



RESEARCH ARTICLE

COMPETITION OF 1.10- PHENANTHROLINE AND L. PROLINE TOWARDSOME  
TRANSITION METAL IONS

\*<sup>1</sup>Reham M. Nori, <sup>1</sup>Salah A. Jassim and <sup>2</sup>Faliah H. Ali

<sup>1</sup>Department of Chemistry, College of Science, University of Diyala, Iraq  
<sup>2</sup>Ministry of Science and Technology, Materials Research Department, Iraq

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ABSTRACT

The competition of both 1.10-Phenanthroline (1.10-Phen.) and L- proline (Pro.) ligands against three transition metals ions, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Co<sup>3+</sup> were studied. <sup>1</sup>H NMR, FTIR, atomic absorption and chlorine contents were used to identify the complex formation. Both Zn<sup>2+</sup> and Cd<sup>2+</sup> were complexed with 1.10-Phen. while Ni<sup>2+</sup> binds only with Pro. Hard soft acid base (HSAB) principle is the main explanation binding mode of metal ions in this work.

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INTRODUCTION

Complexes formation in mixed ligands and their stability are governing through some factors such as pH, ligand types, metal ions, ring size (ThiNhu *et al.*, 2012) steric effects and Hard Soft Acid Base (HSAB) principle (Shukla, 2016). The stability increases with increase dentate factors as follows:

Tetradentate > tridentate > bidentate

Steric factor is also has large effects on competition of more than one ligand toward metal ions due to the repulsion of bulky substituents group on the ligands (Vora *et al.*, 2009). Ring size has been considered as one of the important factors that influence the stability, five and six membered ring are more stable than others (four, seven, eight...etc.) (Dipak *et al.*, 2006). Competition between metal ions toward different ligands using HSAB principle is the main factor that governing the explanation of binding modes in this job.

Experimental Section

1-Reagents and Materials: ZnCl<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, CdCl<sub>2</sub>.2H<sub>2</sub>O and NiCl<sub>2</sub>.6H<sub>2</sub>O are of analar grade.

2- Instruments

- pH meter TWT 7110
- Sensitive balance
- Atomic Absorption spectrophotometer- aurora – Canada FTIR – perkinelmer
- <sup>1</sup>H NMR Synthesis of complex

A 10 mL solution containing (0.002 mol, 0.4753 gm) of NiCl<sub>2</sub>.2H<sub>2</sub>O in absolute ethanol was prepared. Two separated solutions (each one 10 mL of absolute ethanol) were prepared containing 0.002 mol, 0.396 gm of 1,10 phen for the first one and the other one is containing (0.002 mol, 0.23 gm of Pro. and both separated solutions were added gradually to the cobalt ion solution and the mixture was placed on a hotplate/stirrer and heated for 2 hours to reflux at 80°C.

During heating, few drops of KOH solution were added to the mixture to be basic medium at about pH=10. The solution allowed for 24 hours to yield brown precipitate, filtered and washed several times by absolute ethanol and then purified by recrystallization of complex using deionizer water. The same above procedure was followed to prepare the complex of Zn<sup>2+</sup> by dissolve (0.272 gm, 0.002 mol) of ZnCl<sub>2</sub> and Cd<sup>2+</sup> complex by dissolve (0.3663 gm, 0.002 mol) of CdCl<sub>2</sub>.2H<sub>2</sub>O.

\*Corresponding author: Reham M. Nori

Department of Chemistry, College of Science, University of Diyala, Iraq

## RESULTS AND DISCUSSION

## FTIR study

Results obtained in Table-1 show the important bands of the complexes been studied. It is clearly shown that both divalent zinc and cadmium ions are coordinated with 1-10 phen. only due to the shifted observed of C=C, C=N and Benzene ring stretch from 1645, 1562, 1140 (Ismail *et al.*, 2014; Turel *et al.*, 2015; Tai *et al.*, 2014; Abolfazl *et al.*, 2014) to 1625, 1517, 1105  $\text{cm}^{-1}$  respectively in  $\text{Zn}^{+2}$  complex, while  $\text{Cd}^{+2}$  complex is shifted to 1634, 1516, 1103  $\text{cm}^{-1}$  respectively.

Table 1. Vibrational frequencies of 1.10 phen. and Pro. And corresponding metal complexes

	$\text{NH}_2^+_{\text{asy}}$	$\text{COO}^-_{\text{asy}}$	C=C	C=N	Benzen Ring stretch	C-N	$\text{H}_2\text{O}$ Wag.	M-O	M-N
1.10-Phen. Pro.	3421	1624	1645	1562	1140	1037	851		
$\text{Zn}^{2+}$ +1.10-Phen.+pro. ( $\text{Cd}^{2+}$ -1.10phen+pro)			1625	1517	1105				429
$\text{Ni}^{2+}$ +1.10 Phen.+pro.	3486	1580	1634	1516	1103	1045	848	636	517
							931		465

Table 2.  $^1\text{H}$  NMR signals of 1.10 phen. and Pro. and their corresponding metal complexes

