Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 118 (2014) 572–577

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Complexation, thermal and catalytic studies of N-substituted piperazine, morpholine and thiomorpholine with some metal ions

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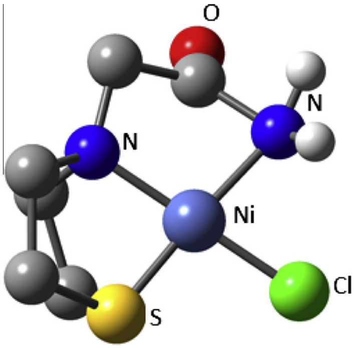
HIGHLIGHTS

- Nine new metal complexes were prepared.
- Catalytic activity of the complexes were studied.
- Thermal stabilities of the complexes were determined.
- Cataltytic epoxidation of cis-diphenylethylene was studied.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 August 2013
Accepted 6 September 2013
Available online 16 September 2013

Keywords:
N-substituted piperazine
Morpholine
Thiomorpholine
Thermal stability
Complexes
Catalytic activity

ABSTRACT

Several Cu(II), Pt(II) and Ni(II) complexes of N-substituted, piperazine (NN donor), morpholine (NO donor) and thiomorpholine (NS donor) derivatives were synthesized and their thermal behavior and catalytic activity in epoxidation reaction of cis-diphenylethylene were studied using oxygen sources NaOCl. The coordination compounds of Cu(II), Pt(II) and Ni(II) having general formula [MLCl]Cl, $[ML_2l]Cl_2$ or $[ML]Cl_2$ with tetra coordinated geometry around metal ions have been isolated as solid. All the ligands and complexes were identified by spectroscopic methods and elemental analysis, magnetic measurements, electrical conductance and thermal analysis. A square planer structures have been proposed for all complexes. The thermal stability of the complexes discussed in terms of ligands donor atoms, geometry and central metal ions. The complexes have a similar thermal behavior for the selected metal ions. The thermogravimetric analyses suggest high thermal stability for most complexes followed by thermal decomposition in different steps. The decomposition processes were observed as water elimination, chloride anion removal and degradation of the organic ligands. Catalytic ability of the complexes were examined and found that all the complexes can effectively catalyze the epoxidation of cis-stilbene with NaOCl.

Introduction

The chelate ligands that contain mixed donor groups comprising morpholines, thiomorpholines, and symmetric donor piperazines are some of the most important pharmacophores in medicinal chemistry [1–3]. Morpholine, thiomorpholine and piperazine with an acetamide pendant group are known to be as tridentate chelates. Nitrogen, oxygen and sulfur-containing heterocyclic frameworks are prevalent subunits in biologically active molecules [4–6] in a variety of biologically active structures such as the antidepressant drug [7] and the antifungal compounds [8]. Similarly, the piperazine moiety is present in various biologically active compounds including the antimicrobial [9] and related quinolones, dopaminergic D3 agents [10], HIV-protease inhibitors [11] and the antidepressants [12]. Piperazine derivatives

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http://dx.doi.org/10.1016/j.saa.2013.09.031

were extensively investigated and used as drugs in the field of medicinal sciences, and actively investigated in antibacterial, antifungal and anti-cancer aspects. The structure of bis-pendant piperazine was published recently [13]. Thiomorpholine analogs are associated with a variety of pharmacological activities including anti mycobacterial [14], antibacterial [15], analgesic [16] and anti-inflammatory [17]. Metal complexes of these compounds have been reported to act as efficient catalyst for the epoxidation of alkenes. Coordination compounds catalyze the transfer of oxygen atoms to organic substrates which are important in the development of efficient catalyst in organic synthesis in laboratory and industry. This fact has opened up of new channel in the field of homogeneous catalysis [18–25]. Epoxidation of alkenes is one of the most used methods in organic synthesis. Epoxides can easily be transformed into a large variety of compounds via ring opening reactions to give diols, amino alcohols, allylic alcohols and ketones [26]. These reactions are important process in commercial polymers like polyurethane, polyamide, epoxy resins, and polyesters. Direct oxygen transfer to the alkene is the most common method of epoxide synthesis. Epoxidation reactions of alkenes can be achieved by a variety of oxidants [27]; NaOCl was used in epoxidation of cis-diphenylethylene. A major breakthrough in this field was the discovery by Jacobsen and co-workers [28]. Catalytic alkene epoxidation with mononuclear nickel complexes have been developed [29]. The complexes of N-substituted morpholine, thiomorpholine and piperazine are of particular interest not only for their ability to form complexes but also high thermodynamic stability and kinetic inertness. The thermal behavior of the complexes with acetamide pendant derivatives of piperazine, morpholine and thiomorpholine have attracted attention in the last years, this attention being focused on the species that could have some practical applications. Here we describe the synthesis, characterization, thermal behaviors and catalytic activity in alkene epoxidation of some metal complexes. The details of synthetic, spectral, magnetic and thermal behaviors of these compounds are described.

