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ORIGINAL ARTICLE

Synthesis and characterization of heterobimetallic complexes of the type [Cu(pn)$_2$][MCl$_4$] where M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II)

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KEYWORDS

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Equilibrium

Abstract A series of new bimetallic transition metal complexes of the type [Cu(pn)$_2$] [MCl$_4$] have been synthesized (where M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), pn = 1,3-diaminopropane) and characterized by elemental analysis, molar conductance, TGA, IR and electronic spectra. All the compounds are 1:1 electrolyte in DMF. The Cu(II) ion is square-planar while metal ions in the anionic moiety acquire their usual tetrahedral arrangement. On the basis of these studies it is concluded that anionic moiety is electrically stabilized by its cationic counterpart.

1. Introduction

Although diamines are well known chelating agents, they also behave as bridging ligand either with cis or trans conformation. The 1,3-diaminopropane is known to form six membered chelate ring with the metal ions (Miyoshi et al., 1972; Allmann et al., 1990). [Cu(pn)$_2$]Cl$_2$ is known to have a tetragonally distorted pseudooctahedral unit with C_{2h} symmetry where chloride ions are weakly bonded and remain uncoordinated (Davey and Stephens, 1971). Chemistry of tetrahalogeno complexes is well established. Such complexes are strictly termed as halide complexes (Hald and Rasmussen, 1978a,b; Ohba and Rasmussen, 1994). After a closer examination of M(en)Cl$_2$ X-ray powder photographs and vibrational data it has been pointed out that Zn(en)Cl$_2$ and Cd(en)Cl$_2$ should not be formulated as [Zn(en)$_2$][ZnCl$_4$] or [Cd(en)$_2$][CdCl$_4$] nevertheless, this type of formulations are reported in the older literature (Sukarova et al., 1993; Fatmi et al., 2007).

Gerken and coworkers have reported the synthesis and stabilization of tetrachloroarsonium and tetrabromoarsonium cations using weakly coordinating bulky anions as counter anions. It has been reported that [AsCl$_4$][As(OTeF$_5$)$_6$] is stable while [AsBr$_4$][As(OTeF$_5$)$_6$] undergoes slow decomposition at room temperature but kinetically more stable than AsF$_6$ and [AsF(OTeF$_5$)$_6$]$^-$ salt, which rapidly decomposes upon warming at room temperature. The synthesis and stabilization of such complexes are recent matter of concern (Pastorek et al.,

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2011; Nami et al., 2010; Beznischenko et al., 2009; Pryma et al., 2003; Gerken et al., 2000; Casteel et al., 1996).

A family of cyanobridged Copper(II)–Copper(I) mixed valence polymers containing diamine ligands of formula $[Cu(pn)_2][Cu_2(CN)_4]$ has been prepared with the aim of analyzing how their architecture may be affected by steric constraints imposed by the diamine ligands (Cui et al., 2011; Colacio et al., 2002). Since the stabilization of tetrachloro-metallate ion by bis-propanediamine cupric ion has not been reported, it is, therefore, considered worthwhile to study and evaluate the phenomenon associated with the formation and stabilization of relatively larger $[MCl_4]^{2-}$ anion by $[Cu(pn)_2]^{2+}$ cation (Ha, 2010; Kim et al., 1998; Sundberg and Uggla, 1997). In continuation of our earlier work on heterobinuclear complexes, we are reporting in this paper, a series of novel bimetallic transition metal complexes of the type $[Cu(pn)_2][MCl_4]$, (M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) (Siddiqi et al., 1993a–d). The ionic nature has been established from their molar conductance in DMF.

2. Experimental

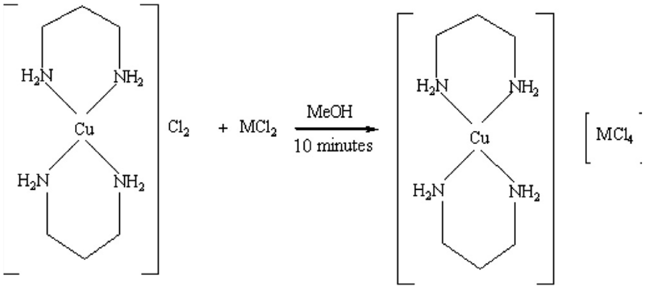
1,3-Diaminopropane (Fluka), MCl_2 (M = Co, Ni, Cu, Zn, Cd and Hg) (BDH) were used as supplied. DMF (Merck), MeOH and Et_2O used in this work were of analytical grade.

