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# Nickel and copper complexes based on tridentate nitrogen donor ligand 2,6-bis-(1-phenyliminoethyl) pyridine: Synthesis, spectral and structural characterization

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#### Abstract

The reaction of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  with 2,6-bis(1-phenyliminoethyl)pyridine (referred hereafter as L) in 1:1 molar ratio in methanol or acetronitrile at room temperature afforded distorted trigonal-bipyramidal complex  $[\text{Cu}(\kappa^3-\text{L})\text{Cl}_2]$ . On the other hand, the reaction of NiCl<sub>2</sub> · 6H<sub>2</sub>O with 2 equivalents of L gave an octahedral complex  $[\text{Ni}(\kappa^3-\text{L})_2]^{2+}$ , which was isolated as  $[\text{Ni}(\kappa^3-\text{L})_2][\text{BF}_4]_2$  using NH<sub>4</sub>BF<sub>4</sub>. The complexes have been characterized by elemental analyses, FAB-MS, IR, EPR and electronic spectral studies. Molecular structures of both the  $[\text{Cu}(\kappa^3-\text{L})\text{Cl}_2](1)$  and  $[\text{Ni}(\kappa^3-\text{L})_2](\text{BF}_4)_2$  (2) have been determined by single crystal X-ray analyses. Weak interaction studies on 1 and 2 revealed stabilisation of the crystal packing by inter and intra-molecular C-H···X (X = F, Cl,  $\pi$ ) interactions. In complex 2 ortho C-H bond from phenyl rings leads to unexpected C-H··· $\pi$  interaction with nickel  $\alpha, \alpha'$ -diimine chelate ring. This provides structural support for metalloaromaticity in the chelate ring of complex 2.

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Keywords: Metal complexes; Bis-immine ligand; X-ray; C-H··· $\pi$  interaction

#### 1. Introduction

Bis-(iminoalkyl)pyridine metal complexes have drawn much attention due to their interesting coordination chemistry and applications in catalysis [1,2]. The donor properties of the N,N,N donor ligands 2,6-diacetylpyridine-bis(imines) derived by Schiff base condensation of 2,6-diacetylpyridine with aromatic amines is comparable to that of terpyridine (terpy). It is well established that they normally behave as planar, tridentate ligand towards various kinetically labile metal ions such as Fe(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) halides, nitrates, perchlorates, and tetrafluoroborate. The resulting products are either five-coordinate complexes with the formulations  $[M(L)X_2]$  or six-coordinate  $[M(L)_2]^{2+}$ ,  $[M(\kappa^2-NO_3)X(L)]$ ,  $[M(\kappa^2-NO_3)(NO_3)(L)]$ ,  $[M(NO_3)(en)(L)]^+$  (M = Ni, Cu, Zn and Cd; X = halide; en = 1,2-diaminoethane) [3]. It has also been shown that reactions of L with the group VI and VII metal carbonyls or their derivatives give complexes in which the potentially tridentate ligands act in a bidentate chelating mode binding to metal centre *via* the pyridyl and just one of the imino nitrogen atoms [4].

CH··· $\pi$  interactions are weakest hydrogen bonds that operate between a soft acid and a soft base  $\pi$  system and play significant roles in the various fields of chemistry and biology [5]. The soft base  $\pi$  system which acts as a CH acceptor comprises not only of an organic moiety such as a double bond, triple bond or a delocalized aromatic ring [6], but also of a metal chelate ring of suitable transition metal complexes [7]. Group of authors in their interesting work have presented a remarkable effort towards

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the definition of structural parameters for the interaction between C–H polar bonds and the whole of a  $\pi$ (metal-chelate ring) system [7]. The concept of "metalloaromaticity" was proposed a long time ago and it is well known that a large variety of transition metal-chelate rings feature this aromaticity [8]. Here we provide structural support for nickel(II) complex in which nickel-diimine chelate ring acts as a CH acceptor.

Because of interests in N,N,N donor ligands, we have examined the reactivity of L with Cu(II) and Ni(II) salts [9]. We describe herein the reproducible synthesis, spectral and structural characterization of five-coordinate copper complex [Cu( $\kappa^3$ -L)Cl<sub>2</sub>] (1) and six-coordinate nickel complex [Ni( $\kappa^3$ -L)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (2) containing 2,6-di-iminopyridyl unit. We also report herein structural evidence for metalloaromaticity in the chelate ring of nickel complex 2.

