Polyhedron 47 (2012) 112-117

Contents lists available at SciVerse ScienceDirect

Polyhedron

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

Synthesis, spectroscopic and structural characterization of Co(II), Ni(II) and Cu(II) complexes of substituted 2-pyridyl amine based [N,N] chelating ligand

Billa Prashanth, Maheswararao Karanam, A.R. Choudhury, Sanjay Singh*

Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali, Knowledge City, Sector 81, SAS Nagar, Mohali 140306, Punjab, India

ARTICLE INFO

Article history: Received 28 May 2012 Accepted 8 August 2012 Available online 17 August 2012

Keywords: Pyridyl amine Cobalt complex Tetrahedral nickel complex Copper complex Hydrogen bonding

ABSTRACT

The reaction of N-benzylaminopyridine with the imidoylchloride of N- $(2.6-iPr_2C_6H_3)$ acetamide in the presence of Et₃N affords a new neutral [N,N] chelating ligand, (PhCH₂)N(2-pyridyl)C{(Me)(=N-2,6-iPr₂C₆₋ H₃)} (L). The reaction of equimolar quantities of L with Cu(NO₃)₂, CuCl₂ and NiBr₂, respectively, in DCM, acetonitrile and DME yields the corresponding mononuclear complexes L-Cu(NO₃)₂ (1), L-CuCl₂ (2) and L·NiBr₂ (**3**). Whereas, the reaction of L with $CoCl_2 \cdot 6H_2O$ leads to the formation of [HL·CoCl₃] (**4**) with pyridine nitrogen coordinated to cobalt. Solid state structure of L and compounds 1-4 have been investigated by single crystal X-ray structural analysis. The ligand L shows the E-anti arrangement in the solid state and its mononuclear complex 1 shows six coordinated Cu in a quasi square planar geometry with two long distanced donors: complexes 2 and 3 show distorted tetrahedral arrangement of the substituents around metal ions. Interestingly, the solid state structure of complex 4 reveals C-H…Cl intra-molecular hydrogen bonding and N-H…Cl and C-H…Cl inter-molecular hydrogen bonds. These hydrogen bonding interactions in complex **4** facilitate the formation of an extended 2D network structure.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Anionic versus neutral ligands and sterically encumbered versus sterically less demanding ligands have provided the chemists with a synthetic tool to control the nuclearity of the metal complexes. This subtle control can further be enhanced by incorporating the chelate character in the ligand. These elegant features can easily be incorporated in the ligand design by using various synthetic methodologies available at hand. It is due to proper design of the ligand that has made possible the syntheses of several interesting molecules [1-5]. In recent years, the bis(2-pyridyl) amine based ligands with C₂N₃ backbone have emerged as potential spectator ligands in view of their strong [N,N] chelation to metals and tuneable steric and electronic factors [6]. Additionally, unlike the mono- or di-anionic ligands these ancillary neutral *bis*(2-pyridyl) amines do not engage covalent valence on the metal center and have proved to be very useful in controlling the coordination number and nuclearity in the metal complexes.

Chart 1 depicts well characterized skeletal arrangement in the ligands with C_2N_3 skeleton as reported in the literature, [7–12]. The ligands are mostly either aryl substituted bis(2-pyridyl) amine (with the substituents located at different positions of the pyridyl ring) and/or on the amine nitrogen connecting the two pyridyl rings (I) or based on quinolylimine (II). However, the pyridylamidines

* Corresponding author. E-mail address: sanjaysingh@iisermohali.ac.in (S. Singh). (III) are comparatively rare and a few of these have been useful in the preparation of metal complexes containing metal-metal bonds [7]. Only one report illustrating the [N,N] chelating 2-pyridylbenzamidine ligand and its Ni complex for ethylene oligomerization appeared in 2009 [8]. This ligand (III) possesses a sterically congested 2,6-*i*Pr₂C₆H₃ group on the benzamidine moiety while the amine N contains H atom. The steric demand of the substituent on the benzamidine N atom and the electronic factors of the



R/R'/R" can be H, alkyl, or aryl group

Chart 1. Common [N,N] chelate ligands based on C₂N₃ skeleton.





^{0277-5387/\$ -} see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2012.08.019

substituents on pyridyl ring can influence the structure and reactivity of the metal complex. A report on the copper complexes with bis(2-pyridyl) amine ligands (type I) show that the steric effect of the substituents on the remote amine N can also play an important role on the reactivity of the metal complexes [9,10]. These copper complexes were used for the separation of olefins. Only one ligand (IV) contains the sterically demanding substituents on amidine nitrogen as well as on the remote amine nitrogen. The catalyst prepared *in-situ* from PdCl₂ and IV has been used in Suzuki–Miyaura reaction however, no attempt was made to characterize the metal complex [12].