Experimental

Materials

The high purity reagents were obtained commercially and used as received without further purification. Spectroscopic grade and argon saturated methanol was used for the syntheses of the compounds.

Physical measurements

IR spectra (KBr disks, 4000–400 cm^{-1}) were recorded using a Perkin Elmer BXII spectrometer. ^{1}H (300.0 MHz) and ^{13}C NMR spectra were recorded on a Varian NMR spectrometers. Chemical shifts are referred to the detoured solvent chemical shift. Mass spectra were acquired with GC–MS in Electron impact mode with a Thermo Finnigan Trace DSQ. Molar conductance was measured using a WTW inolab cond 720 conductivity meter where the cell constant was calibrated with 0.001 M KCl solution, and nitromethane was used as solvents. Thermal studies were made with a Seiko SII TG-DTA 6300 TG/DTA analyzer heated from 20 to 1200 °C under dry air. The end products in thermogravimetric study were analyzed by a Bruker D2 Phaser XRD. UV–vis spectra were recorded at 25 °C in aqueous solution on an Agilent 4583 diode array spectrometer. Solid-state magnetic susceptibility data were collected on a powdered microcrystalline sample using a Sherwood Scientific Magnetic Susceptibility Balance at room temperature. Elemental analysis for C, H and N were determined on dried samples using a Perkin–Elmer 2400 CHN analyzer.

General syntheses of the ligands

2,2′-piperazine-1,4-diyldiacetamide, L^1

(0.86 g, 10 mmol) piperazine was dissolved in THF and (2.76 g, 20 mmol) potassium carbonate was added and mixture was stirred at room temperature for 20 min and then (2.90 g, 21 mmol) 2-bromoacetamine was added. The mixture was stirred for 15 h and the completion of the reaction was monitored by TLC analysis and upon the completion, the solid was filtered with sintered glass funnel. The filtrate was evaporated by rotary evaporator and the residue was dried in vacuum desiccator. The best yields of the desired products were obtained when the reaction was carried out in THF at room temperature with a 1:2 mole ratio of the reagents. Formation of HBr is eliminated with subsequent treatment of this salt with saturated aqueous sodium carbonate. The white crystals were obtained. The compound was characterized using different spectroscopic techniques, including IR, NMR and MS, elemental analyses. Reaction scheme is given in Scheme 1.

Yield: 77%, 1.6 g. Anal. calcd. for $C_8H_{16}N_4O_2$, (200.24 g/mol): C 47.99%; H 8.05%; N 27.98%. Found: C 47.83%; H 8.14%; N 27.82%. FT-IR (KBr, cm^{-1}): 1675 ν(C = 0, amide), 3323, 3213, 3146 ν(N—H). ^{1}H NMR (δ, ppm, CD_3OD): 7.33 (NH_2, s, 4H), 3.91(s, CH_2—N, 4H), 3.50–3.60 (d t, piperazine ring, 8H), ^{13}C NMR (δ, ppm, $CDCl_3$): 167.89 (C=O), 56.79 (CH_2—N, 2C), and 49.74 (piperazine ring, 4C). GS MS (EI, m/z): $[M]^+$, 200.99.

2-morpholin-4-ylacetamide, L^2

Yield: (73%) 2.11 g. Anal.calcd. for $C_6H_{12}N_2$ O_2 (144.17): C 49.98%; H 8.39%; N 19.43%. Found: C 49.81%; H 8.27%; N 19.34%. IR (KBr, cm^{-1}): 1695 (C=O), 3369, 3154 ν(N—H) ^{1}H NMR (δ, ppm, CD_3OD): 7.32 (s, NH_2), 3.95–4.45 (t, O—CH_2, 4H), 3.89 (s, N—CH_2, 2H), 3.28–3.80 (t, N—CH_2 ring, 4H). ^{13}C NMR (δ, ppm, CD_3OD): 166.87 (C=O), 64.05 (O—CH_2, 2C), 57.37 (N—CH_2), and 52.78 (N—CH_2 ring, 2C). MS (m/z, EI): $[M]^+$, 145.05.