#### 2. Results and discussion

#### 2.1. Synthesis

The reactions of  $CuCl_2 \cdot 2H_2O$  with L in methanol or acetronitrile in equimolar ratio under stirring conditions at room temperature gave neutral complex with the formulations  $[Cu(\kappa^3-L)Cl_2]$  (1). On the other hand, the reaction of two equivalents of L with NiCl<sub>2</sub> · 6H<sub>2</sub>O under analogous conditions afforded the corresponding bis-(ligand) complex cation  $[Ni(\kappa^3-L)_2]^{2+}$  (2) which was isolated as the BF<sub>4</sub><sup>-</sup> salt by using NH<sub>4</sub>BF<sub>4</sub>. Synthesis of 2 has previously been described by Schroder et al. following a quite different procedure but no structural data were reported [3b]. A simple scheme showing the syntheses of the complexes is given below. consistent with the formulations of the respective complexes. Infrared spectra in nujol displayed bands corresponding to v(C=N) at ~1585 cm<sup>-1</sup> and bands around 289–330 cm<sup>-1</sup> assignable to v(Cu-Cl). Bands at 1060–1055 and 525–530 cm<sup>-1</sup> are assigned to the asymmetric stretching B–F vibrations and B–F bending, respectively. The absorption spectra of 1 and 2 in DMSO displayed bands at ~489 nm and an intense higher-energy band at 249–296 nm. The lowest-energy bands in the range of 489 nm can be assigned to metal to ligand charge transfer transition MLCT  $[M(II) \rightarrow \pi_L^*]$ . The intense band in the region 249–296 nm has been assigned to L-centered intraligand  $(\pi-\pi^*)$  transitions.

Information regarding the immediate environment about the metal centre in complex 1 was obtained from ESR spectral studies. The X-band ESR spectra of 1 in DMSO were recorded at liquid-nitrogen and room temperatures (Fig. 1). The spectrum at room temperature shows one intense band in the high field while in frozen state it shows four well resolved peaks. Three bands are at a higher field and one is at a lower field than the relative to that of TCNE. Complex 1 in the solid state afforded a broad spectrum. The copper complex exhibits the  $g_{\parallel}$  value of 2.274 and  $g_{\perp}$  2.092. These values indicate that the ground state of Cu(II) is predominant [10].

### 2.3. Molecular structures

Molecular structures of 1 and 2 were determined by single-crystal X-ray diffraction studies. The details about data collection, solution and refinement are recorded in Table 1. The molecular structures of complexes 1 and 2 with atom numbering scheme are shown in Fig. 2 and the important



The complexes are air stable, non-hygroscopic shiny crystalline solids, sparingly soluble in common organic solvents, and insoluble in diethyl ether and petroleum ether. The complexes were fully characterised by IR, UV–Vis, FAB-MS and EPR spectroscopies. Analytical data of the complexes (recorded in the experimental section) corroborated well their respective formulations. The FAB-MS spectra of the complexes correspond to their respective formulations. The positions of various peaks and overall fragmentation patterns (recorded in the Section 4) are geometrical parameters are recorded in Table 2. Complex 1 crystallizes in the orthorhombic space group *Pbca* and the crystallographic asymmetric unit contains two independent molecules, which have almost identical geometry, while 2 crystallizes in the monoclinic space group  $P2_1/n$ . The molecular structure of 1 shows a distorted square-bipyramidal geometry consisting of two axial imino N-atoms N<sub>2</sub> and N<sub>3</sub>, and two Cl-ions and a pyridyl N1-atom as equatorial ligands (see Table 2). The Cu–N distances are longer compared to the values reported in the literature [1a,11], indicating that the ligand is more loosely bound with the metal centre. The N–Cu–N angle is 154.8° and this





Fig. 1. (a) EPR spectra of 1 at RT; (b) at LNT.