We were interested in designing a neutral pyridylamidine ligand based on the C_2N_3 backbone that will offer a [N,N] bidentate chelate to the metal ions and with the aim to incorporate sterically demanding substituents on the amidine as well as on the remote amine nitrogen atom. Consequently, we report here on the synthesis, characterization and structure of the [N,N] donor neutral chelate ligand (PhCH₂)N(2-pyridyl)C{(Me)(=N-2,6-*i*Pr₂C₆H₃)} (L) and its mononuclear complexes with Co(II), Ni(II) and Cu(II). The steric effect of the substituents on acetamidine N as well as that of the amine N have also been explored.

2. Experimental

2.1. General procedures

All chemicals were purchased from Sigma–Aldrich and used without further purification. Solvents were distilled by standard methods prior to use. The imidoylchloride, $2,6-iPr_2C_6H_3N=C(Me)Cl$ was prepared following the reported procedure [13]. IR spectra of the complexes were recorded in the range 4500–400 cm⁻¹ using a Perkin Elmer Lambda 35-spectrophotometer. ¹H and ¹³C NMR spectra were recorded with Brucker 400 MHz spectrometer with TMS as an external reference. Elemental analyses were recorded with Thermo Scientific Flash 2000 Series and mass spectrometry was performed with Thermo Scientific LTQ XL instrument at NIPER

Table 1

Crystal	lographic	data	for	L and	1-4
---------	-----------	------	-----	-------	-----

Mohali. The UV–Vis spectra of the complexes were recorded with LABINDIA[®] UV3000⁺ UV–Vis spectrophotometer.

2.2. X-ray crystallography: compounds L and 1-4

Single crystal X-ray diffraction data were collected on a Bruker AXS KAPPA APEX-II CCD diffractometer (monochromatic MoKa radiation) equipped with Oxford cryosystem 700 plus at 100 K (except L). Data collection and unit cell refinement for the data sets were done using the Bruker APPEX-II suite, data reduction and integration were performed by SAINTV 7.685A (Bruker AXS, 2009) and absorption corrections and scaling were done using sad-ABSV2008/1 (Bruker AXS, 2009). The crystal structures were solved by using either olex2 or WINGX package using SHELXS-97 and the structure were refined using SHELXL-97 [14]. Single crystal data and refinement results are listed in Table 1. All non hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at geometrically calculated positions and were refined using riding model except H3a of complex 4. The H(3a) in 4 was located from difference Fourier map and refined isotropically. DIAMOND version 2.1d was used to generate graphics for the X-ray structures.

2.2.1. Synthesis of $(PhCH_2)N(2-pyridyl)C\{(Me)(=N-2,6-iPr_2C_6H_3)\}$ (L)

To a solution of NEt₃ (35 g, excess) and N-benzylaminopyridine (7.50 g, 40 mmol) in 150 mL dry toluene was added 2,6-*i*Pr₂C₆H₃. N=C(Me)Cl, (10.20 g, 43 mmol) dropwise at 0 °C. The mixture was refluxed for 6 h. After removal of all volatiles under *vacuo* the residue was taken in 200 mL dichloromethane (DCM) and washed with H₂O (3 × 100 mL), the organic layer was dried over MgSO₄, filtered and all volatiles were removed to afford light brown solid. This was recrystallized from acetone in 77% yield (11.87 g, 30.8 mmol). X-ray quality crystals were grown by slow evaporation from acetone. Mp: 120 °C. *Anal.* Calc. for C₂₆H₃₁N₃: C, 81.00; H, 8.10; N, 10.90. Found: C, 80.27; H, 8.02; N, 10.82%. ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.94 (d, *J* = 6.8 Hz, 6H, *Me*₂CH), 1.04 (d, *J* = 7.2 Hz, 6H, *Me*₂CH), 1.72 (s, 3H, C=NMe), 2.71 (sept, *J* = 7.2 and 6.8 Hz, 2H, Me₂CH), 5.30 (s, 2H, CH₂Ph), 6.87–6.90 (m, 2H, Ar), 6.95–6.97