2-thiomorpholin-4-ylacetamide, L^3

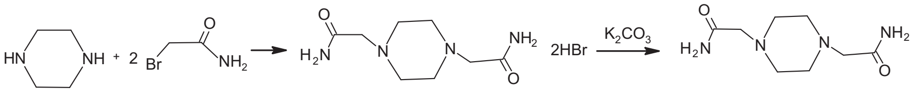
Yield: 58%, 1.85 g. Anal. calcd. for $C_6H_{12}N_2OS$ (160.24): C 44.97%; H 7.55%; N 17.48%. Found: C 45.11%; H 7.59%; N 17.37%. FT-IR (KBr, cm^{-1}): 1686 ν(C=O). ^{1}H NMR (δ, ppm, CD_3OD): 7.92 (s, NH_2), 3.02 (s, N—CH_2, 2H), 2.79 (t, N—CH_2, 4H), 2.72 (t, S—CH_2 ring, 4H). ^{13}C NMR (δ, ppm, $CDCl_3$): 167.97 (C=O), 61.54 (N—CH_2), 55.25 (N—CH_2 ring, 2C), 27.40 S—CH_2 ring, 2C). MS (EI, m/z): $[M]^+$, 161.97.

2.4 General synthesis of the complexes

All the complexes of acetamide pendant piperazine, morpholine and thiomorpholine with Pt(II), Ni(II) and Cu(II) were prepared by following general method. The metal salt (10 mmol) was dissolved in 40 mL argon saturated methanol and the solution was added to a stirred solution of ligands (11 mmol) in 30 mL methanol solution at room temperature. On addition of metal to ligand solution immediate color change was observed according to the metal ions. Then the solution was warmed up to 40 °C and stirred for 8 h and then solution was concentrated on rotary evaporator. Solutions were left for crystallization but amorphous powders were obtained and dried at vacuum oven at room temperature. The proposed structures of the complexes and ligands are given in Fig. 1.

Ni-L^1

Yield: 63%. FTIR (KBr cm^{-1}): 3270, 3174, 1663, 459 (M—N). UV–vis (H_2O nm; (ε, M^{-1} cm^{-1})): 310(1466), 425(566), 490(510). Anal. calcd. for $C_8H_{18}N_4O_3Cl_2Ni$ (Fw: 347.85): C 27.62, H 5.22, N 16.11. Found: C 27.51, H 5.14, N 16.25.



Scheme 1. Reaction scheme of the piperazine derivative.