Table 1 Crystal data for **1** and **2** 

	1	2
Empirical formula	C <sub>21</sub> H <sub>19</sub> Cl <sub>2</sub> N <sub>3</sub> Cu	C42H38B4F8N6Ni
Formula weight	447.83	880.73
Colour and habit	yellow red needle	red needle
Crystal size (mm)	$0.50\times0.30\times0.20$	$0.30 \times 0.25 \times 0.20$
Crystal system, space group	orthorhombic, Pbca	monoclinic, $P2_1/n$
a (Å)	15.6109(9)	14.0472(16)
b (Å)	20.1076(11)	13.9261(16)
<i>c</i> (Å)	24.8441(13)	20.729(2)
β (°)	90	97.064
$V(\text{\AA}^3)$	7798.5(7)	4024.4(8)
$Z, D_{\rm c}  ({\rm g}  {\rm cm}^{-3})$	15, 1.430	4, 1.454
$\mu (\mathrm{mm}^{-1})$	1.317	0.560
<i>T</i> (K)	373(2)	293(2)
λ (Mo Kα) (Å)	0.71073	0.71073
Number of reflections/unique	37 246/9675	26468/9838
Number of refined parameters	221	536
<i>R</i> factor $[I \ge 2\sigma(I)]$	0.0582	0.0703
$wR_2 [I \ge 2\sigma(I)]$	0.1548	0.1567
<i>R</i> factor (all data)	0.0835	0.1417
$wR_2$ (all data)	0.1875	0.2013
Goodness-of-fit	1.193	0.934



angle in the other symmetrically identical molecule is 155.5, which is lower than the expected *trans* N–Cu–N angle. The Cu–Cl distances are comparable to the values reported in the literature [12].

The molecular structure of 2 shows two molecules of L coordinated to the nickel centre in a meridional manner. The geometry around the Ni<sup>II</sup> is distorted octahedral with four imino N-atoms bound in an equatorial plane Ni-N3a 2.117(3), Ni-N2a 2.149(3), Ni-N2b 2.135(3), Ni-N3b 2.145(3) and the two pyridyl N-atoms occupying the axial positions Ni-Npy1a 1.980(3), Ni-Npy1b 1.976(3) Å. The Ni-Nimine and Ni-Npy separations are comparable to those in the closely related complexes [3b,1b,11]. The dihedral angle between two pyridyl rings is 89.9°. The N-Ni-N angles are markedly distorted from 90° with N1a-Ni-N3a, 77.32(13)°, N1a-Ni-N2a, 76.93(13)°, N1b-Ni-N1a, 166.71 (14)°, N1b–Ni–N2b, 77.37(13)°, N1b–Ni–N3b, 76.55(13)°. In the solid-state structure, two of the phenyl rings (i.e. centroids of the rings) of each tridentate ligand extend away from the metal centre beyond the coordination sphere of other coordinated ligands and are situated with

Fig. 2. ORTEP views of 1 (top) and 2 (bottom) with thermal ellipsoids shown at the 30% level; hydrogen atoms were omitted for clarity.

the four positions of the phenyl ring lying at distances of 7.68 and 5.28 Å from one another.

Crystal packing in 1 is stabilized by C-H···Cl type interand intra-molecular hydrogen bonds, which lead to straight chain motif in which the phenyl rings attached to imino nitrogen are perpendicular to this chain (Fig. 3). Contact distances between C-H···Cl are in the range of 2.64–2.92 Å and angles are in the range of 153.6–160.6°. Extra stabilization of the phenyl rings has been found in both complexes 1 and 2 by intramolecular C-H···F weak interactions (Fig. 4). The inter-molecular C-H···F weak interactions that are present in complex 2 result in parallel chain like structure, which expands the motif in the crystal lattice through these interactions (Figs. 5a and 5b). Contact

Table 2 Selected bond lengths (Å) and bond angles (°) for 1 and 2

Complex 1		2	
Cu–N1a	1.947(3)	Ni–N1b	1.976(3)
Cu–N3a	2.084(3)	Ni–N1a	1.980(3)
Cu–N2a	2.109(3)	Ni–N3a	2.117(3)
Cu–Cl2a	2.226(11)	Ni–N2b	2.135(3)
Cu–Cl1a	2.405(11)	Ni–N2a	2.149(3)
Cu–N1b	1.961(3)	Ni–N3b	2.145(3)
Cu–N3b	2.080(3)	N3a–C2a	1.288(5)
Cu–N2b	2.115(3)	N2b–C8b	1.287(5)
Cu–Cl1b	2.246(9)	N2a–C8a	1.285(5)
Cu-Cl2b	2.402(9)	N2b-C16b	1.436(5)
N3a–C16a	1.433(4)	N3b-C2b	1.286(5)
N2a-C10a	1.442(4)	N2b-C16b	1.436(5)
N2b-C10b	1.432(4)	N2a-C16a	1.436(4)
N3b-C16b	1.425(4)	N3a–C10a	1.436(5)
N1a–Cu–N3a	77.71(11)	N1b–Ni–N3b	76.55(13)
N1a–Cu–N2a	77.94(12)	N1a–Ni–N3a	77.32(13)
N3a–Cu–N2a	154.82(11)	N1b–Ni–N2b	77.37(13)
N1a–Cu–Cl2a	151.94(8)	N1b–Ni–N1a	166.71(14)
N1b-Cu-N3b	77.92(11)	N1a–Ni–N2a	76.93(13)
N1b-Cu-N2b	77.64(11)		
N3b–Cu–N2b	155.51(11)		

