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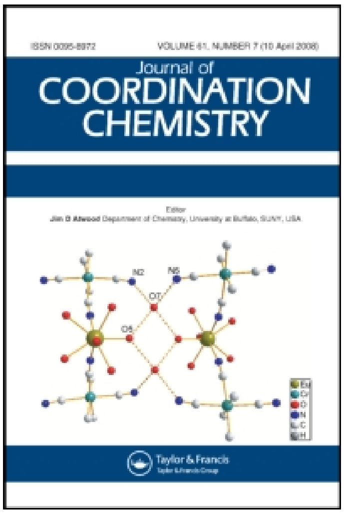

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Interaction of Co(II), Ni(II), Cu(II), and Zn(II) with 12- and 14-membered macrocycles containing O_2N_2 donors

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The 12- and 14-membered diazadioxo macrocyclic ligands, 1,2 : 7,8-diphenyl-6,9-diaza-3,12-dioxocyclododecane (L^1) and 1,2 : 8,9-diphenyl-7,10-diaza-3,14-dioxocyclotetradecane (L^2), were synthesized by condensation between *o*-phenylenediamine, 1,2-dibromoethane/1,3-dibromopropane, and catechol. Metal complexes [ML^1Cl_2] and [ML^2Cl_2] [M = Co(II), Ni(II), Cu(II), and Zn(II)] were prepared by interaction of L^1 or L^2 with metal(II) chlorides. The ligands and their complexes were characterized by elemental analyses, IR, ^1H, and ^{13}C NMR, EPR, UV-Vis spectroscopy, magnetic susceptibility, conductivity measurements, and Electrospray ionization-mass spectral (ESI-MS) studies. The results of elemental analyses, ESI-MS, Job's method, and conductivity measurements confirmed the stoichiometry of ligands and their complexes while absorption bands and resonance peaks in IR and NMR spectra confirmed the formation of ligand framework around the metal ions. Stereochemistry was inferred from the UV-Vis, EPR, and magnetic moment studies.

Keywords: Diazadioxo macrocyclic ligands; Spectral studies; Octahedral complexes; Transition metals; Job's method

1. Introduction

Synthetic macrocycles have been known for over 75 years, although a real spate of publication in this area was observed in the late 1960s [1]. Nature prefers macrocyclic derivatives for many fundamental biological functions, such as photosynthesis and transport of oxygen in mammalian and other respiratory systems [2]. Hence, the synthesis and studies of model systems show important properties, such as thermodynamic and kinetic stability [3], electron transfer and magnetic interactions between metal centers [4]. These are affected by ring size, coordination sites, and electronic effects [5] of the ligand. The stability of a macrocyclic metal complex depends upon number and type of donors present in the ligand, their relative positions within the macrocyclic skeleton, and number and size of the chelate rings formed on complexation [6]. Macrocyclic ligands with additional donors appended to the ring have considerable interest because

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of their capacity to bind and transport metal ions, for the potential to prepare and study mixed-valence forms, and as models for metalloproteins [7, 8]. Macrocycles offer exciting possibilities to construct supramolecular assemblies that are capable of performing highly specific molecular functions. Molecular recognition between these compounds and their guests, mostly transition metal ions or biomolecules (nucleic acids, proteins, etc.), provides a good opportunity for studying key aspects of supramolecular chemistry, significant in a variety of disciplines including bioorganic chemistry, biocoordination chemistry, biology, medicine, and related science and technology [9–11]. Multi-donor ligands and particularly mixed donors are important due to the presence of several potential donor centers and their flexibility to bind with biomolecules or to coordinate with various metal ions. Mixtures of two or more donor sites have also been employed to tune selectivity and stability [12]. A number of mixed donor macrocycles have been reported [5, 7, 13–15] incorporating O_2N_2, O_3N_2, O_2N_3, or N_4O_2 donor sets. To extend the chemistry of mixed N or O donor ligands, we report herein the synthesis of the 12–14 membered diazadioxo macrocycles, their complexes with Co(II), Ni(II), Cu(II), and Zn(II) and their physico-chemical properties.