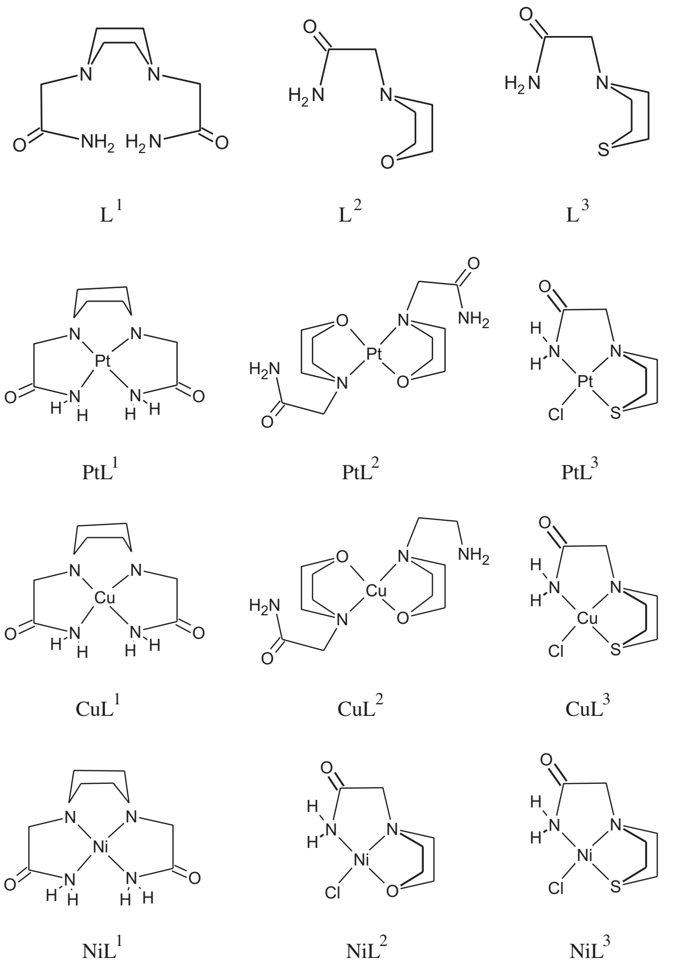


Fig. 1. Proposed structures of the ligands and complexes. Counter ions and waters are omitted.

Cu-L¹

Yield: 66%. FTIR (KBr cm^{-1}): 3502, 3309, 1675, 429 (M—N). UV–vis (H_2O nm; (ε, M^{-1} cm^{-1})): 357(1240), 540(520). Anal. calcd. for $C_8H_{20}N_4O_4Cl_2Cu$ (Fw: 370.72): C 25.91, H 5.44, N 15.11. Found: C 25.85, H 5.33, N 15.24. Paramagentic with 1.88 BM.

PtL¹

Yield: 63%. FTIR (KBr cm^{-1}): 3313, 3167, 1676, 438 (M—N). UV–vis (H_2O nm; (ε, M^{-1} cm^{-1})): 430(1125). Anal. calcd. for $C_6H_{20}N_4O_4Cl_2Pt$ (Fw: 502.25): C 19.13, H 4.01, N 11.16. Found: C 19.01, H 3.96, N 11.23.

Ni-L²

Yield: 71%. FTIR (KBr cm^{-1}): 3477, 3148, 1668, 1418, 549 (M—O), 466 (M—N). UV–vis (H_2O nm; (ε, M^{-1} cm^{-1})): 375(1355), 450(488), 480(390). Anal. calcd. for $C_6H_{24}O_8N_2Cl_2Ni$ (Fw: 381.87): C 18.87, H 6.33, N 7.34. Found: C 18.79, H 6.45, N 7.39.

Cu-L²

Yield: 78%. FTIR (KBr cm^{-1}): 3366, 1656, 1578, 528 (M—O), 416 (M—N). UV–vis (H_2O nm; (ε, M^{-1} cm^{-1})): 355(1113), 556(396). Anal. calcd. for $C_{12}H_{28}N_4O_6Cl_2Cu$ (Fw: 458.83): C 31.41, H 6.15, N 12.21. Found: C 31.22, H 6.18, N 12.32. Paramagnetic with 1.81 BM.

PtL²

Yield: 61%. FTIR (KBr cm^{-1}): 3384, 3183, 1691, 576 (M—O), 472 (M—N). UV–vis (H_2O. nm; (ε, M^{-1} cm^{-1})): 443(1020). Anal. calcd. for $C_{12}H_{24}N_4O_4Cl_2Pt$ (Fw: 554.33): C 26.00, H 4.36, N 10.11. Found: C 26.10, H 4.28, N 10.27.

Ni-L³

Yield: 66%. FTIR (KBr cm^{-1}): 3399, 1568, 1418, 433 (M—N). UV–vis (H_2O nm; (ε, M^{-1} cm^{-1})): 290(1277), 344(388), 466(371). Anal. calcd. for $C_6H_{14}O_2Cl_2N_2NiS$ (Fw: 307.86): C 23.41, H 4.58, N 9.10. Found: C 23.28, H 4.27, N 9.15.

Cu-L³

Yield: 79%. FTIR (KBr cm^{-1}): 3390, 3123, 1672, 446 (M—N). UV–vis (H_2O nm; (ε, M^{-1} cm^{-1})): 320(1231), 540(377). Anal. calcd. for $C_6H_{12}N_2O_2Cl_2CuS$ (Fw: 294.70): C 24.45, H 4.10, N 9.51. Found: C 24.31, H 4.32, N 9.26. Paramagnetic 1.79 BM

Pt–L³

Yield: 56%. FTIR (KBr cm^{-1}): 3398, 3179, 1684, 442 (M—N). UV–vis (H_2O nm; (ε, M^{-1} cm^{-1})): 448(1322). Anal. calcd. for $C_6H_{14}N_2O_2Cl_2PtS$ (Fw: 445.25): C 16.19, H 3.14, N 6.29. Found: C 16.27, H 3.23, N 6.11.

