Five-coordinate dicarboxylate complexes of copper (+2) and zinc (+2)

Bhaskar Nath [a], Dipjyoti Kalita [a] & Jubaraj B. Baruah [a]

[a] Department of Chemistry , Indian Institute of Technology
Guwahati , Guwahati 781 039, Assam, India
Published online: 26 Jul 2011.

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Five-coordinate dicarboxylate complexes of copper (+2) and zinc (+2)

BHASKAR NATH, DIPJYOTI KALITA and JUBARAJ B. BARUAH*

Department of Chemistry, Indian Institute of Technology Guwahati,
Guwahati 781 039, Assam, India

A new dicarboxylic acid, **LH₂**, derived from 2-[(2-hydroxy-3,5-dimethylphenyl) (phenyl)methyl]-4,6-dimethylphenol (**1**) was prepared by reacting it with methyl bromoacetate followed by alkaline hydrolysis. Two five-coordinate mononuclear complexes of **L** with zinc (+2) and copper (+2), $[Zn(L)(py)_2(H_2O)] \cdot H_2O \cdot py$ (**IV**), and $[Cu(L)(py)_2(H_2O)]$ (**V**), were prepared (py = pyridine) and characterized. The packing patterns of these two complexes are different and the H-bond interactions in their lattices are controlled by the presence or absence of water molecules. This difference arises from subtle change in the orientation of carbonyl groups of the carboxylates.

1. Introduction

There are a number of examples of five-coordinate complexes of zinc [1–12] and copper [13–19]. Five-coordinate complex formation is not a regular feature for these metals, but has been prepared with specific ligands designed to provide the required geometrical constraints to form five-coordinate complex [19–27]. For the synthesis of such five-coordinate complexes, side-arm bearing tripodal amines [17–24] are used; such complexes are suggested to bear bio-mimicking features [10, 27, 28]. We have chosen **LH₂** (figure 1a) derived from *bis*-phenol with the anticipation that it would maintain a propeller-like structure [29, 30]. Such geometry of this ligand would make cyclic structures with metal ions, as shown in figure 1(b). Such cyclic structures having two ether oxygens in the ring would provide weak macrocyclic effect restricting the coordination number to be lower than six. One such possibility to form a five-coordinate complex is shown in figure 1b. In this work we synthesized, characterized **LH₂** and its binding properties with copper and zinc are presented.

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*Corresponding author. Email: juba@iitg.ernet.in

(a)   (b)
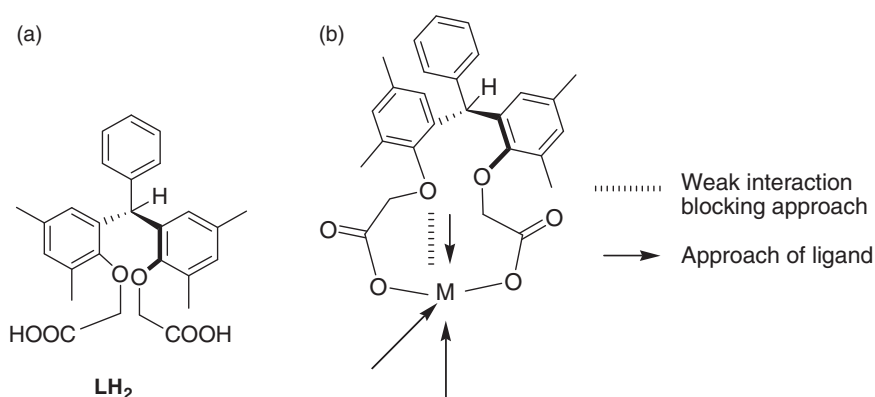
Figure 1.   Schematic representation of (a) ligand; (b) binding to metal ion leading to five-coordination.
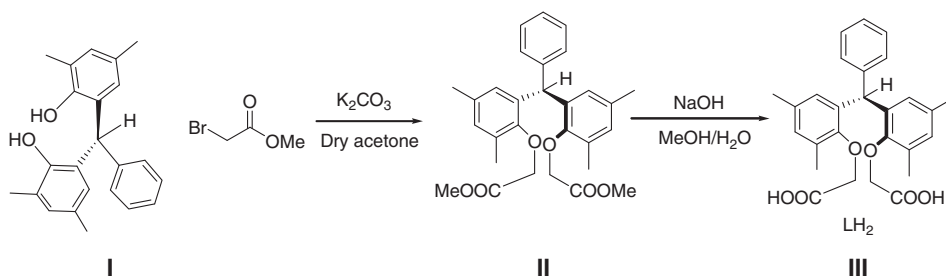
Scheme 1.   Synthesis of **LH₂**.