2. Experimental

2.1. *Materials and methods*

Metal salts (all Merck) were used as received. *o*-Phenylenediamine (Reachim), catechol (Central Drug House, India), 1,2-dibromoethane, and 1,3-dibromopropane (both Merck) were commercially pure compounds and used as received. Solvents were reagent grade and purified by usual methods.

2.2. *1,2 : 7,8-Diphenyl-6,9-diaza-3,12-dioxocyclododecane (L^1)*

Hot ethanolic solutions (~25 cm^3) of *o*-phenylenediamine (1.0 mmol) and 1,2-dibromoethane (2.0 mmol) were mixed slowly with constant stirring. To this mixture was added an ethanolic solution (~25 cm^3) of catechol (1.0 mmol) in the presence of a few drops of aqueous sodium hydroxide and refluxed for 6 h. Cooling gives a brown precipitate, which was filtered and washed several times with EtOH to remove any traces of starting materials. Finally the product was washed with diethyl ether and dried in a vacuum desiccator over anhydrous calcium chloride.

2.3. *1,2 : 8,9-Diphenyl-7,10-diaza-3,14-dioxocyclotetradecane (L^2)*

The same procedure as above for the synthesis of L^2 except that 1,3-dibromopropane was used instead of 1,2-dibromoethane.

2.4. *Preparation of [ML^1Cl_2] [M = Co(II), Ni(II), Cu(II), and Zn(II)]*

Hot ethanolic (~25 cm^3) solutions of L^1 (0.27 g, 1.0 mmol) and corresponding metal salt (1.0 mmol) were mixed together with constant stirring. The mixture was refluxed for

2–4 h, giving a colored complex. It was filtered, washed with ethanol, and dried under vacuum over anhydrous $CaCl_2$.

2.5. *Preparation of [ML^2Cl_2] [M = Co(II), Ni(II), Cu(II), and Zn(II)]*

A similar procedure was adopted for the synthesis of complexes of L^2 (0.298 g, 1.0 mmol) as for complexes derived from L^1.

