	344	239	221	180	105	77		
L^2	480	344	240	181	105	77			
L^3	578	392	283	220	185	124	105	77	
L^4	510	360	253	178	105	77	57		
NiL^1	537	401	343	298	239	183	122	105	77
NiL^2	537	403	338	280	236	180	124	105	77
NiL^3	635	448	393	345	285	169	77		
NiL^4	567	418	345	240	183	137	105	77	
NiL^5	537	400	295	238	179	124	105		
ZnL^1	543	407	343	302	238	185	105	77	
ZnL^2	543	406	347	301	243	180	77		
ZnL^3	641	456	393	351	287	170	105	77	
ZnL^4	573	424	344	318	240	177	137	105	77
ZnL^5	543	407	342	239	180	123	77		
CuL^1	542	406	343	303	185	123	105	77	
CuL^2	542	408	302	179	122	105	77		
CuL^3	639	453	392	377	169	105	77		
CuL^4	572	406	345	301	183	105	77		
CuL^5	542	343	330	180	124	105	77		

TABLE VI. The formation constants, log K_f, and the thermodynamic free energy for the complexes of the ligands with the metal ions at 25 °C, in DMF and at I = 0.1 mol dm^{-3} ($NaClO_4$)

Ligand	Cu^{2+}		Ni^{2+}		Zn^{2+}	
	log K_f	$\Delta G^{\ominus}$ / kJ mol^{-1}	log K_f	$\Delta G^{\ominus}$ / kJ mol^{-1}	log K_f	$\Delta G^{\ominus}$ / kJ mol^{-1}
L^1	5.42(0.48)	–30.92(1.11)	5.63(0.04)	–32.10(0.32)	5.33(0.24)	–30.39(0.12)
L^2	5.84(0.43)	–33.30(0.76)	6.13(0.22)	–34.96(0.19)	5.11(0.30)	–29.14(0.74)
L^3	5.31(0.26)	–30.28(0.19)	5.41(0.04)	–30.85(0.37)	4.14(0.02)	–23.61(0.44)
L^4	3.67(0.01)	–20.93(0.07)	4.85(0.01)	–27.66(0.44)	2.42(0.63)	–13.80(1.31)
L^5	5.60(0.30)	–31.93(0.09)	5.79(0.06)	–33.02(0.19)	5.20(0.32)	–29.65(0.74)

The metal effect

The trend of the complex formation of the metal ions with a given ligand is as follows: $Ni^{2+} > Cu^{2+} > Zn^{2+}$.

The crystal field stabilization energy, *CFSE*, affects the stability of the produced complexes. Ni^{2+} has the highest *CFSE*; hence, it has the highest formation constant. The coordination around nickel is essentially square planar with a small tetrahedral distortion. The molecular structure of [Ni(salen)],[33] [Ni(cd$_5$Clsalen)][34] and [Ni(cdsalen)][35] were determined previously and may be compared with the structure of the present complexes NiL$^{1–5}$.

Zn(II), with a d^{10} configuration, has more potency to take a tetrahedral configuration; hence, it has the smallest formation constant, while Cu(II), with a d^9 configuration, tends to have a distorted square planar geometry because of the Jahn–Teller effect[36] (Table VI).

The electronic effect of para-*substituted Schiff base ligands*

For studying the electronic effect of *para* substitution on the Schiff base ligands, some different substituents were used. In the *para*-substituted Schiff base ligands, the formation constants vary as could be expected according to the electronic effect of the substituents at the *para* position. Thus, the formation constants decrease according to the sequence OMe > Br > NO_2. An electron-withdrawing functional group, such as NO_2, makes the Schiff base a poorer donor ligand and decreases the formation constant, while an electron-donor group, such as OMe, increases the formation constant. Therefore, the ligands having Br and NO_2 groups, (L^3) and (L^4), respectively, have the smallest formation constants, while the ligands with an OMe group have the highest (Table VI).[37,38]

The effect of the position of the methoxy substituent on the Schiff base

The results show the following trend of complex formation of either nickel(II) and copper(II) with the Schiff bases (Table VI): 5-OMe (L^2) > 3-OMe (L^5) > > 4-OMe (L^1).

In the case of L^2, the methoxy group was situated in the *para* position to the phenolic oxygen of the N_2O_2 backbone, which can release an electron directly to the phenyl ring compared with that of the *meta* and *ortho* positions in L^1 and L^5, respectively.[39]

The trend of the formation constant for the Zn^{2+} complexes is as follows: 5-OMe (L^2) < 3-OMe (L^5) < 4-OMe (L^1).

It seems, due to the preference of Zn^{2+} for a tetrahedral geometry, the steric factor predominates over the electronic factor.

CONCLUSIONS

Some new symmetrical di-imino tetradentate Schiff base ligands and their complexes with Ni(II), Cu(II) and Zn(II) were synthesized and characterized. The thermodynamic formation constants, K_f, were determined spectrophotometrically at 25 °C. By considering the formation constants and the free energy changes, the following conclusions were drawn.

The complex formation constant for Ni(II) was higher than Cu(II) and Zn(II) has the smallest formation constant: Ni(II) > Cu(II) > Zn(II).

An electron-donor group increases the formation constant, while an electron-withdrawing functional group decreases it. The trend of the formation constant is as follows: $ML^{1,2,5} > ML^{3} > ML^{4}$, M = Cu(II), Zn(II) and Ni(II).

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ИЗВОД

СИНТЕЗА ТЕТРАДЕНТАТНИХ ЛИГАНАДА ТИПА ШИФОВИХ БАЗА ПОЛАЗЕЋИ ОД 3,4-ДИАМИНОБЕНЗОФЕНОНА: СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И ТЕРМОДИНАМИЧКЕ КОНСТАНТЕ ФОРМИРАЊА КОМПЛЕКСА Ni(II), Cu(II) И Zn(II)

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У реакцији између 3,4-диаминобензофенона и деривата салицилалдехида, као што су [3,4-бис(((2-хидрокси-4-метоксифенил)метилен)амино)фенил]фенилметанон (L^1), [3,4-бис-(((2-хидрокси-5-метоксифенил)метилен)амино)фенил]фенилметанон (L^2), [3,4-бис(((5-бромо-2-хидроксифенил)метилен)амино)фенил]фенилметанон (L^3) и [3,4-бис(((2-хидрокси-5-нитрофенил)метилен)амино)фенил]фенилметанон (L^4), синтетисани су нови тетрадентатни лиганди типа Шифових база. Поред тога, у овом раду описана је синтеза тетрадентатног лиганда [3,4-бис(((2-хидрокси-3-метоксифенил)метилен)амино)фенил]фенилметанона (L^5), који такође припада типу Шифових база. Добијени лиганди су употребљени за синтезу одговарајућих Ni(II), Cu(II) и Zn(II) комплекса. За карактеризацију ових комплекса употребљени су елементарна микроанализа, инфра-црвени, електронски, масени спектри. Поред тога, за карактеризацију комплекса, осим за Cu(II) комплексе, употребљени су и њихови ^{1}H-NMR спектри. Дате су вредности за константе грађења комплекса, као и вредности за неке термодинамичке параметре, који су одређени помоћу UV–Vis спектрофотометрије у 0,10 M $NaClO_4$ на 25 °C у диметилформамиду (DMF) као растварачу.

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