Compound	L	1.HNO3	2 ·CH ₃ CN	3 .0.5DME	4
Empirical formula	C ₂₆ H ₃₁ N ₃	C26H32N6CuO9	C ₂₆ H ₃₁ N ₃ CuCl ₂ ·CH ₃ CN	$C_{26}H_{31}N_3NiBr_2 \cdot 0.5(DME)$	C26H32N3Cl3C0
Formula mass	385.54	636.12	561.03	649.13	551.83
T (K)	298(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	C2/c	PĪ	C2/c	$P2_1/c$
a (Å)	9.962(5)	36.666(3)	9.485(1)	37.849(5)	7.691(2)
b (Å)	18.377(10)	8.467(6)	10.584(1)	8.435(1)	22.879(4)
c (Å)	15.640(9)	19.4913(14)	14.067(1)	19.621(3)	16.761(3)
α (°)	90.00	90.00	79.222(2)	90.00	90.00
β(°)	126.87(4)	96.154(4)	87.074(1)	114.099(1)	112.566(2)
γ (°)	90.00	90.00	80.665(1)	90.00	90.00
$V(Å^3)$	2291.0(2)	6016.0(7)	1368.65(1)	5718.52(2)	2723.57(2)
Ζ	4	8	2	8	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.118	1.405	1.36	1.51	1.346
μ (MoK α) (mm ⁻¹)	0.066	0.786	1.017	3.498	0.943
F(000)	832	2648	586	2648	1148
θ range (°)	1.97-25.03	2.1-25.02	2.2-25.0	1.2-29.6	1.8-25.0
Index range	$-11\leqslant h\leqslant 10$	$-43 \leqslant h \leqslant 43$	$-9 \leqslant h \leqslant 11$	$-52 \leqslant h \leqslant 51$	$-7\leqslant h\leqslant 9$
	$-21 \leqslant k \leqslant 21$	$-10 \leqslant k \leqslant 9$	$-12 \leqslant k \leqslant 12$	$-11 \leqslant k \leqslant 11$	$-25\leqslant k\leqslant 27$
	$-18\leqslant l\leqslant 18$	$-23 \leqslant l \leqslant 22$	$-16 \leqslant l \leqslant 15$	$-26 \leqslant l \leqslant 27$	$-19\leqslant l\leqslant 19$
Reflections collected	15821	29231	13981	35239	14000
Independent reflections	4030	5311	4827	8012	4751
Data/restraints/parameters	4030/0/267	5311/0/473	4827/0/322	8012/0/441	4751/0/295
R_1 , $wR_2 [I > 2\sigma(I)]^a$	0.060, 0.163	0.055, 0.134	0.028, 0.066	0.032, 0.072	0.055, 0.120
R_1 , wR_2 (all data) ^a	0.117, 0.215	0.070, 0.134	0.036, 0.069	0.051, 0.086	0.104, 0.140
GOF	1.046	1.044	1.045	1.064	0.996
$\Delta ho_{ m max}$, $\Delta ho_{ m min}$ (e Å ³)	0.241, -0.404	1.336, -0.903	0.365, -0.292	0.556, -0.510	0.964, -0.758

^a $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$. $wR_2 = [\Sigma w (|F_0^2| - |F_c^2|)^2 / \Sigma w |F_0^2|^2]^{1/2}$.

(m, 3H, Ar), 7.08–7.09 (m, 1H, Ar), 7.15–7.18 (m, 2H, Ar), 7.23 (m, 2H, Ar), 7.45–7.49 (m, 1H, Ar), 8.31–8.33 (m, 1H, Ar). 13 C NMR (100 MHz, CDCl₃, δ ppm): 18.42, 23.07, 23.57, 28.08, 29.77, 30.96, 52.57, 119.23, 119.61, 122.45, 122.83, 126.64, 126.86, 127.38, 128.02, 128.24, 137.65, 137.95, 139.57, 145.80, 148.67, 155.05, 157.46. IR (ν cm⁻¹, KBr): 2953, 2922, 2862, 1632, 1582, 1474, 1438, 1374, 1321, 1275, 1227, 1197. EI-MS (*m*/*z*): 386 [M]⁺.

2.2.2. Synthesis of $L \cdot Cu(NO_3)_2$ (1)

To a solution of L (0.19 g, 0.50 mmol) in DCM (30 mL) was added Cu(NO₃)₂·3H₂O (0.12 g, 0.50 mmol) in portions. An immediate green color developed which was stirred for 15 h. This was followed by filtration through celite and slow evaporation of the solvent to afford green crystals suitable for X-ray analysis. The crystals were isolated from the mother liquor and washed with hexane. This gave analytically pure compound as green solid in 74% yield (0.21 g, 0.37 mmol). Drying the crystals under vacuum for longer duration leads to the evaporation of HNO₃ molecules present in the crystal lattice. The data reported below corresponds to this material. Mp: 220 °C. *Anal.* Calc. for C₂₆H₃₁N₅CuO₆: C, 54.49; H, 5.45; N, 12.22. Found: C, 53.92; H, 5.42; N, 11.45%. IR (ν cm⁻¹, KBr): 2966, 2927, 2868, 1601, 1559, 1483, 1441, 1398, 1286, 1136, 1088, 1005. EI-MS (m/z): 510 [M–NO₃]⁺; 386 [M–Cu(NO₃)₂]⁺. UV–Vis [CHCl₃, λ_{max} , nm]: 716, 384.