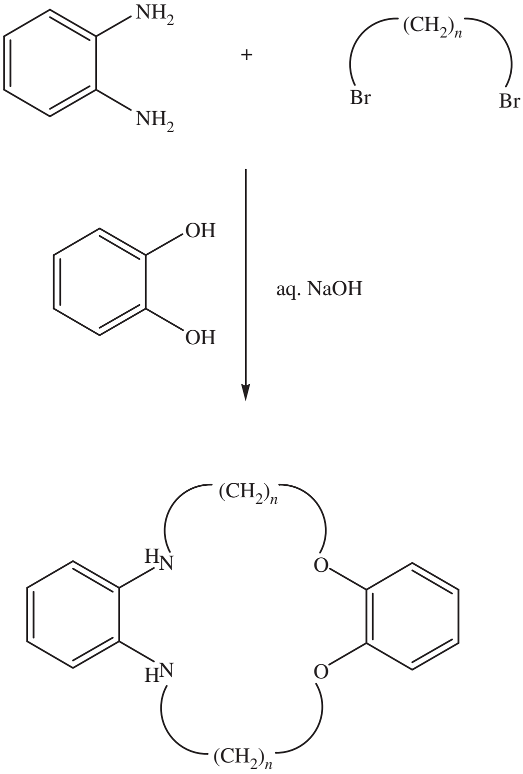
2.6. *Physical measurements*

Elemental analyses were obtained from the Microanalytical laboratory of the Central Drug Research Institute (CDRI), Lucknow, India. IR spectra (4000–200 cm^{-1}) were recorded as KBr/CsI discs on a Perkin Elmer – 2400 spectrometer. Metals and chloride were determined volumetrically [16] and gravimetrically [17], respectively. ^1H and ^{13}C-NMR spectra were recorded in DMSO-d_6 using a Bruker Avance II 400 NMR spectrometer with Me_4Si as an internal standard from SAIF, Punjab University, Chandigarh. Electrospray ionization-mass spectra (ESI-MS) of the ligands and their complexes were recorded on a micromass quattro II triple quadruple mass spectrometer. Magnetic susceptibility measurements were carried out using a Faraday balance at 25°C. The UV-Vis spectrophotometric studies of the freshly prepared 10^{-3} mol L^{-1} DMSO solutions of the complexes from 200 to 1100 nm were conducted using a Cintra 5 GBC scientific spectrophotometer at room temperature. EPR spectra were recorded at room temperature on a Varian E-4 X-band spectrometer using TCNE as the g-marker. Electrical conductivities (10^{-3} mol L^{-1} solution in DMSO) were obtained on a Systronic type 302 conductivity bridge equilibrated at 25.00 ± 0.05°C.

3. Results and discussion

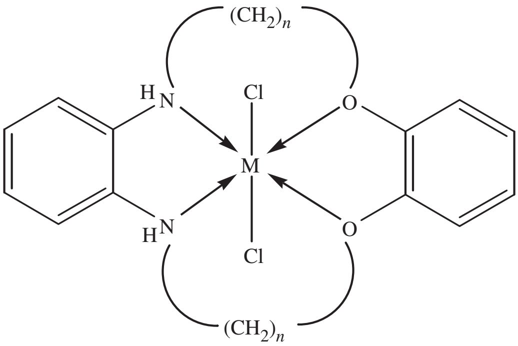
The diazadioxo macrocyclic ligands (L^1 and L^2) have been synthesized by the reaction of *o*-phenylenediamine, 1,2-dibromoethane/1,3-dibromopropane, and catechol in 1 : 2 : 1 molar ratio in ethanol (scheme 1). The isolated ligands remain unchanged at room temperature for extended times and were soluble in DMSO, DMF, and THF. Macrocyclic complexes, [ML^1X_2] and [ML^2X_2] [M = Co(II), Ni(II), Cu(II), and Zn(II)], were obtained by the reaction of L^1 and L^2 with metal salts in 1 : 1 molar ratio in ethanol (scheme 2). The ligands and their complexes were checked by comparing the TLC with the starting materials, showing a single spot different from the starting materials indicating that the compounds are pure.

The formation of ligand frameworks and their complexes was deduced on the basis of elemental analyses, molecular ion peaks in ESI-MS (table 1), characteristic bands in the FT-IR (table 2), and resonance signals in the ^1H and ^{13}C NMR spectra. The overall geometry of the complexes was inferred from the observed magnetic moments and the position of bands in the EPR and electronic spectra (table 3). Molar conductivities in DMSO indicate that all the complexes are nonelectrolytes [18].



where $n=2$ and 3 for L^1 and L^2, respectively.

Scheme 1. Formation and suggested structure of macrocyclic ligands.



Scheme 2. Suggested structure of complexes, M = Co(II), Ni(II), Cu(II), and Zn(II).

3.1. *Infrared spectra*

The absence of bands corresponding to the free primary amino group and the phenolic group in IR spectra (table 2) indicates the formation of the macrocyclic framework.

Table 1. Elemental analyses, m/z values, colors, yields, molar conductances, and melting points of the ligands and their complexes.