2.1. Preparation of [Cu(pn)$_2$]Cl$_2$

$[Cu(pn)_2]Cl_2$ was synthesized by literature method with a slight modification (Siddiqi et al., 1993a–d). To a hot solution of $CuCl_2{\cdot}2H_2O$ (1.66 g, 0.01 mol) in MeOH (25 cm^3) was added dropwise 1,3-diaminopropane (1.671 ml, 0.02 mol) dissolved in the same solvent. The dark blue precipitate formed instantaneously was refluxed for 5–6 h (Scheme 1) and left for nearly ten days which yielded dark blue flakes. It was washed with MeOH followed by Et_2O and dried in vacuum for seven days. M.P. ~190–200 °C.

2.2. Preparation of [Cu(pn)$_2$][MCl$_4$]

To a methanolic solution (15 cm^3) of $[Cu(pn)_2]Cl_2$ (0.01 mol) was added divalent metal chloride dissolved in the same solvent (0.01 mol). On stirring the mixture for ten min dark coloured precipitates (Table 1) were obtained (Scheme 2). It was filtered and washed with MeOH followed by Et_2O and dried in vacuum over anhydrous $CaCl_2$ for 7 days. Any attempt to prepare such complexes with Cr(II), Mn(II) and Fe(III) was unsuccessful. The quantity used and per cent yield of all the complexes are given below.



Scheme 2 Synthesis of $[Cu(pn)_2]$ $[MCl_4]$.

2.3. No. of moles, weight (g) of the reactants and per cent yield of the products

$$\text{(1)}\quad \underset{0.01\text{ mol }(1.66\text{ g})}{Cu(pn)_2Cl_2} + \underset{0.01\text{ mol }(2.91\text{ g})}{CoCl_2\cdot 6H_2O} \rightarrow \underset{\text{yield}=32\%}{[Cu(pn)_2][CoCl_4]}$$

$$\text{(2)}\quad \underset{0.01\text{ mol }(1.66\text{ g})}{Cu(pn)_2Cl_2} + \underset{0.01\text{ mol }(2.71\text{ g})}{NiCl_2\cdot 6H_2O} \rightarrow \underset{\text{yield}=41\%}{[Cu(pn)_2][NiCl_4]}$$

$$\text{(3)}\quad \underset{0.01\text{ mol }(1.66\text{ g})}{Cu(pn)_2Cl_2} + \underset{0.01\text{ mol }(1.70\text{ g})}{CuCl_2\cdot 2H_2O} \rightarrow \underset{\text{yield}=45\%}{[Cu(pn)_2][CuCl_4]}$$

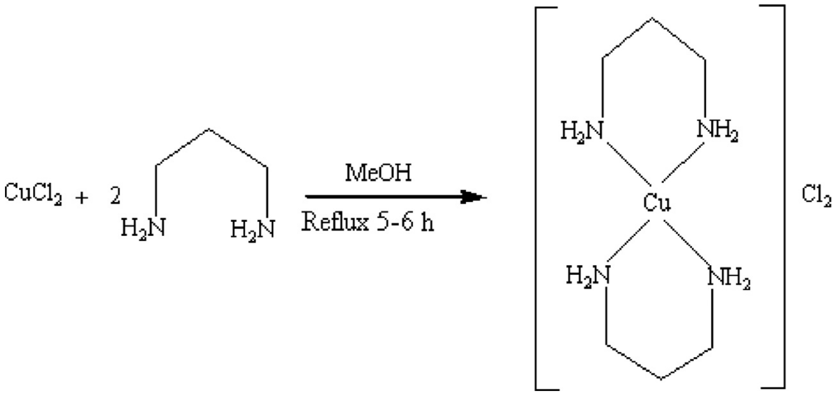
$$\text{(4)}\quad \underset{0.01\text{ mol }(1.66\text{ g})}{Cu(pn)_2Cl_2} + \underset{0.01\text{ mol }(1.66\text{ g})}{ZnCl_2} \rightarrow \underset{\text{yield}=45\%}{[Cu(pn)_2][ZnCl_4]}$$

$$\text{(5)}\quad \underset{0.01\text{ mol }(1.66\text{ g})}{Cu(pn)_2Cl_2} + \underset{0.01\text{ mol }(1.82\text{ g})}{CdCl_2} \rightarrow \underset{\text{yield}=57\%}{[Cu(pn)_2][CdCl_4]}$$

$$\text{(6)}\quad \underset{0.01\text{ mol }(1.66\text{ g})}{Cu(pn)_2Cl_2} + \underset{0.01\text{ mol }(2.71\text{ g})}{HgCl_2} \rightarrow \underset{\text{yield}=54\%}{[Cu(pn)_2][HgCl_4]}$$

2.4. Physical measurements

Elemental analyses were carried out with Carlo-Erba 1106. Molar conductance was measured with ELICO Conductivity Bridge CM 183. The IR spectra (600–4000 cm^{-1}) were recorded with Interspec 2020 FTIR SPECTROLAB, UK as KBr pellet. Far IR spectra (200–500 cm^{-1}) were recorded using CsBr. Electronic spectra were recorded with UV–vis spectrophotometer UV min-1240. Chlorine was analyzed as AgCl.