2.2.3. Synthesis of $L \cdot CuCl_2$ (2)

A solution of L (0.38 g, 1.0 mmol) in dry acetonitrile (10 mL) was added drop wise to a solution of CuCl₂ (0.13 g, 1.0 mmol) in dry acetonitrile (25 mL) at room temperature. The color of the solution immediately turned to dark brown. Stirring was continued for 12 h followed by removal of the solvent under vacuum to 10 mL. Storage at -30 °C afforded brown crystals of **2** in 1 week. Drying the crystals under vacuum eliminates the solvated acetonitrile and the following data reported is for this material. Crystalline 60% yield (0.31 g, 0.6 mmol). Mp: 158 °C. *Anal.* Calc. for C₂₆H₃₁N₃CuCl₂: C, 60.05; H, 6.01; N, 8.08. Found: C, 60.04; H, 5.99; N 8.09%. IR (ν cm⁻¹, KBr): 2960, 2926, 1597, 1554, 1476, 1436, 1396, 1363, 1258, 1223, 1027. EI-MS (m/z): 483 [M–Cl]⁺. UV–Vis [CHCl₃, λ_{max} , nm]: 775, 428.

2.2.4. Synthesis of L·Ni Br_2 (3)

A solution of NiBr₂ (0.43 g, 2.0 mmol) in dry DME (20 mL) was prepared at room temperature. To it was added drop wise a solution of L in 20 mL dry DME (0.77 g, 2.0 mmol) at room temperature. Color of the solution slowly changed from yellow-brown to deep purple. The solution was stirred overnight followed by concentration of the solution under vacuum and storage at -30 °C afforded purple colored X-ray quality crystals. Drying the crystals under vacuum leads to the loss of DME molecules present in the crystal lattice. The following data pertains to this material. Crystalline 88% yield (1.06 g, 1.76 mmol). Mp: 255 °C. Anal. Calc. for C₂₆H₃₁N₃. NiBr₂: C, 51.70; H, 5.17; N, 6.96. Found: C, 52.56; H, 5.18; N, 6.95%. IR (ν cm⁻¹, KBr): 2962, 2922, 1601, 1560, 1475, 1458, 1436, 1349, 1261, 1107. EI-MS (m/z): 605 [M]⁺; 526 [M–Br]⁺; 386 [M–NiBr₂]⁺. UV–Vis [CHCl₃, λ_{max} , nm]: 983, 503.

2.2.5. Synthesis of [HL·CoCl₃] (4)

To a solution of L (0.19 g, 0.5 mmol) in DME (30 mL) was added $CoCl_2 \cdot 6H_2O$ (0.12 g, 0.5 mmol). Color of the solution gradually turned to blue and stirring was continued for 20 h. The blue solution was filtered through celite and removal of DME under reduced pressure afforded blue solid which was washed with hexane and dried under *vacuo*. Crystalline 56% yield (0.15 g, 0.28 mmol). Mp: 235 °C. *Anal.* Calc. for $C_{26}H_{32}N_3CoCl_3$: C, 56.59; H, 5.84; N, 7.61. Found: C, 58.74; H, 6.03; N, 7.35%. IR (ν cm⁻¹, KBr): 3428, 2963, 2923, 1599, 1435, 1390, 1260, 1095, 1025. EI-MS (m/z): 538

 $[M-CH_3]^+$; 519 $[M-2CH_3-H]^+$; 503 $[M-CH_3-CI]^+$; 386 $[M-CoCl_{3-}-H]^+$. UV-Vis $[CHCl_3, \lambda_{max}, nm]$: 637, 567.

3. Results and discussion

3.1. Ligand synthesis and molecular structure

The ligand $(PhCH_2)N(2-pyridyl)C\{(Me)(=N-2,6-iPr_2C_6H_3)\}$ (L) was synthesized in a single step by the reaction of N-benzylaminopyridine with the imidoyl chloride, $2,6-iPr_2C_6H_3N=C(Me)Cl$ in the presence of Et₃N (Scheme 1). Compound L is a white crystalline solid soluble in common organic solvent. It was characterized by IR, ¹H and ¹³C NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. Sharp absorption bands around 1632 and 1582 cm⁻¹ in the IR spectrum of L can be attributed to the imine stretching frequency. The ¹H NMR spectrum of L exhibits resonances in accordance with the expected chemical shifts and pattern. The benzylic CH_2 appears as singlet at 5.30 ppm whereas the methyl groups of *iso*-propyl moiety appear as two doublets (0.94 and 1.04 ppm) and CH of the same is seen as a septet at 2.71 ppm. The backbone methyl group appears as a singlet at 1.72 ppm. The base peak in the EI mass spectrum of L at m/z 386 corresponds to the molecular ion peak [M]⁺. The molecular structure of L has been determined by single crystal X-ray diffraction (Fig. 1). Single crystals of L suitable for X-ray structural analysis were obtained by slow evaporation from acetone. Compound L crystallizes in the monoclinic system with space group $P2_1/c$ (Fig. 1 and Table 1).