Complexes	m/z Found (Calcd)	Color	Yield (%)	m.p. (°C)	Molar conductivity ($\Omega^{-1}\,cm^2\,mol^{-1}$)
Ligand L^1 $C_{16}H_{18}N_2O_2$	270.326320 (270.327237)	Gray	66	178	–
Ligand L^2 $C_{18}H_{22}N_2O_2$	298.379480 (298.378856)	Gray	62	186	–
$[CoL^1Cl_2]$ $C_{16}H_{18}N_2O_2CoCl_2$	399.197225 (399.198134)	Dark brown	64	244	18
$[CoL^2Cl_2]$ $C_{18}H_{22}N_2O_2CoCl_2$	427.250385 (427.251243)	Dark brown	72	230	17
$[NiL^1Cl_2]$ $C_{16}H_{18}N_2O_2NiCl_2$	398.957425 (398.956416)	Dark brown	61	267	24
$[NiL^2Cl_2]$ $C_{18}H_{22}N_2O_2NiCl_2$	427.010585 (427.011676)	Dark brown	63	282	19
$[CuL^1Cl_2]$ $C_{16}H_{18}N_2O_2CuCl_2$	403.810025 (403.812113)	Dark brown	69	232	22
$[CuL^2Cl_2]$ $C_{18}H_{22}N_2O_2CuCl_2$	433.707185 (433.704534)	Dark brown	71	255	25
$[ZnL^1Cl_2]$ $C_{16}H_{18}N_2O_2ZnCl_2$	405.654025 (405.653267)	Dark brown	60	224	20
$[ZnL^2Cl_2]$ $C_{18}H_{22}N_2O_2ZnCl_2$	433.707185 (433.708621)	Dark brown	65	215	17

Table 2. IR spectral data of the ligands and their complexes (cm^{-1}).

Complexes	ν(N–H)	ν(C–N)	ν(C–O)	ν(M–O)	ν(M–N)	ν(M–Cl)
L^1	3280	1160	1345	–	–	–
L^2	3290	1175	1330	–	–	–
CoL^1Cl_2	3260	1140	1340	560	425	324
CoL^2Cl_2	3265	1155	1310	555	445	339
NiL^1Cl_2	3220	1130	1325	575	420	321
NiL^2Cl_2	3270	1150	1310	525	460	319
CuL^1Cl_2	3245	1145	1335	540	470	335
CuL^2Cl_2	3260	1135	1320	515	465	313
ZnL^1Cl_2	3210	1125	1330	535	455	320
ZnL^2Cl_2	3200	1160	1310	565	475	315

This was further corroborated [19] by ν(C–N) and ν(C–O) bands at 1160–1175 and 1345–1330 cm^{-1}, respectively, for L_1 and L_2.

Bands due to coordinated N–H at 3200–3290 cm^{-1} [20] shifted to lower frequencies by 10–30 cm^{-1} after complexation with the metals. Low-frequency vibrations due to M–O and M–N stretching provide direct evidence for complexation. Bands due to ν(M–Cl) were observed at 339–313 cm^{-1}, characteristic of chloro complexes. The bands due to phenyl ring vibrations appeared at their expected positions.

Table 3. Magnetic moments, electronic spectral bands (cm^{-1}) with their assignments and EPR data of the complexes.

Complexes	μ_{eff} (BM)	Band position (cm^{-1})	Assignments	EPR parameters $g_{\parallel}$	$g_{\perp}$	G
$[CoL^1Cl_2]$	4.55	13,900	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	–	–	–
		20,100	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$			
$[CoL^2Cl_2]$	4.58	14,200	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	–	–	–
		20,260	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$			
$[NiL^1Cl_2]$	3.17	11,300	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	–	–	–
		17,250	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$			
$[NiL^2Cl_2]$	3.14	11,405	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	–	–	–
		17,300	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$			
$[CuL^1Cl_2]$	1.75	15,700	$^2B_{1g} \rightarrow {}^2B_{2g}$	2.23	2.12	1.91
		18,400	$^2B_{1g} \rightarrow {}^2E_g$			
$[CuL^2Cl_2]$	1.72	15,720	$^2B_{1g} \rightarrow {}^2B_{2g}$	2.26	2.14	1.85
		18,440	$^2B_{1g} \rightarrow {}^2E_g$			