Scheme 1 Synthesis of $[Cu(pn)_2]Cl_2$.

Table 1 Analytical data, color, melting point and conductance.

S.No.	Compounds	Elemental analysis found (Calcd.), %				Color	m.p. (°C)	Molar conductance ($Scm^2 mol^{-1}$)
		C	H	N	Cl			
1.	$[Cu(pn)_2]Cl_2$	12.93 (12.50)	3.75 (4.01)	10.01 (9.87)	25.98 (26.01)	Dark blue	200	120.90
2.	$[Cu(pn)_2][CoCl_4]$	17.01 (16.50)	4.04 (4.35)	12.91 (12.48)	26.45 (26.78)	Light blue	190	65.16
3.	$[Cu(pn)_2][NiCl_4]$	17.49 (17.06)	3.96 (4.35)	13.39 (12.80)	27.60 (27.12)	Light blue	200	74.89
4.	$[Cu(pn)_2][CuCl_4]$	17.94 (17.46)	4.95 (4.85)	14.08 (13.58)	26.75 (27.05)	Light blue	190	76.34
5.	$[Cu(pn)_2][ZnCl_4]$	17.47 (17.02)	5.00 (5.27)	13.34 (13.63)	25.93 (26.23)	Dark purple	180	73.51
6.	$[Cu(pn)_2][CdCl_4]$	14.86 (14.34)	3.83 (4.32)	11.20 (11.15)	26.21 (26.89)	Purple	175	69.42
7.	$[Cu(pn)_2][HgCl_4]$	13.27 (13.20)	3.40 (3.89)	10.06 (9.48)	27.38 (27.83)	Light purple	175	63.73

The TGA was done with Mettler Star^e SW 8.10 under nitrogen atmosphere using Al_2O_3 as reference.

3. Results and discussion

The elemental analysis is consistent with the proposed formulation of the complexes and they decompose only above 200 °C (Table 1). The reaction of $[Cu(pn)_2]Cl_2$ with MCl_2 leads to the formation of $[Cu(pn)_2][MCl_4]$. The complex $[Cu(pn)_2]Cl_2$ may be pseudo octahedral. It is apparent that during its reaction with MCl_2, the chloride ion may be transferred in order to maintain equilibrium between the two species. In such complexes, the central metal ion in cationic form explicitly exists in square-planar environment although the larger anionic counterpart maintains its ubiquitous tetrahedral configuration and is stabilized by $[Cu(pn)_2]^{2+}$cation. The structure of $[Cu(pn)_2]^{2+}$ is known to be square-planar (Kang et al., 2007; Mondal et al., 2001). There is no speculation about it. They are moderately soluble in DMSO and DMF, stable to heat and light and can be stored in an open atmosphere without any decomposition.