2. Results and discussion

2.1. *Ligand synthesis*

LH₂ was prepared by two-step procedure starting from *bis*-phenol **I**. In the first step *bis*-phenol **I** was reacted with methylbromoacetate to obtain the corresponding diester (**II**) (scheme 1). This diester was hydrolyzed by methanolic sodium hydroxide to obtain the desired dicarboxylic acid **LH₂** (scheme 1). The ligand was characterized by IR, ^{1}H NMR, ^{13}C NMR, and mass spectra, showing the desired ^{1}H NMR spectra and characteristic peaks in ^{13}C to confirm the structure. For example, in ^{13}C NMR spectra, it has signals at 15.9 and 20.7 ppm due to carbon on methyl attached to aromatic rings, methylene carbon at 43.1 ppm, and methine carbon at 69.3 ppm. The signal from carbon of carboxylic acid appears at 170.3 ppm. The OH of carbonyl appears at 3440 cm^{-1}. The crystal structure of the ligand was also determined (figure 2). **LH₂** forms H-bonded assemblies with two methanols and two water molecules.

2.2. *Synthesis and characterization of five-coordinate complexes*

Reaction of $Zn(O_2CCH_3)_2 \cdot 4H_2O$ or $Cu(O_2CCH_3)_2 \cdot H_2O$ with **LH₂** in the presence of sodium hydroxide led to insoluble mass. The precipitate thus obtained was dissolved in py led to $[Zn(L)(py)_2(H_2O)] \cdot H_2O \cdot py$ (**IV**) and $[Cu(L)(py)_2(H_2O)]$ (**V**), respectively

Figure 2. Structure of $LH_2 \cdot MeOH \cdot H_2O$ (drawn with 50% thermal ellipsoids; hydrogens on O atoms of methanol and O7 of water are omitted).

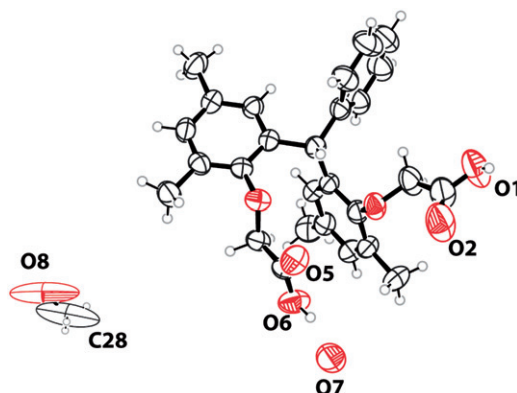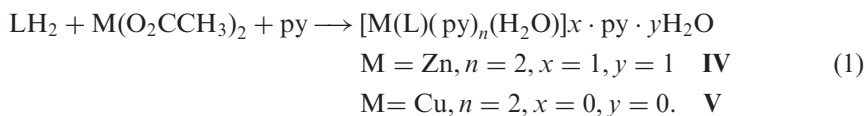(equation 1). Upon complexation, the carbonyl frequency shifts drastically to $1631\,cm^{-1}$ and $1599\,cm^{-1}$ in zinc and copper complexes, respectively. The ^1H NMR of the zinc complex suggests it to have three pyridines along with one **L**. The crystal structures of both complexes are determined, showing five-coordinate, mononuclear complexes with trigonal bipyramidal geometries. Both complexes have one **L** per metal and **L** forms cyclic structure with metal by coordinating through two monodentate carboxylates. Each complex has one coordinated water molecule along with **L** making the trigonal plane, whereas the two pyridines are axial.

$$LH_2 + M(O_2CCH_3)_2 + py \longrightarrow [M(L)(py)_n(H_2O)]x \cdot py \cdot yH_2O$$
$$M = Zn, n = 2, x = 1, y = 1 \quad \mathbf{IV} \qquad (1)$$
$$M = Cu, n = 2, x = 0, y = 0. \quad \mathbf{V}$$