In the solid state L exists as a monomer with E-anti geometry similar to [N,N]-phenylpyridylbenzamidine [7] that exists as a dimer due to intermolecular hydrogen bonding but contrary to [N,N] 2-pyridylbenzamidine ligand [8] which exist as a monomer with E-syn configuration. The N(2)–C(6) and C(6)–N(3) bond length of 1.396(3) and 1.277(3) Å, respectively, correspond to the amino and imino nature of the bonds which is in good agreement with the similar moieties reported earlier [7,8]. The C(1)–N(1) distance



Scheme 1. Synthesis of the [N,N] chelating ligand L.



Fig. 1. Molecular crystal structure of L. All hydrogen atoms have been omitted for clarity. Thermal ellipsoids have been drawn at 50% probability.

within the pyridine ring is 1.330(3) Å. The N(2)–C(6)–N(3) of the ligand is arranged in a non linear fashion with an angle of $116.30(2)^{\circ}$. The angles C(1)–N(2)–C(6) and N(1)–C(1)–N(2) are $122.8(2)^{\circ}$ and $117.4(2)^{\circ}$, respectively, which are similar to the reported values [7,8].

3.2. Copper(II) complexes (1 and 2) and their crystal structure

Reaction of L with 1 equiv of Cu(NO₃)₂·3H₂O in DCM affords L·Cu(NO₃)₂ (**1**). Compound L·Cu(NO₃)₂ is a green crystalline solid that melts at 220 °C. The IR spectral analysis gave the preliminary indication of formation of the metal complexes with L in addition to the color change and improved solubility of the metal salts. The IR spectrum of **1** shows C=N vibrations at 1600 and 1559 cm⁻¹ which is around 30 cm⁻¹ red shifted as compared to the ligand. The nitrate absorption bands appear at 1483, 1286 and 1005 cm⁻¹. The UV–Vis spectrum shows a broad absorption centered at 13965 cm⁻¹ (ε = 291 L mol⁻¹ cm⁻¹) assignable to the ²E_g \rightarrow ²Tg_{2g} transition for an octahedral geometry of the complex [15]. Another high energy band at 26040 cm⁻¹ (ε = 1650 L mol⁻¹ - cm⁻¹) may be assigned to a charge transfer transition.

Compound L·Cu(NO₃)₂ crystallize in monoclinic system with space group C2/c (Table 1). The molecular structure of this complex reveals the nitrate coordination to copper in a bidentate mode which was also initially envisaged by the IR spectrum of this complex. The C₂N₃Cu six member ring is non planar in a boat conformation with Cu(1) and N(2) forming the bow and stern of the boat. The C(13)–N(1), C(22)–N(3) and C(13)–N(2) bond lengths of 1.304(5), 1.343(5) and 1.386(5) Å, respectively, are slightly longer than that of the free ligand, vide-supra. The Cu atom in this complex resides in a quasi square-planar geometry and two additional long distanced oxygen ligands at axial positions making Cu as six coordinated. The quasi square plane consists of two oxygen atoms from two nitrate molecules [Cu(1)-O(1) 2.045(3) and Cu(1)-O(4) 1.994(3) Å] and two nitrogen atoms [Cu(1)-N(1) 1.965(3) and Cu(1)-N(3) 1.950(5)Å] of the ligand. The oxygen atoms O(2) and O(5) of two nitrate ions coordinate to Cu(1) as distant axial sites with a distance of 2.457(4) and 2.433(3) Å, respectively (Fig. 2). The N(1)-Cu(1)-N(3) and O(1)-Cu(1)-O(4) angles in the quasi



Fig. 2. Molecular structure of copper nitrate complex (1) with the ligand L. The HNO_3 molecule present in lattice has been deleted. All hydrogen atoms have been deleted for clarity. Thermal ellipsoids are drawn at 50% probability.



Fig. 3. Molecular structure of L-CuCl₂ complex **2**. All hydrogen atoms and solvated acetonitrile molecule have been deleted for clarity. Thermal ellipsoids are drawn at 50% probability.

suare plane are $91.36(3)^{\circ}$ and $86.61(1)^{\circ}$, respectively. The angle around Cu(1) with the distanced oxygen atoms O(2)–Cu(1)–O(5) is $130.32(1)^{\circ}$. Other metric parameters for **1** agree well with that of similar moieties [16–19].