3.2. ^{1}H NMR spectra

The absence of proton signals of free NH_2 and OH groups indicates that condensation of primary amines and phenol with dibromoalkane has taken place. The ^{1}H NMR spectra of the ligands recorded in DMSO-d_6 show a multiplet at 6.41 ppm ascribed [21] to secondary amino protons (–NH, 2H) of the *o*-phenylenediamine. The ^{1}H NMR spectra of L^1 and L^2 gave a multiplet at 3.08–3.19 ppm, which corresponds to methylene protons (N–CH_2–C, 4H) adjacent to nitrogen of the amine. Another multiplet at 2.45 ppm for L^2 may be assigned [22] to the middle methylene protons (C–CH_2–C, 4H) of the propane chain. A multiplet at 1.85 ppm is attributed to methylene protons (O–CH_2–C, 4H) adjacent to oxygen of the catechol and a multiplet at 7.18–7.30 ppm may be assigned to aromatic protons. The ^{1}H NMR spectra of the Zn complexes recorded in DMSO-d_6 exhibits resonance peaks comparable to that of the ligands with a slight downfield shift suggesting coordination of macrocyclic ligand with the metal center.

3.3. ^{13}C NMR

The ^{13}C NMR spectra of the ligands in DMSO-d_6 at room temperature are consistent with the proposed macrocyclic framework. The resonances at 65.1–65.6 and 51.2–51.7 ppm are indicative [23] of two types of methylene carbons in the macrocyclic framework for L^1 and L^2. An additional peak for L^2 at 26.5 ppm corresponds to central methylene carbon of the propane chain. The peaks at 112.4–113.1, 119.8–120.7, 131.8–133.0, 139.3–140.1, and 156.9–157.4 ppm regions corresponds to carbons of the phenyl ring. The ^{13}C NMR spectra of Zn complexes exhibit resonances with their chemical shift slightly downfield.

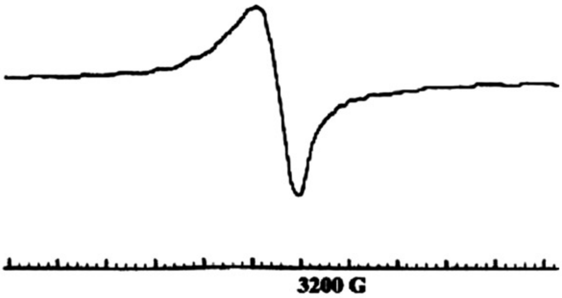


Figure 1. EPR spectrum of [CuL^1Cl_2] at room temperature.

3.4. *EPR spectra*

The EPR spectra of Cu(II) complexes were recorded as powders on X-Band at 9.1 GHz under 3100 G magnetic field strength with scan rate 1000 at room temperature. The $g_{\|}$ and $g_{\perp}$ values were computed from the spectrum using TCNE free radical as "g" marker. In distorted octahedral geometry, the unpaired electron lies in the $d_{x^2}-d_{y^2}$ orbital giving $^2B_{1g}$ as the ground state with $g_{\|} > g_{\perp}$. The observed g values (table 3) are characteristic of a distorted octahedral geometry in [CuL^1X_2] and [CuL^2X_2] (figure 1). Kivelson and Neiman [24] have reported the $g_{\|} < 2.3$ for covalent character of the metal ligand bond and $g_{\|} > 2.3$ for ionic character. Applying this criterion the covalent character of the metal–ligand bond in the complexes under study can be predicted. The trend $g_{\|} > g_{\perp} > g_e$ (2.0023) observed for these complexes show that the unpaired electron is localized in $d_{x^2}-d_{y^2}$ orbital of Cu(II). The g values are related by the expression

$$G = (g_{\|} - 2)/(g_{\perp} - 2)$$

measuring the exchange interaction between the copper centers in the solid. If $G > 4$, the exchange interaction is negligible and if $G < 4$ considerable exchange interaction occurs in solid complexes [25]. The G values of 1.85–1.91 indicate considerable interaction between two copper centers.