distances between C–H···F are in the range of 2.38–2.62 Å and angles are in the range of 126–151°.

The most noteworthy structural feature of complex 2 is that two ortho-H atoms from phenyl ring point towards the centre of the corresponding nickel- $\alpha, \alpha'$  dimine chelate ring (Fig. 6). Comprehensive analysis was carried out with the program PLATON, and relevant structural parameters are listed in Table 3 [13]. The H-ring centroid  $(H \cdot \cdot \cdot Ct)$  distance is of 2.68–2.94 Å,  $C \cdots Ct$  distance is in the range of 3.379–3.416 Å, H. . . ring plane (H. . .  $\perp$ ) distance is in the range of 2.66–2.88 Å and the C-H···Ct angle is 111–  $136.0^{\circ}$ , still below the optimal value (180°) for the strongest C–H··· $\pi$  interactions, which may be due to the steric constraint in the molecule. The  $\gamma$  angle is found to be 5.41– 11.58° and is within the range reported in the literature [14]. This indicates that  $C-H\cdots\pi$  interactions occur between ortho-CH bonds and the whole of an electronically delocalized nickel chelate ring in complex 2. On the basis of the reported metalloaromaticity in aryl metal chelate rings [7,8], this kind of C–H··· $\pi$  (planar chelate ring) interaction in complex 2 is thought to be structural support for metalloaromaticity.

#### 3. Conclusions

In this work, we have presented synthesis, spectral and structural properties of the Cu(II) and Ni(II) complexes derived from 2,6-bis-(1-phenyliminoethyl) pyridine. Weak interaction studies on the nickel complex indicated the occurrence of metalloaromaticity in this complex.

# 4. Experimental

#### 4.1. Materials and physical measurements

All the synthetic manipulations were performed under oxygen free nitrogen atmosphere. The solvents were dried and distilled before use following the standard procedures. Ammonium tetrafluoroborate (Aldrich), copper chloride dihydrate, and nickel chloride hexahydrate were used as received. 2,6-bis(1-phenyliminoethyl) pyridine was prepared and purified following the literature procedure [15].

Elemental analyses were performed at Sophisticated Analytical Instrumental Facility, Central Drug Research Institute, Lucknow. Infrared spectra and Electronic spectra were obtained on a Perkin–Elmer 577 and Shimadzu UV-1601 spectrometer, respectively. Electron paramagnetic resonance (EPR) spectra were recorded with a Varian E-line Century Series EPR Spectrometer equipped with a dual cavity and operating at X-band of 100 kHz modulation frequency. Tetracyanoethylene was used as a field marker (g = 2.00277). The FAB mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using Xenon (6 kV, 10 mA) as the FAB gas. Accelerating voltage was 10 kV and the spectra were recorded at room temperature with *m*-nitrobenzyl alcohol as the matrix.

#### 4.2. Synthesis

# 4.2.1. $Cu[(\kappa^3-L)Cl_2](1)$

To a suspension of  $CuCl_2 \cdot 2H_2O(0.170 \text{ g}, 1.0 \text{ mmol})$  in 20 mL of acetonitrile or methanol, L (0.313 g, 1.0 mmol) was added and the resulting solution was stirred at room temperature for 30 min. Slowly, the color of the solution changes from green to yellow and yellow coloured precipitate separated out. The resulting precipitate was filtered



Fig. 3. C-H···Cl interactions lead to a straight chain motif in which the phenyl rings attached to imino nitrogen are perpendicular to this chain in 1.



Fig. 4. Intra-molecular C–H··· $\pi$  interactions in (a) 1 and (b) 2.