Epoxidation of cis-1,2-diphenylethylene

The epoxidation reactions were carried out in in CH_2Cl_2 at room temperature with constant stirring. The composition of reaction medium was 2 mmol cis-1,2-diphenylethylene, 6 mmol NaOCl, 0.040 mol complex in 10 mL of dichloromethane. The solution was buffered to pH: 11 using a NaH_2PO_4–NaOH buffer. The mixture was stirred at room temperature for 7 h. For each complex the reaction time for the maximum epoxide yield was determined by withdrawing small amount of aliquots from reaction mixture. The disappearance of cis-1,2-diphenylethylene was checked with TLC. After the conversion of cis-1,2-diphenylethylene to epoxide, the mixture was loaded to a short celite column and the filtrate was extracted twice with CH_2Cl_2 dried over anhydrous Na_2SO_4 and filtered. Reactions were run at least in duplicate. The solvent was removed and the substance was analyzed for the epoxide in $CDCl_3$ with NMR. For the NMR experiments epoxides were prepared following the procedure described [30]. The cis-1,2-diphenylethylene oxide has a singlet for the aliphatic proton at δ 4.21 and trans-1,2-diphenylethylene oxide has a singlet at δ 3.83 ppm.

Result and discussion

Infrared spectra

A high intensity bands observed in ligand in between 3370 and 3100 cm^{-1} are attributed to the ν(N—H) vibration for the ligands L^1, L^2 and L^3. The frequencies in between 1695 and 1675 cm^{-1} are due to ν(C=O) of the ligands. The frequency 718 cm^{-1} is due to υ(C—S—C) of L^3, 1085 cm^{-1} is due to υ(C—O—C) of L^2 and 1023–1010 cm^{-1} due to υ(C—N—C) of all ligands. In the case of

Table 1
Thermal analysis data of the complexes.

Complex	Step	Onset/°C	Endset/°C	Leaving group	Mass loss/%		Residue Exp. (Calc.)
					Exp.	Calc.	
[NiL^1] Cl$_2$·H$_2$O	1	25	298	H_2O	5.1	5.1	
	2	298	478				
	3	478	609	L^1 + Cl$_2$	77.2	77.9	NiO 17.7(16.9)
[PtL^1]Cl$_2$·2H$_2$O	1	25	229	2H$_2$O	6.6	7.1	
	2	229	367				
	3	367	580	L^1 + Cl$_2$	58.7	54.4	PtO 35.3/38.7
[CuL^1]Cl$_2$·2H$_2$O	1	25	198	2H$_2$O	9.6	9.7	
	2	198	315				
	3	315	588	L^1 + Cl$_2$	75.1	73.1	CuO 15.3/17.1
[NiL^{2}Cl]Cl·6H$_2$O	1	25	140	6H$_2$O	28.8	28.0	
	2	140	394				
	3	394	619	L^1 + Cl$_2$	55.3	56.3	NiO 16.1/15.4
[PtL$^2_2$]Cl$_2$	1	25	302				
	2	302	556				
	3	556	974	$L^2_3 + Cl_2$	65.3	64.8	PtO 34.6/35.2
[CuL$^2_2$l]Cl$_2$ · 2H$_2$O	1	25	274	2H$_2$O	7.6	7.8	
	2	274	486				
	3	486	652	L^2 + Cl$_2$	80.3	78.3	CuO 12.1/13.8
[NiL^{3}Cl]Cl·H$_2$O	1	25	92	H_2O	6.1	5.9	
	2	92	406	L^3 + Cl$_2$	73.3	75.1	NiO 20.4/19.1
[PtL^{3}Cl]Cl·H$_2$O	1	25	97	H_2O	2.0	4.1	
	2	97	463				
	3	463	546	L^3 + Cl$_2$	53.4	52.1	PtO 46.1/44.4
[CuL^{3}Cl]Cl	1	25	189				
	2	189	359				
	3	359	585	L^3 + Cl$_2$	77.5	78.4	CuO 22.9/21.5