3.5. *Electronic spectra and magnetic moments*

The electronic spectral and magnetic moment data (table 3) recorded at room temperature for all the metal complexes are consistent with the proposed structure. The Co(II) complexes show bands at 13,900–14,200 and 20,100–20,260 cm^{-1} corresponding to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, characteristic of an octahedral geometry [26]. The observed values of magnetic moment for cobalt(II) complexes are generally diagnostic of the coordination geometry. Both tetrahedral and high-spin octahedral cobalt(II) complexes possess three unpaired electrons but may be distinguished by the magnitude of the deviation of μ_{eff} from the spin-only value. The magnetic moment of tetrahedral cobalt(II) complexes with an orbitally nongenerate ground term is increased above the spin-only value *via* contribution from higher orbitally degenerate terms and occurs in the range 4.2–4.4 BM [27]. Octahedral cobalt(II) complexes however maintain a large contribution due to ^4T_g ground term and exhibit μ_{eff} in the range 4.5–5.2 BM [28]. The magnetic measurements on the complexes reported herein 4.55–4.58 BM show high-spin octahedral configuration.

Electronic spectra of the Ni(II) complexes show two main bands centered at 11,300–11,405 and 17,250–17,300 cm^{-1}, which may be assigned to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively, similar to an octahedral [29] Ni(II). Magnetic behavior of octahedral nickel(II) complexes is relatively simple. Nickel(II) has the electronic configuration 3d^8 and should exhibit a magnetic moment higher than expected for two unpaired electrons in octahedral (2.8–3.2 BM) and tetrahedral (3.4–4.2 BM) complexes whereas its square planar complexes would be diamagnetic. This increase in the magnetic moment value from that of the spin-only value has been discussed by Figgis and Nyholm [30], who considered it to be due to some "mixing in" of upper state *via* spin–orbit coupling. The paramagnetism observed for the present complexes range from 3.17 to 3.14 BM (table 3), consistent with octahedral complexes.

The complexes derived from Cu(II) exhibit bands at 15,700–15,720 and 18,400–18,440 cm^{-1}, assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2Eg$ transitions, respectively, for distorted octahedral geometry [31] for Cu(II). The magnetic moment values further complement the electronic spectral data.

In order to determine if the metal complexes undergo solvatochromic shifts in different solvents, the complexes were dissolved in a variety of polar solvents like DMSO, DMF, THF, $CHCl_3$, and their UV-Vis spectra were recorded. Since the spectra do not exhibit any variation in the absorption pattern as a function of solvent, binding of solvent to the metal ions does not occur. Thus the geometry of the metal does not change in solution.

3.6. *Job's plot*

Data from the spectroscopic titrations have been analyzed using Job's method of continuous variations [32], commonly used for determining the composition of complexes in solution. These solutions are prepared such that the total analytical concentration of metal plus ligand is maintained constant while the ligand : metal ratio varies from flask to flask, i.e.

$$C_M + C_L = k,$$

where C_M and C_L are the analytical concentrations of metal and ligand, respectively, and k is a constant. The absorbance is plotted as a function of mole fraction (X) of ligand (X_L) or metal (X_M) in the flask. Job's diagram (figure 2) obtained for the nickel and zinc complexes at $\lambda_{\max}$ 570 and 600 nm, respectively, consists of two straight lines intersecting at $X = 0.5$, suggesting a complex of 1 : 1 composition. The same profile was observed when the diagram was constructed at different wavelengths.

3.7. *Mass spectra*

Mass spectra of the complexes play an important role in confirming the monomeric [1 + 1] (dicarbonyl and diamine) nature of the complexes. The fragments observed in the mass spectrum of the complexes are useful for the characterization of the complexes [33, 34]. The mass spectra of the complexes are described below and the values are in