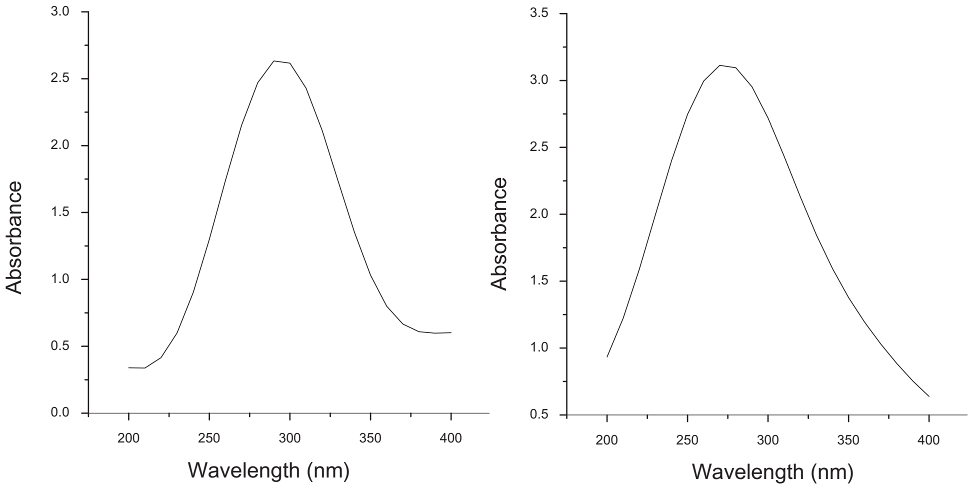
It evident by their room temperature molar conductivity (1 mM) measured in DMF (60–90 $Scm^{-2} mol^{-1}$) that $[Cu(pn)_2]Cl_2$ behaves as 1:2 electrolyte while $[Cu(pn)_2][MCl_4]$ is 1:1 electrolyte in the same solvent. It is known that molar conductance of 1 mM solution of 1:1 electrolyte falls between (65–90 $Scm^2 mol^{-1}$). Our values are within this limit (Table 1) and therefore it is suggested that the complexes are 1:1 electrolyte. Although different ranges for 1:1 electrolyte in this solvent have been quoted and an average of 65 $Scm^2 mol^{-1}$ for 1 mM solution has been accepted. The complexes are non-electrolyte if they have molar conductance values below the above range. It has been reported that the values for 1:2 electrolyte in DMF generally falls between 130–170 $Scm^2 mol^{-1}$. However, for ionic compounds of this type, such as tetra phenyl borate the conductance is as low as 115 $Scm^2 mol^{-1}$ (Geary, 1971). Since the molar conductance of $[Cu(pn)_2Cl_2]$ is 120 $Scm^2 mol^{-1}$, it is suggested to be 1:2 electrolyte (Table 1). The quantitative estimation of Cl^- ion as AgCl confirms the presence of four chloride ions in the bimetallic species. Formation of the bimetallic complex by transfer of chloride ion is also evidenced by reaction of $[Cu(pn)_2]Cl_2$ with $[M(PPh_3)_2Cl_2]$ where M = Co(II), Ni(II) (Scheme 3). Precipitation of triphenyl phosphine in this reaction indicates that it is replaced by chloride ions of the precursor.

3.1. Electronic spectra

Two types of absorption bands were observed for all the complexes in their UV–visible spectra (Figs. 1a, 1b). The intense band ranging from 250 to 300 nm is unambiguously attributed to the L → M charge transfer (Bernhardt et al., 2001). All compounds of Cu(II) with diamines exhibit a band around 250 nm which is assigned to ligand to metal charge transfer. Zelenak and co-workers have recently reported from the electronic spectral study and crystal structure that the UV band at 250 nm in $[Cu(pn)_2Cl_2]$ is attributed to ligand to metal charge transfer (Zelenak et al., 2006). Intraligand charge transfer does not occur in such complexes. Secondly, the Lapporte-forbid-

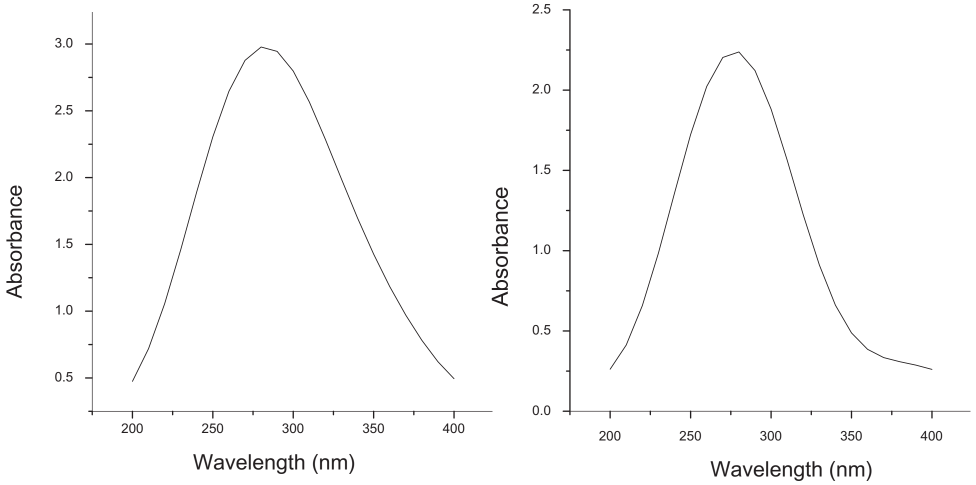
Table 2 Electronic spectra.