The reaction of L with one equivalent of anhydrous CuCl_2 in dry acetonitrile easily affords L·CuCl₂ (**2**). Compound **2** is a red-brown solid that melts at 158 °C. The IR spectrum of **2** shows the ligand C=N vibrations (1597 and 1554 cm⁻¹) which show negative shift as compared to the free ligand and also in consistence with the formation of complex **1**. Crystals of **2** suitable for X-ray structure analysis were grown from acetonitrile at -30 °C. Complex **2** crystallizes in triclinic system with $P\bar{1}$ space group. The UV–Vis spectrum shows a broad absorption centered at 12900 cm⁻¹ (ε = 178 L mol⁻¹ cm⁻¹) due to d–d transition for tetrahedral geometry of Cu(II) [15]. The other high energy band at 23360 (ε = 1318 L mol⁻¹ cm⁻¹) may be assigned to a charge transfer transition.

The molecular structure of 2 shows the expected chelate complex with Cu residing in a distorted {~11%, considering the observed sum of the bond angles around Cu and comparing this value with that for an ideal T_d (656.8°) and for D_{4h} (720.0°)} tetrahedral arrangement of two N atoms of the ligand and two chloride ions (Fig. 3 and Table 1). The C₂N₃Cu six member ring is puckered, the Cu(1)-N(1) and Cu(1)-N(3) bond lengths of 1.970(2) and 1.965(2) Å are in good agreement with **1**. The C(13)–N(3), C(13)– N(2), C(5)–N(2) and C(5)–N(1) bonds in the C_2N_3Cu chelate ring, respectively, are 1.297(3), 1.387(3), 1.414(3) and 1.343(3) Å, which are slightly longer than the corresponding distances in free ligand. The Cu-Cl distances are 2.249(5) and 2.224(6) Å similar to the reported values [7]. The N(3)-Cu(1)-N(1) angle of $89.92(7)^{\circ}$ in 2 is narrower than that in **1**. The other bond angles Cl(1)-Cu(1)-Cl(2)N(3)-Cu(1)-Cl(1)139.25(5)°, 99.20(2)°, N(3)-Cu(1)-Cl(2)103.81(5)°, N(1)-Cu(1)-Cl(1) 97.71(5)°, and N(1)-Cu(1)-Cl(2) 134.08(5)° also show significant deviation from the regular tetrahedral bond angle.

3.3. Nickel complex (3) and its molecular structure

Reaction of L with 1 equiv of NiBr₂ in dimethoxyethane (DME) affords L·NiBr₂ (**3**). Compound **3** is a purple crystalline solid that melts at 255 °C. It has been characterized by IR, elemental analysis and its structure elucidated by single crystal X-ray technique. IR spectrum of **3** shows C=N vibrations at 1601 and 1560 cm⁻¹ which



Fig. 4. Molecular crystal structure of L-NiBr₂ (3). DME molecule and all hydrogen atoms have been deleted for clarity. Thermal ellipsoids are drawn at 50% probability.

is around 30 cm⁻¹ red shifted as compared to the free ligand and consistent with that of the L·Cu(NO₃)₂ complex. The electronic spectrum of the complex **3** shows absorption bands at 10170 ($\varepsilon = 81.5 \text{ Lmol}^{-1} \text{ cm}^{-1}$) and 19880 cm⁻¹ ($\varepsilon = 224.5 \text{ Lmol}^{-1} \text{ cm}^{-1}$) attributable to the ${}^{3}T_{1}(F) \rightarrow {}^{3}A_{2}(\nu_{2})$ and $\rightarrow {}^{3}T_{1}(P)$ transitions, respectively, for the tetrahedral geometry of the complex.

Crystals of **3** suitable for X-ray structural analysis were grown from DME at -30 °C. Compound L-NiBr₂ crystallizes in monoclinic system with space group *C*2/*c*. Asymmetric unit of **3** contains a molecule of L-NiBr₂ and half a molecule of DME. The molecular structure of **3** shows distorted tetrahedral geometry around nickel (Fig. 4 and Table 1).