Pt(II), Ni(II) and Cu(II) complexes we observed the following changes. The N—H bands in the ligands shift up on complexation. The small shift to lower frequencies of the C—O—C, C—S—C, C—N—C bands affords evidence of the coordination of O, S and N atom of the morpholine, thiomorpholine and piperazine. In addition the Pt(II), Ni(II) and Cu(II) complexes exhibit a broad band at *ca.* 3400 cm^{-1}; which was attributed to the —OH stretching frequencies of coordinated water molecule. In the far IR spectra of the complexes, the non-ligand bands were observed at 450–500 cm^{-1} region assigned to M—N stretch [31]. Another bands in far IR region around 530–560 cm^{-1} were observed which are assigned to M—O stretch [32]. The important features of the infrared spectra of all the complexes are the appearance of two weak bands at 536–554 cm^{-1} region are assignable ν(M—O) and those in the region 462–499 cm^{-1} to ν(M—N) vibrations, respectively. Thus, the IR spectral results provide strong evidence for the complexation of the potentially tri and tetradentate ligands.

Electronic spectra

Electronic spectra of the complexes show high intensity band, d–π^* Metal-Ligand Charge Transfer (MLCT) transitions were observed in the region 320–375 nm. The third expected low-energy ligand field bands observed in between 430 and 646 nm range and are assigned as *d*–*d* transitions. The Ni(II) complexes are diamagnetic and the bands around 362–375 nm could be consistent with low spin square-planar geometry. Pt(II) complexes are all four coordinated; therefore square planer geometry around the metal is expected. Cu(II) complexes show d–π^* metal-ligand charge transfer (MLCT) transitions in the region 320–355 nm. A broad band around 540 nm which are attributed to $^2B1g \rightarrow {}^2A_{1g}$ transition strongly favors the square planer geometry around metal ion [33]. The electronic spectra show that absorption bands in Ni(II) complexes observed below 550 nm. A lack of any electronic transition at longer wavelengths indicates a large crystal field splitting is consistent with square planer geometry of Ni(II) complexes [34,35].

^{1}H and ^{13}C NMR spectra

The ^{1}H and ^{13}C NMR spectra of the ligands were recorded at room temperature in CD$_3$OD. All the protons and carbons in NMR spectra found to be in their expected regions. The data are summarized in the synthesis of ligands. All the ligands show characteristic carbon peak for C═O at 167.89, for L^1, 166.87 for L^2 and 167.97 for L^3 in ^{13}C NMR

Molar conductance

The complexes of Cu(II), Ni(II) and Pt(II) were dissolved in nitromethane and the molar conductivities of 10^{-3} M of their solutions at 25 ± 2 °C were measured. It is concluded from the results that all the complexes are considered 1:1 or 1:2 electrolytes with the molar conductance values in between 73 and 112 Ω^{-1} mol^{-1} cm^2 indicating the ionic nature of these complexes.

Thermal analysis

The molecular composition of the complexes has been verified by thermogravimetric analyses. Thermal analysis data show that some complexes follow similar type of decomposition pattern confirming their similar formulation. Complexes start losing water first up to 200 °C and then ligands decompose in several steps. Thermal stabilities increase as PtL^2 > NiL^2 > CuL^2 but with the different ligands this sequence will changes such as CuL^1 > NiL^1 > CuL^1 and CuL^3 > PtL^3 > NiL^3. Complexes with L^3 ligands much more stable than L^1 and L^3 ligand complexes. The thermal behavior of the PtL^{2}complex is discussed as an example. Thermal analysis data of the complexes are summarized in Table 1. The TG curves show mainly three stages in the decomposition process. The first stage

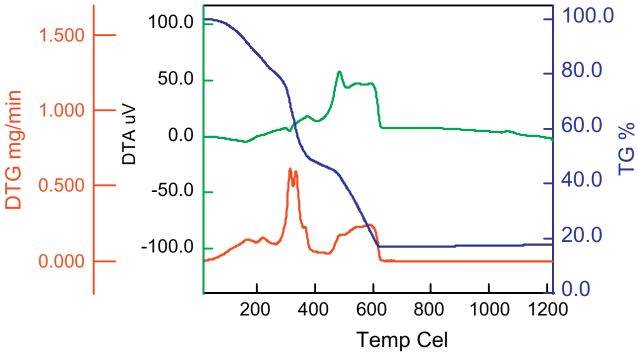


Fig. 2. The TG–DTG–DTA curves of the NiL^1 complex.