S.No.	Compounds	UV spectral region		Visible spectral region	
		λ (nm)	Abs.	λ (nm)	Abs.
1.	$[Cu(pn)_2]Cl_2$	272	3.08	660	0.122
2.	$[Cu(pn)_2][CoCl_4]$	289	3.37	670	0.613
3.	$[Cu(pn)_2][NiCl_4]$	279	3.33	675	0.593
4.	$[Cu(pn)_2][CuCl_4]$	279	2.27	680	0.543
5.	$[Cu(pn)_2][ZnCl_4]$	280	3.90	650	0.419
6.	$[Cu(pn)_2][CdCl_4]$	271	3.03	620	0.127
7.	$[Cu(pn)_2][HgCl_4]$	279	2.61	619	



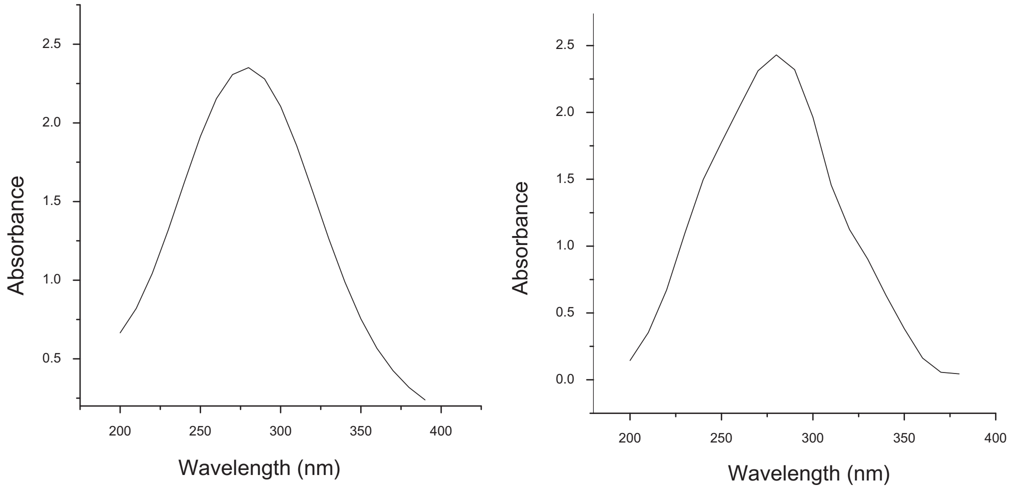
$[Cu(pn)_2][CoCl_4]$

$[Cu(pn)_2][NiCl_4]$



$[Cu(pn)_2][CuCl_4]$

$[Cu(pn)_2][ZnCl_4]$

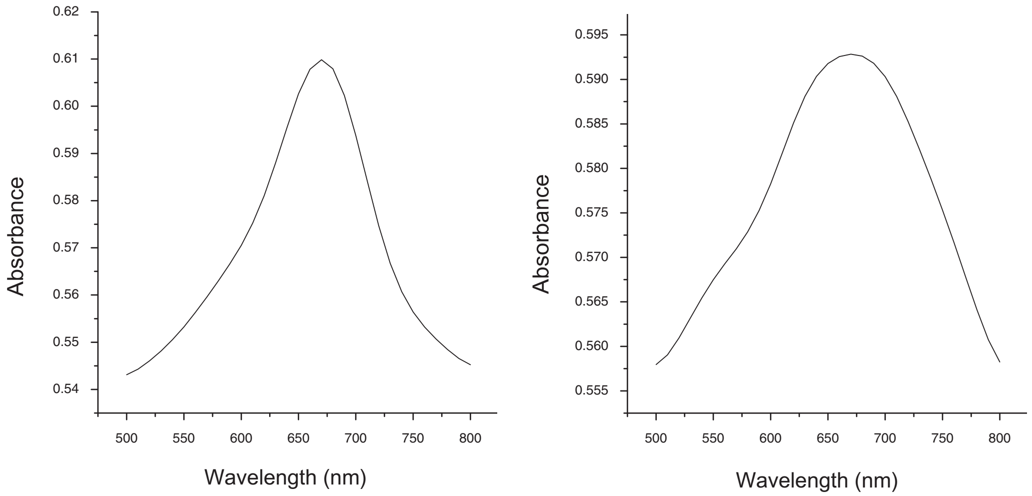


$[Cu(pn)_2][CdCl_4]$

$[Cu(pn)_2][HgCl_4]$

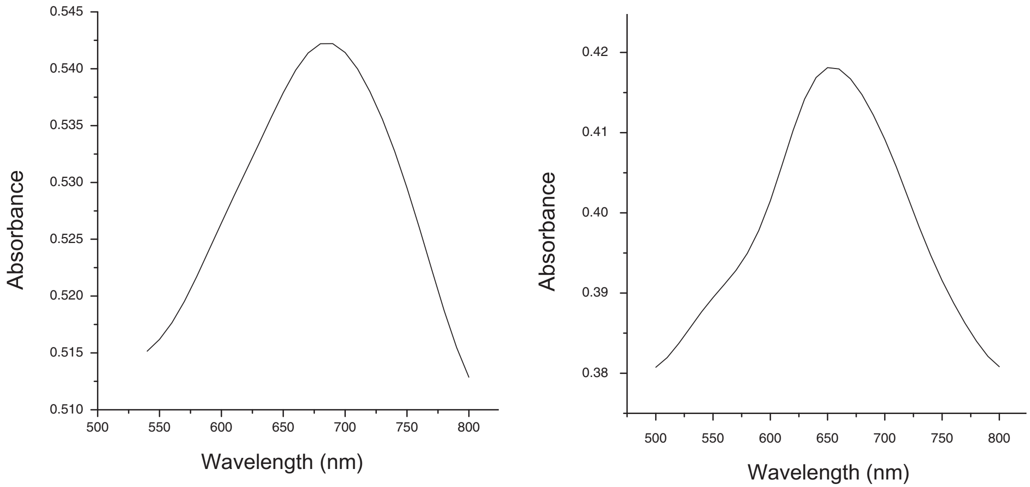
Figure 1a UV spectra of complexes.