The C₂N₃Ni six-member ring is non planar in a boat conformation with Ni(1) and N(2) forming the bow and stern of the boat, this is very similar to that of [2,6-*i*Pr₂C₆H₃-N=C(Ph)–NH–Py]NiBr₂. The N(1)–C(5), C(5)–N(2), N(2)–C(13), and C(13)–N(3) bond distances 1.347(3), 1.408(3), 1.390(3), and 1.299(3) Å, respectively, within the C₂N₃Ni ring are slightly longer than the free ligand, and comparable with [2,6-*i*Pr₂C₆H₃–N=C(Ph)–NH–Py]NiBr₂. The Ni(1)–N(1) and Ni(1)–N(3) of the C₂N₃Ni ring are 1.980(2) and 1.972(2) Å. The Ni(1)–Br(1) 2.375(4) and Ni(1)–Br(2) 2.347(4) Å bond distances agree well with that reported for [2,6-*i*Pr₂C₆H₃–N=C(Ph)–NH–Py]NiBr₂ [8]. The N(1)–Ni(1)–N(3) angle of 90.14(7)° in **3** is comparable to the same angle reported for [2,6-*i*Pr₂C₆H₃–N=C(Ph)–NH–Py]NiBr₂ [92.6(1)°] but the Br(1)–Ni(1)–Br(2) angle of 114.20(1)° in **3** is narrower than that in [2,6-*i*Pr₂C₆H₃–N=C(Ph)–NH–Py]NiBr₂ [123.94(3)°] [8].

3.4. Cobalt complex (4) and its crystal structure

The reaction of $CoCl_2 \cdot GH_2O$ with the ligand L affords the complex [HL-CoCl₃] (**4**) featuring a tetrahedral Co(II) ion. Contrary to the Cu or Ni complexes it does not form the usual chelate and the cobalt is seen to coordinate with the pyridine nitrogen only in addition to three chloride ions leaving cobalt ion in a tetrahedral arrangement and the imine nitrogen of the 2,6-*i*Pr₂C₆H₃ bears a proton to maintain the electrical neutrality. It is presumed that hydrolysis of cobalt(II) chloride occurs followed by generation of HCl which protonates the ligand to produce [HL-CoCl₃] (**4**). The by-product of the reaction is a yellow solid which has been investigated by IR spectroscopy; a sharp band at 3552 cm^{-1} assigned to OH functionality of cobalt hydroxo species. The powder X-ray diffraction pattern of this material (see Supplementary data) is identical to that reported for ClCo(OH) in a similar study [27]. The IR spectrum of **4** shows the NH stretching frequency at 3428 cm^{-1} and the C=N stretch is observed at 1599 and 1559 cm^{-1} . The complex shows two bands at 15700 cm^{-1} ($\varepsilon = 284 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$) and 17635 cm^{-1} ($\varepsilon = 201 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$) which are the split components of ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$ (ν_{3}) transition in a tetrahedral geometry of the complex [15].

Blue block like crystals of 4 were obtained by slow diffusion of pentane into a DME solution of **4**. Compound **4** crystallizes in the monoclinic system with space group $P2_1/c$ (Fig. 5 and Table 1). The C(1)-N(1) and C(13)-N(3) bond length of 1.338(6) and 1.320(6) Å are slightly longer than the corresponding bonds in free ligand [1.330(3) and 1.277(3) Ål, indicative of the coordination of N(1) to cobalt and protonation of the imine, respectively. The average Co-Cl bond length is 2.249(1) Å, which is comparable to the Co-Cl bond length found in the related compound (C₉H₈N)[CoCl₃ (C₉H₇N)] (2.2541(8)Å) [20]. The Co(1)–N(1) bond length of 2.071(4) Å is also similar to that in $(C_9H_8N)[CoCl_3(C_9H_7N)]$ (2.0643(19) Å) [20]. The tetrahedral arrangement around Co(1) comprising of N(1)-Co(1)-Cl angles lie in the range 101.23(10)-114.91(11)°. It has been well documented in the literature that metal bound halide ions can act as good hydrogen bond acceptors with O-H and N-H donors [21] in the form of M-Cl...H interaction and this hydrogen bonding interaction leading to extended 2D or 3D structure is more common in halide rich complexes [22-24].

In chlorine rich complex **4** three chlorine atoms on cobalt participate in hydrogen bonding (Fig. 6). The iminium cation links the neighboring Co(II) anion *via* N(3)–H(3a)···Cl(1) hydrogen bond to form 1D network. The H(3a)···Cl(1) contact range is 2.37(2) Å and the N(3)–H(3a)···Cl(1) angle is 154(1)°, this is in the normal accepted range of strong N–H···Cl hydrogen bonding interaction in such complexes [25–27]. In addition, the weak C–H···Cl interactions along with N(3)–H(3a)···Cl(1) interactions lead to the formation of 2D network in the solid state structure of **4** (supplementary information includes distances and angles of these interactions).

In conclusion, we have reported on the synthesis and structure of 2-pyridyl amine based [N,N] chelating ligand and its complexes with Co(II), Ni(II) and Cu(II).



Fig. 5. Crystal structure of [LH-CoCl₃] (**4**). All hydrogen atoms except H(3a) have been deleted for clarity. Thermal ellipsoids are drawn at 50% probability.