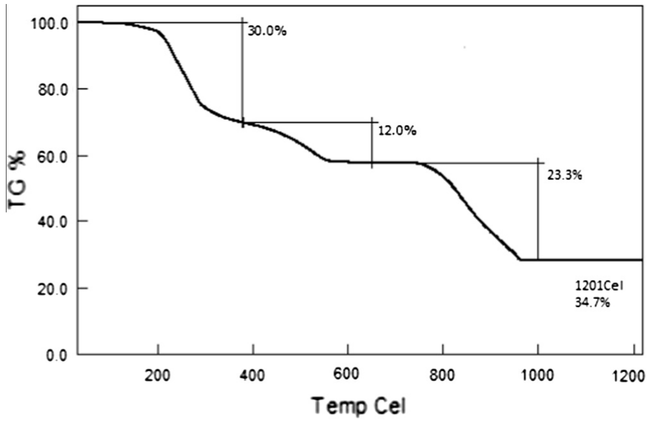


Fig. 3. The labeled mass loss of the PtL^2 complex.

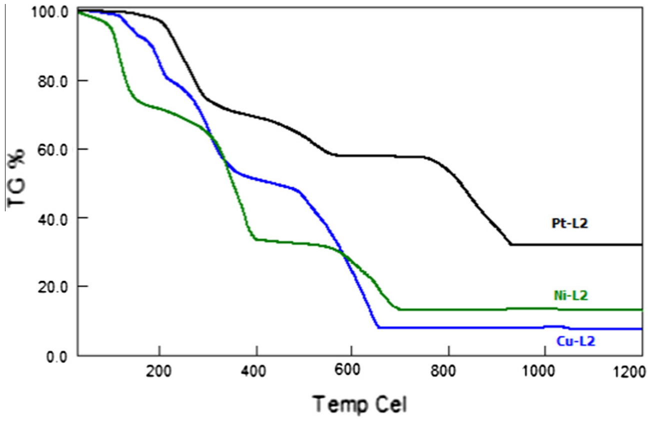


Fig. 4. TG curves of L^2 complexes.

decomposition temperature is in the range of 25–302 °C, with a mass loss of 30%, is probably attributed to the decomposition of a group in the ligand. The second stage of decomposition was observed in the 302–556 °C range and the third stage decompositions take places in between 556 and 974 °C a with a mass loss of 12% and 23.3%. Total mass loss is 65.3% (calculated 64.8%). The final product is the PtO (34.6%, calcd.35.20%). These results are in good agreement with the composition of the complexes. All thermal events are exothermic process in dry air atmosphere. The thermogravimetric analyses reveal greater thermal stability of the L^2(N_2O donor set) complexes over the L^1 and L^3 complexes. It is confirmed that most of the complexes contain water in the structure. As a

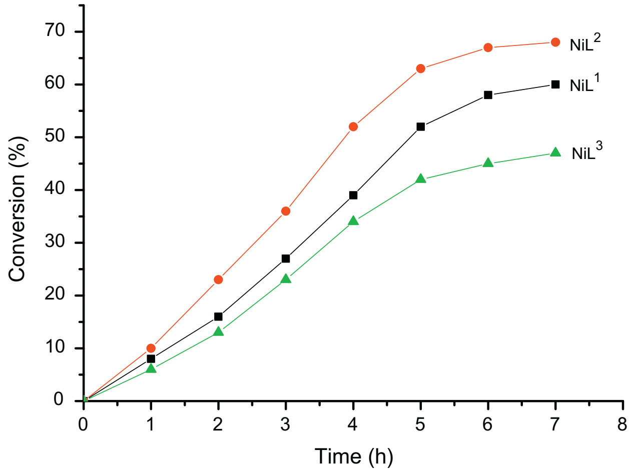


Fig. 5. The effect of time on epoxidation of cis-1,2-diphenylethylene using Ni(II) complexes.

result of the thermal study, qualitative conclusion can be done for the stability of the complexes. PtL^2 complex is the most stable one and NiL^3 complex is the least stable one. The group TG, labeled mass loss and TG–DTG–DTA curves of the complexes are given in Figs. 2–4.

Magnetic susceptibility measurements

The measurement of the magnetic moment of a coordination compounds containing unpaired electron spin is useful in the establishment of the valency of the metal atom, and in many cases also helps to determine the geometrical structure of the complex. The magnetic susceptibilities of the solid-state complexes under discussion were measured by the Gouy balance method. The magnetic moments of Ni(II) and Pt(II) complexes were measured at room temperature and were found in the range 0.15–0.33 BM, consistent with no unpaired electrons in the nickel(II) ion. The magnetic moment of copper complexes is in the range 1.79–1.88 BM.