den *d*–*d* transition (400–800 nm) is due to d^9 of Cu(II) ion (Nami et al., 2010). The precursor complex $[Cu(pn)_2]Cl_2$ shows a broad *d*–*d* band at 630 nm which indicates an octahedral geometry. However in bimetallic complex the same band



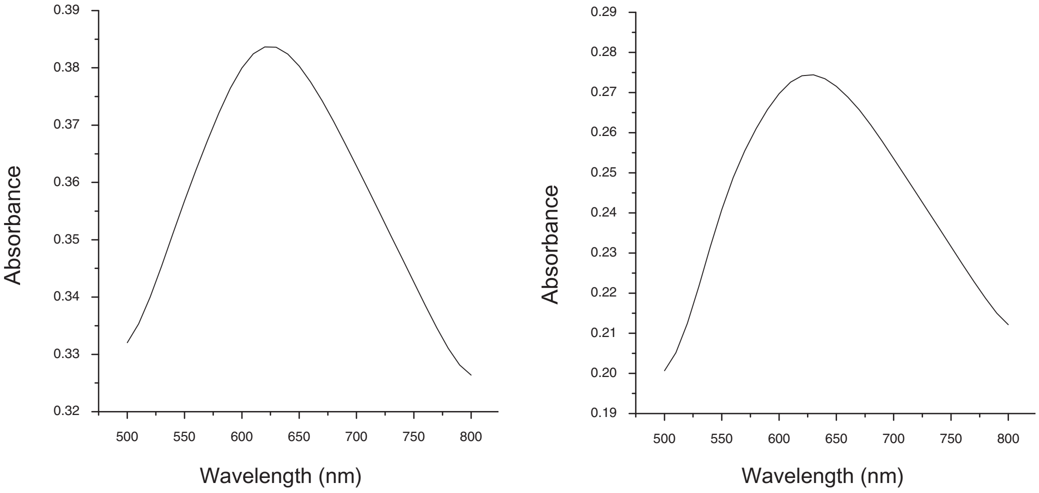
[Cu(pn)$_2$][CoCl$_4$]

[Cu(pn)$_2$][NiCl$_4$]



[Cu(pn)$_2$][CuCl$_4$]

[Cu(pn)$_2$][ZnCl$_4$]



[Cu(pn)$_2$][CdCl$_4$]

[Cu(pn)$_2$][HgCl$_4$]

Figure 1b Visible spectra of complexes.

appears at ca. 680 nm, indicating the presence of square-planar geometry (Gaura et al., 1982). The spectra slightly differ from each other with regard to the position of the *d–d* band, while the absorption band in the UV region remains nearly unaltered

Table 3 IR spectra.