Fig. 5a. Parallel chains structure made through C–H–F interactions in complex (side view).



Fig. 5b. Apical view of chains made through C-H-F interactions in complex 2.



Fig. 6. The ortho C–H bond from the phenyl ring produces unexpected C–H··· $\pi$  interactions with the nickel- $\alpha$ , $\alpha'$ -diimine chelate ring in **2**.

and washed with diethyl ether. It was dissolved in methanol and layered with diethyl ether and left in a refrigerator for slow crystallization. In a couple of days reddish yellow needle shaped diffraction quality crystals separated. These were separated and washed with diethyl ether. Yield: 0.317 g (71%). *Anal.* Calc. for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>Cl<sub>2</sub>Cu: C, 56.37; H, 4.25; N, 9.39. Found: C, 56.20; H, 4.10; N, 9.29%. FAB-MS *m*/*z*: 447(445), 5 [Cu( $\kappa^3$ -L)Cl<sub>2</sub>]; 411(411), 20 [Cu( $\kappa^3$ -L)Cl]; 375(376) [Cu( $\kappa^3$ -L)]; 313(314), 5 [( $\kappa^3$ -L)]. UV–Vis {DMSO,  $\lambda_{max}$  (nm) ( $\epsilon/M^{-1}$  cm<sup>-1</sup>)}: 294(3502), 486(1432).

Table 3 Intramolecular "CH··· $\pi$ (chelate ring)" interaction parameters for **2** 

# 4.2.2. $[Ni(\kappa^3-L)_2] (BF_4)_2 (2)$

Complex 2 was prepared following the above procedure from the reaction of NiCl<sub>2</sub>  $\cdot$  6H<sub>2</sub>O (0.238 g, 1.0 mmol) in methanol (10 mL) with L (0.626 g, 2.0 mmol). The color of the solution changes from green to vellowish red. The resulting solution was filtered to remove any solid residue. The filtrate was concentrated under reduced pressure to one fourth of its volume and a saturated solution of ammonium tetrafluoroborate dissolved in methanol was added and left for slow crystallization in the refrigerator at  $\sim$ 4 °C. Slowly, a microcrystalline product was obtained, which was separated by filtration and washed repeatedly with diethyl ether and dried in vacuo. Dark red needle shaped crystals suitable for X-ray diffraction studies were grown by diffusion method from methanol-diethyl ether. Yield: 0.354 g (80%). Anal. Calc. for C42H38N6B2F8Ni: C, 58.67; H, 4.42; N, 9.78. Found: C, 58.30; H, 4.12; N, 9.60%. FAB-MS *m*/*z*: 772(771), 5  $[Ni(\kappa^3-L)_2]^+(BF_4);$ 685(684), 50  $[Ni(\kappa^3-L)_2]^{2+}$ ; 372(371), 100  $[Ni(\kappa^3-L)_2]^{2+}$ . UV-Vis {DMSO,  $\lambda_{max}$  nm ( $\epsilon/M^{-1}cm^{-1}$ )}: 302 (24221), 489 (2103).

### 4.3. X-ray crystallographic study

Crystals suitable for single-crystal X-ray analyses for the complexes  $[Cu(\kappa^3-L)Cl_2](1)$  and  $[Ni(\kappa^3-L)_2](BF_4)_2(2)$  were grown at room temperature. Preliminary data on the space group and unit cell dimensions as well as intensity data were collected on Enraf-Nonius MACH3 diffractometer using graphite monochromatized Mo K $\alpha$  radiation. The crystal orientation, cell refinement and intensity measurements were made using the program CAD-4 PC. The structure was solved by direct methods and refined by using MAXUS (1999) and SHELX-97 [16]. The non-hydrogen atoms were geometrically fixed and allowed to refine using a riding

CH-chelate ring	H···Cg (Å)	H…(ring plane) (Å)	$C \cdots Cg$ (Å)	C–H···Cg (°)	r (°)
C11aH11a…(NiN1bN3b)	2.68	2.669	3.416	136	5.41
C17aH17a···(NiN1bN3b)	2.94	2.880	3.379	111	11.58

model. The computer program PLATON was used for analyzing the interaction and stacking distances [17].

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#### Appendix A. Supplementary material

CCDC 602708 and 602709 contain the supplementary crystallographic data for 1 and 2. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallo-graphic 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 doi: 10.1016/j.ica.2006.12.031.

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