	Ar-H	N-H amine	$\text{CH}_2^1, \text{CH}_2^2, \text{CH}_2^3$	CH
1,10phen.	7.64-9.25			
L-Pro.		1.85-5	2.37-3.81, 3.46	3.97
$\text{Zn}^{2+}$ +1.10-phen.+ pro. $\text{Cd}^{2+}$ + 1.10 Phen.+ pro.	7.80-8.56 8.18-9.22		2.95 3.65	
$\text{Ni}^{2+}$ +1.10 Phen. + pro.		1.91		

Table 3. Metal and chlorine content in each complex

	Chemical formula	Chlorine %		metal %		M:L Ratio	Mol. Weight
		Calc.	Found	M calc.	M found		
A <sub>3</sub>	[Zn (phen.) Cl <sub>2</sub> ]	21	19	19.55	18.85	1:1	316.49
A <sub>6</sub>	[Cd(phen.)Cl H <sub>2</sub> O]	9.62	8.5	30.8	31	1:1	346.09
A <sub>12</sub>	[Ni(pro).2H <sub>2</sub> O]	0	1.5	27.98	25.98	1:1	208.85

Table 3. Metal and chlorine content in each complexes

$\text{Zn}^{+2}$ + 1-10 phen. +Pro.	$\text{Zn}^{+2}$ + 1-10 phen.	Softer- Softer
$\text{Ni}^{+2}$ + 1-10 phen. +Pro.	$\text{Ni}^{+2}$ + 1-10 phen.	Harder - Harde
$\text{Cd}^{+2}$ + 1-10 phen. +Pro.	$\text{Cd}^{+2}$ + pro.	Softer- Softer

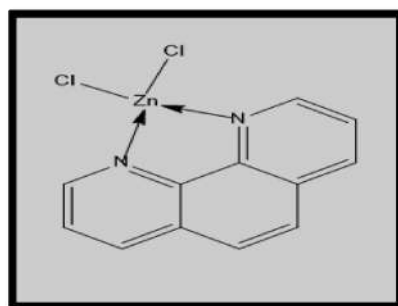


Fig. 1. Zinc complex geometry

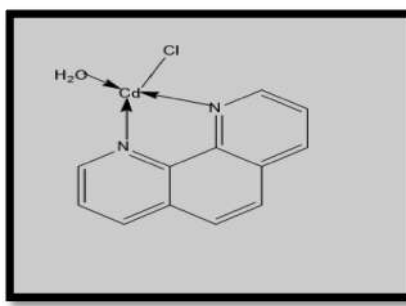


Fig. 2. Cadmium complex geometry

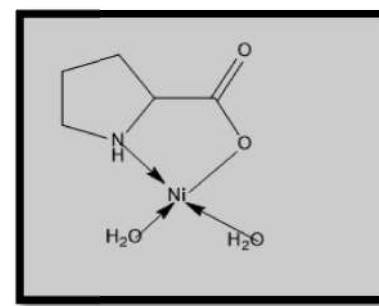


Fig. 1. Nickel complex geometry

$\text{Ni}^{+2}$  complexes differ from the last two complexes, none of aromatic rings corresponding to 1-10 phen. were appeared but the bands of pro.  $\text{NH}_2^+_{\text{asy}}$ ,  $\text{COO}^-_{\text{asy}}$ , C-N Shifted as seen in the table (Wagner *et al.*, 2008; AL-Noor and AbdulKarim, 2015; Gunasekaran *et al.*, 2009). New bands M-O and M-N are appeared which confirm the modes of coordination.

 $^1\text{H}$  NMR study

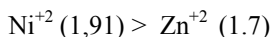
as shown in table-2, the chemical shifts of the all signals referring to the ligands and their corresponding metal ions complexes formed. Results obtained is clearly confirmed that both  $\text{Zn}^{+2}$  and  $\text{Cd}^{+2}$  are coordinated with 1-10 phen. only due to the appearance of aromatic protons (Kavitha *et al.*, 2006; Nagababu *et al.*, 2009; Adeloje and Ajibade, 2010; Grimes, 1982) in their  $^1\text{H}$ -NMR Spectrum. For  $\text{Ni}^{+2}$  complex the disappearance of the aromatic protons and the appearance of other signals defiantly confirms the coordination of nickel ion with pro.

## Metal and chlorine contents

Table-3: illustrate the metal and chlorine contents in the complexes. Both zinc and cadmium ions coordinate with tetrahedral while  $\text{Ni}^{+2}$  with square planar and the M:L ratio for all of them are 1:1. Fig(1-3).

### Competition study:

The competition between ligands toward metal ions is governing by the hard soft acid base (HSAB) principles. It can be classified the studied metal ion as follows:  $\text{Ni}^{+2}$  (border line acid),  $\text{Zn}^{+2}$  (border line acid),  $\text{Cd}^{+2}$  (soft acid).  $\text{Ni}^{+2}$  is harder than  $\text{Zn}^{+2}$  because the higher the electronegativity of metal ions the harder acid(15) as follows:



The ionic size also give an indication for the hardness, the smallest ion is the harder (Paolo *et al.*, 2013; Ei-Ichiro, 1987)

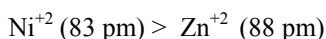


Table -3 show the classification of competition:

1-10 phen. is softer than Pro. Because of the presence of two nitrogen donors which has been softer than the ligand own oxygen and nitrogen donors (Chandratilaka *et al.*, 2013)

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