S.No.	Compounds	ν(NH)	ν(C–C)	ν(C–N)	Ring vib.	ν(Cu–N)	ν(M–X)
1.	$[Cu(pn)_2]Cl_2$	3404 3236	1027	1440 1399	495	405	268
2.	$[Cu(pn)_2][CoCl_4]$	3281 3230	1028	1460 1395	500	417	283
3.	$[Cu(pn)_2][NiCl_4]$	3279 3232	1028	1463 1396	501	416	283
4.	$[Cu(pn)_2][CuCl_4]$	3283 3228	1028	1455 1396	501	416	284
5.	$[Cu(pn)_2][ZnCl_4]$	3282 3236	1022	1465	495	401	281
6.	$[Cu(pn)_2][CdCl_4]$	3270 3229	1022	1462	493	404	234
7.	$[Cu(pn)_2][HgCl_4]$	3277 3231	1022	1465	491	418	227

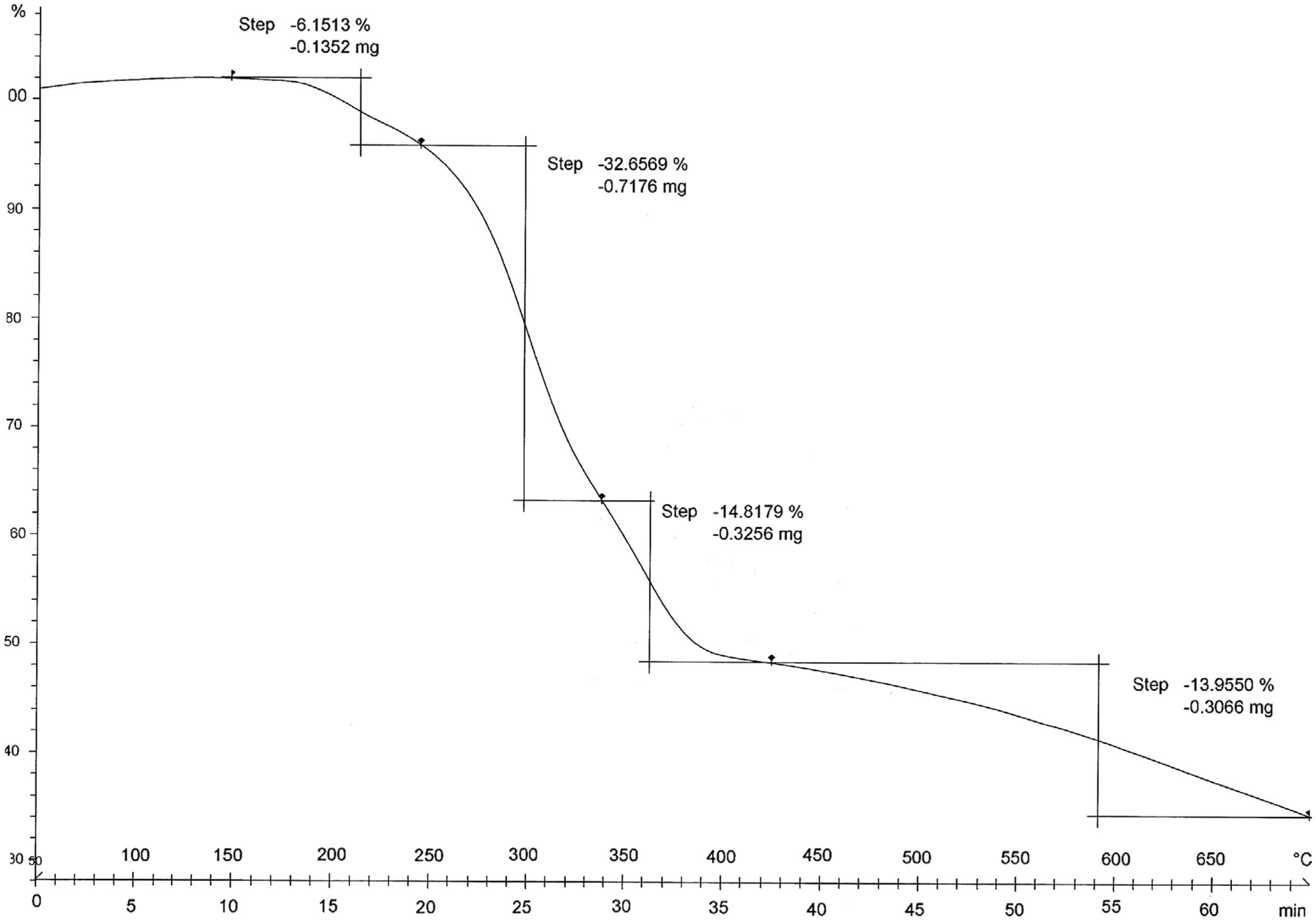


Figure 2 Thermogram of $[Cu(pn)_2][CuCl_4]$.