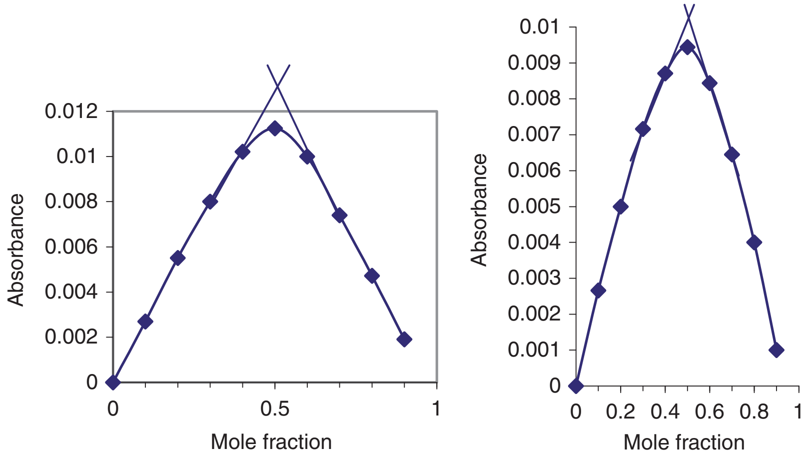


Figure 2. Job's diagram for nickel and zinc complexes.

good agreement with the respective weights of the complexes on the basis of proposed molecular formula.

L1: 261 (18%), 262 (27%), 263 (49.3%), 264 (80%), 265 (35%), 266 (100%), 267 (68.5%), 268 (7.6%), 269 (13%), 270 (6%).

L2: 288 (10%), 289 (27%), 290 (49%), 291 (79.3%), 292 (100%), 293 (27%), 294 (65%), 295 (17%), 296 (20%), 297 (5%), 298 (3%).

[CoL_1Cl_2]: 389 (23%), 390 (51.9%), 391 (86%), 392 (50%), 393 (100%), 394 (31%), 395 (70%), 396 (16%), 397 (23.9%), 398 (5.5%), 399 (3.6%).

[CoL_2Cl_2]: 417 (3%), 418 (23%), 419 (54.5%), 420 (80%), 421 (55.4%), 422 (100%), 423 (42.3%), 424 (72%), 425 (23.3%), 426 (8%), 427 (4%).

[NiL_1Cl_2]: 390 (20.6%), 391 (47.6%), 392 (87%), 393 (52.3%), 394 (100%), 395 (36.2%), 396 (68%), 397 (23.3%), 398 (7.2%), 399 (9%).

[NiL_2Cl_2]: 416 (2%), 417 (26%), 418 (76.9%), 419 (49%), 420 (100%), 421 (25.4%), 422 (70%), 424 (17%), 425(23%), 426 (6.3%), 427 (2.9%).

[CuL_1Cl_2]: 392 (60.2%), 393 (50%), 394 (30.5%), 395 (60.5%), 396 (70.5%), 397 (40.7%), 398 (100%), 399 (30.5%), 400 (49%), 401 (25%), 402 (13%), 403 (5%), 404(7%).

[CuL_2Cl_2]: 421 (80.3%), 622 (22%), 424 (30.6%), 425 (60.1%), 426 (30.8%), 427 (100%), 428 (49%), 430(30%), 431 (13%), 432 (23%), 434 (14%).

[ZnL_1Cl_2]: 397 (23%), 398 (51.9%), 399 (86%), 400 (50%), 401 (100%), 402 (31%), 403 (70%), 404 (23.9%), 405 (5.5%), 406 (3.6%).

[ZnL_2Cl2]: 425 (20.6%), 426 (47.6%), 427 (87%), 4288 (52.3%), 429 (100%), 430 (36.2%), 431 (68%), 432 (23.3%), 433 (7.2%), 434 (9%).

4. Conclusions

The 12- and 14-membered N_2O_2 macrocyclic ligands and their complexes have been synthesized *via* condensation of 1,2-diaminoethane or 1,3-diaminopropane, *o*-phenylenediamine and catechol. The formation of the proposed macrocyclic framework has been inferred by the absence of bands corresponding to the free primary amino and phenol and corresponding proton resonance signals in the ^{1}H NMR. This study revealed octahedral geometry around Co(II), Ni(II), Cu(II), and Zn(II) with *o*-phenylenediamine and catechol acting as neutral bidentate ligands coordinating through nitrogen and oxygen to form stable five-membered chelates.

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