Fig. 6. The 2D network structure of 4 arising due to the inter-molecular hydrogen bonds [N(3)–H(3a)···Cl(1) along a axis] and [C(2)–H(2)···Cl(2) along b axis].

Acknowledgments

B.P. and S.S. acknowledge the financial support, Grant No. SR/ FT/CS-009/2009, from Department of Science and Technology (DST), India. M.K. thanks DST for a fellowship. The authors thank IISER Mohali for NMR and X-ray facility and for all other infrastructural support.

Appendix A. Supplementary data

CCDC 882164, 882165, 882166, 882167, and 882168 contain the supplementary crystallographic data for L, 1, 3, 2, and 4, respectively. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.08.019.

References

- [1] C. Cui, H.W. Roesky, H. Hao, H.-G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, Angew, Chem., Int. Ed. 39 (2000) 4274.
- [2] L.W. Pineda, V. Jancik, H.W. Roesky, D. Neculai, A.M. Neculai, Angew. Chem., Int. Ed. 43 (2004) 1419.
- [3] G. Bai, S. Singh, H.W. Roesky, M. Noltemeyer, N.S. Hosmane, J. Am. Chem. Soc. 127 (2005) 3449.
- [4] M.S. Hill, P.B. Hitchcock, R. Pongtavornpinyo, Science 311 (2006) 1904.

- [5] (a) T. Nguyen, A.D. Sutton, M. Brynda, J.C. Fettinger, G.J. Long, P.P. Power, Science 310 (2005) 844;
 - (b) Y.-C. Tsai, H.-Z. Chen, C.-C. Chang, J.-S.K. Yu, G.-H. Lee, Y. Wang, T.-S. Kuo, J. Am. Chem. Soc. 131 (2009) 12534;
- (c) A. Sekiguchi, R. Kinjo, M. Ichinohe, Science 305 (2004) 1755.
- V. Chandrasekhar, T. Senapati, R. Clérac, Eur. J. Inorg. Chem. (2009) 1640.
- [7] F.A. Cotton, P. Lei, C.A. Murillo, L.-S. Wang, Inorg. Chim. Acta 349 (2003) 165. [8] F.-S. Liu, H.-Y. Gao, K.-M. Song, L. Zhang, F.-M. Zhu, Q. Wu, Polyhedron 28 (2009) 1386.
- [9] J.J. Allen, C.E. Hamilton, A.R. Barron, Dalton Trans. 39 (2010) 11451.
- [10] J.J. Allen, C.E. Hamilton, A.R. Barron, J. Chem. Crystallogr. 40 (2010) 130. [11] T. Schareina, G. Hillebrand, H. Fuhrmann, R. Kempe, Eur. J. Inorg. Chem. (2001) 2421.
- C. Tan, F.-S. Liu, D.-S. Shen, T. Cheng, Z.-Z. Zhou, Catal. Lett. 141 (2011) 1332.
- [13] R.T. Boeré, V. Klassen, G. Wolmershäuser, J. Chem. Soc., Dalton Trans. (1998) 4147
- [14] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
- [15] A.B.P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier, Amsterdam, 1984.
- [16] Y.H. Oh, J.Y. Kim, Y.J. Park, Bull. Korean Chem. Soc. 22 (2001) 379.
- [17] D. Liu, Y.Z. Zhou, Chin. J. Inorg. Chem. 25 (2009) 1797.
- [18] C.M. Fitchett, P.J. Steel, Polyhedron 26 (2007) 400.
- [19] G.A. Van Albada, A. Mohamadou, I. Mutikainen, U. Turpeinen, J. Reedijk, Eur. J. Inorg. Chem. (2004) 3733.
- [20] T.-T. Pan, D.-J. Xu, Acta Crystallogr., Sect. E 60 (2004) m56.
- [21] P.K. Thallapally, A. Nangia, Cryst. Eng. Commun. 27 (2001) 1.
- [22] G.R. Lewis, A.G. Orpen, Chem. Commun. (1998) 1873.
- [23] B. Dolling, A.L. Gillon, A.G. Orpen, J. Starbuck, Xi.-M. Wang, Chem. Commun. 44 (2001) 567
 - [24] A.L. Gillon, A.G. Orpen, J. Starbuck, X.-M. Wang, Chem. Commun. (1999) 2287.
 - [25] L. Brammer, E.A. Bruton, P. Sherwood, Cryst. Growth Des. 1 (2001) 277.
 - [26] T. Steiner, Angew. Chem., Int. Ed. 41 (2002) 48.

 - [27] G. Zhang, G. Yang, N. Wu, J.S. Ma, Cryst. Growth Des. 6 (2006) 229.