Effect of time on the epoxidation of cis-1,2-diphenylethylene

The epoxidation of cis-1,2-diphenylethylene was carried out at various times starting from 1 h up to 10 h at 25 °C. There is a general trend of increasing conversion of cis-1,2-diphenylethylene with increasing reaction time up to 7 h. After 7 h, the conversion of epoxide does not change appreciably. The conversion of cis-1,2-diphenylethylene as a function of time at 25 °C with different catalyst was given in Fig. 5. The effect of the temperature on epoxidation reaction was also studied. There is a gentle increase in conversion of cis-1,2-diphenylethylene with increase in temperature over room temperature. Blank experiments were carried out in each case using the same experimental conditions without the catalyst; no epoxide was formed under the same condition.

Epoxidation

Nine Ni(II), Cu(II) and Pt(II) complexes bearing N-substituted piperazine, morpholine and thiomorpholine in square planer coordination were tested as catalyst for cis-diphenylethylene epoxidation. In the presence of complex, NaOCl reacts with cis-1,2-diphenylethylene to produce trans and cis-epoxides. With [NiL^{1}Cl]Cl epoxides were produced in 53% yield with cis: trans = 25:75, and with [NiL^2]Cl_2, epoxides were produced in 51% yield with cis: trans = 18:82 and with [NiL^{3}Cl]Cl is 39% yield with

Table 2
Cis-stilbene epoxidation with NaOCl catalyzed by complexes in CH_2Cl_2.

Catalysts	Time/h	Tot. conversion (%)[a]	Epoxide Yield (%)[b]
$[NiL^1]Cl_2{\cdot}H_2O$	6	58	53
$[PtL^1]Cl_2{\cdot}2H_2O$	7	48	44
$[CuL^1]Cl_2{\cdot}2H_2O$	7	53	46
$[NiL^2Cl]Cl{\cdot}6H_2O$	6.5	66	51
$[PtL_2^2]Cl_2$	6	54	48
$[CuL_2^2]Cl_2 \cdot 2H_2O$	7	63	60
$[NiL^3Cl]Cl{\cdot}H_2O$	6	46	39
$[PtL^3Cl]Cl{\cdot}H_2O$	7	41	37
$[CuL^3Cl]Cl$	6.5	39	33

[a] Conversion was determined by ^1H NMR spectroscopy by integration of alkene/epoxides.
[b] Isolated yield.

cis:trans 30:70. These data show that cis-diphenylethylene produced higher yield of trans-epoxide and relative yield of epoxidation by using NiL^1 complex is higher than the other Ni(II) complexes as catalyst. The same trend was observed in the epoxidation of cis-olefin catalyzed by Mn(selen) complexes which favor the production of trans epoxide [36–38]. Among all, N_2O donor containing ligand shows high catalytic activity. The catalytic activity of complex is found to correlate with a high cationic charge on the complex +2 charged complexes are much more active when compared with +1 charged one. These data clearly show that the cis-diphenylethylene produced higher yields of trans-epoxide. In summary, the results indicate that under the same conditions, epoxidation of cis-1,2-diphenylethylene with NaOCl catalyzed by nickel complexes provided 46–66% conversion for trans-diphenylethylene oxide but only 37–48% conversion, while when catalyzed by platinum complexes. The results of epoxidation of cis-diphenylethylene by some complexes with NaOCl were summarized in Table 2.

Conclusion

In this article, we presented copper(II), nickel(II) and platinum(II) complexes of three tridentate and tetradentate ligands. The metal centers in all complexes are four coordinated with square planar geometry for Pt(II), Cu(II) and Ni(II). All the complexes are mono nuclear. The structures of the complexes are well sustained by the other spectral, magnetic, thermal, and conductometric studies. Platinum complexes have the same environments with copper but thermal stabilities of the platinum complexes are much more than copper. Most of the complexes show three step decompositions. The results of catalytic studies indicate that epoxidation of cis-diphenylethylene with NaOCl catalyzed by complexes provide trans-diphenylethylene oxide in various conversions with different complexes. The results show that yield and cis-trans selectivity in epoxidation reaction are strongly dependent on steric and electronic effect of the ligands [39–41].

Acknowledgement

We thank the Trakya University TBAP 2010-113 for the financial support.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.09.031.

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