(Table 2). The peak in the visible region varies according to the nature of the metal. The λ_{max} in the visible region slightly increases with decreasing ionic radii of the metal ions.

Talbert et al. (1970), have suggested that $[Cu(pn)_2][CuCl_4]$ is a complex salt with tetrahedrally coordinated chloro anion. We have observed a broad band at 279 nm in its electronic spectrum which is probably due to charge transfer from ligand to metal. It is also supported by additional (Cu–Cl) bands at 284 cm^{-1} and 234 cm^{-1} in its IR spectrum which is in agreement with values previously reported for $[CuCl_4]^{2-}$ ion (Figgis, 1976). The geometry of $[CuCl_4]^{2-}$ is, therefore, suggested to be tetrahedral stabilized by $[Cu(pn)_2]^{2+}$ ion (Parent et al., 2007) .

$$Cu(pn)_2Cl_2 + [M(PPh_3)_2Cl_2] \xrightarrow{MeOH} [Cu(pn)_2][MCl_4] + 2PPh_3$$

Scheme 3 Precipitation of triphenylphosphine.

3.2. IR spectra

As a consequence of the reaction of $CuCl_2$ with 1,3-diaminopropane a square-planar Cu chelate complex is formed bearing two chloride ions out of the coordination sphere. The IR spectrum of the 1,3-diaminopropane (Table 3) shows two strong (N-H) absorption bands in 3450–3250 cm^{-1} region which undergoes a negative shift after chelation with copper(II) forming a six membered ring (Feerrari et al., 1991; Silverstien et al., 1981; Nakamoto, 1986). The in-plane vibration of the six membered rings so formed may be expected to be coupled mechanically to some extent with metal nitrogen vibrational modes.

On the basis of normal coordinate analysis of the $[M(en)_2]^{2+}$ ion with C_{2h} symmetry Omura et al. (1971) have assigned the ν(Cu–N) band in 472–412 cm^{-1} region. We have noted strong bands in 400–420 cm^{-1} region for all the complexes (Malik et al., 1983). The M–Cl stretching frequency (Kabanos et al., 1992) in the 250–380 cm^{-1} region in our case indicates the presence of tetrahedral tetrachlorometallate anion (Exarchos et al., 2001). The bands in the 600–400 cm^{-1} are assigned to in-plane ring deformation and NH_2 rocking modes (Nami and Siddiqi, 2004). All the ν(Cu–N) and ν(M–Cl) were placed on a firm basis by the initial studies on stretching vibrations of the MX_4^{2-}. However, it is clear from the previous work on ν(Cd–Cl) that these are invariably below 200 cm^{-1} in octahedral complexes and only slightly above 200 cm^{-1} in tetrahedral complexes. An additional IR band is observed in the region 230–350 cm^{-1} which is assigned to M-Cl stretching frequency of $[MCl_4]^{2-}$ moiety (Clark, 2010).

3.3. Thermogravimetry

The TGA profile of all the complexes are essentially similar and consists of four well defined stages implying their similar structural features. The weight loss data corresponding to various steps in thermogram were compared with those calculated. The thermal analysis of $[Cu(pn)_2][CuCl_4]$ was studied (Fig. 2) in the temperature range 50–700 °C at a heating rate of 10 °C min^{-1}. During first break in the temperature range 150–250 °C, the weight loss of ~6.15% (cal. 6.01%) could be accounted for the loss of 3/2 mol of H_2O from the complex which is believed to be absorbed during storage. In the second step (250–340 °C) the weight loss of ~32.65% (cal. 33.33%) corresponds to the elimination of two moles of 1,3-diaminopropane moiety. In the third and fourth step two chloride ions are lost one by one at each step (340–430 °C) a weight loss of ~14.81% (Cal. 15.98%) and (430–700 °C) a weight loss of 13.95% (Cal. 15.98%). In the end the residue 28.63% corresponds to Cu bimetals (Materazzi et al., 2002).

4. Conclusion

The reaction of $[Cu(pn)_2]Cl_2$ with MCl_2 leads to the formation of $[Cu(pn)_2][MCl_4]$. As a consequence of the reaction of $CuCl_2$ with 1,3-diaminopropane a square-planar Cu(II) chelate complex is formed with two chloride ions out of the coordination sphere. The complex $[Cu(pn)_2]Cl_2$ may be pseudo octahedral but in its reaction with MCl_2, the chloride ion may be transferred to maintain an equilibrium between the two species. In such complexes, the central metal ion in cationic form explicitly exists in square–planar environment, however, the anionic counterpart maintains its ubiquitous tetrahedral configuration.

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