Besides **L**, the Zn-complex **IV** has two coordinated pyridines and one water molecule (figure 3a) with a pyridine and a water molecule of crystallization. The Zn–O4 distance is 2.56 Å and thus O4 is non-interacting with zinc, but blocks a coordination site. So, O4 of the ether linkage is responsible for guiding the system to be five-coordinate. There is an example of five-coordinate zinc carboxylate prepared by a H-bond blocking the approach of ligand from a side of an octahedron [2]. Five-coordinate zinc complexes were earlier prepared by using macrocyclic ligands using the crown effect [3]. The asymmetric unit contains one molecule of **IV**, half of solvated pyridine, and half of a water molecule of crystallization (occupancy of the oxygen is 0.5 in the asymmetric unit). The complex forms a layered structure with hydrogen bonding between interstitial water and carboxylate. These layers intercalate pyridines to form assemblies of layers and repeats along the *a*-crystallographic axis (figure 3b). Thus, there are two independent environments for py-molecules in the crystal lattice. The interstitial py-molecules are held between 1-D hydrogen-bonded chains through C–H $\cdots \pi$ interactions, thereby forming a 2-D sheet-like structure (figure 3b). The hydrogen bonds involved in the formation of the layered structures are listed in table 1.

Copper complex **V** has a similar structure to **IV** (figure 4a) but does not have pyridine and water molecule of crystallization. The complex has hydrogen-bonded layered
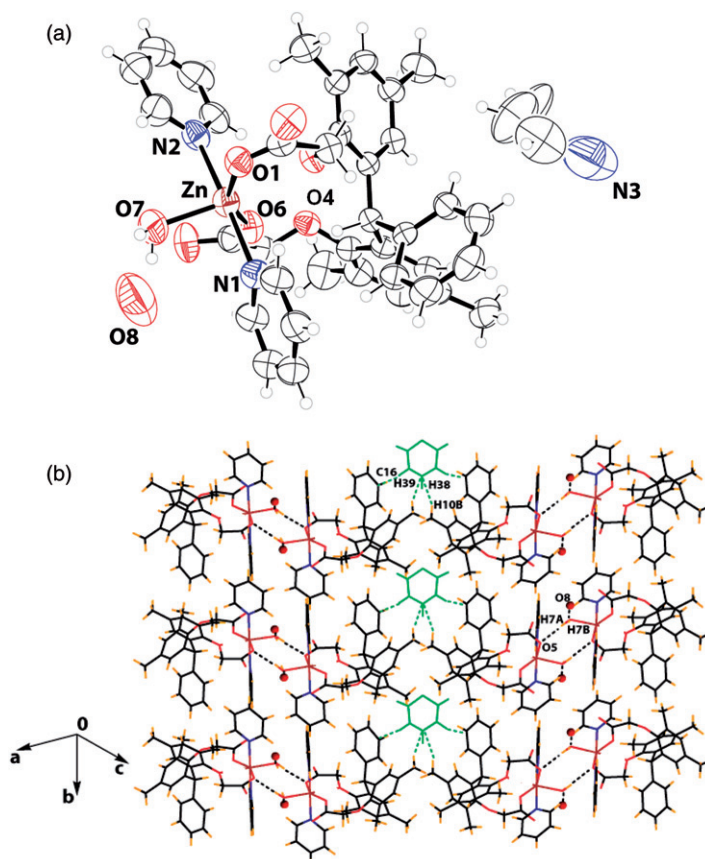
Figure 3.   (a) Asymmetric unit of **IV** (drawn with 50% thermal ellipsoids); (b) short-range interaction in the layers of **IV** showing the encapsulation of the solvated pyridines.

Table 1.   Hydrogen bond parameters for **IV**.

D–H···A	d_{D-H} (Å)	$d_{H···A}$ (Å)	$d_{D···A}$ (Å)	∠D–H···A (°)
O(7)–H(7A)···O(5) [i]	0.78(4)	2.32(4)	2.90(5)	132(5)
O(7)–H(7A)···O(6) [ii]	0.78(4)	2.27(5)	3.02(5)	165(5)
O(7)–H(7B)···O(8)	0.82	2.14	2.75(6)	130
C(2)–H(2A)···O(5) [iii]	0.97	2.49	3.31(5)	142
C(35)–H···O(5) [iv]	0.93	2.42	3.30(6)	159

i = −*x*, 1 − *y*, 1 − *z*; ii = −*x*, 1 − *y*, 1 − *z*; iii = *x*, 1 − *y*, −1/2 + *z*; iv = *x*, 1 + *y*, *z*.

structures formed by H-bond interactions between carbonyl oxygen of carboxylate and coordinated water molecule (figure 4b). In **V**, as shown in figure 4, Cu–O4 distance is 2.56 Å, which suggests a weak interaction between O4 and copper, preventing the approach of another ligand to copper. Five-coordinate copper complexes are interesting from a biological point of view [27, 28] and show structural flexibility [16], undergoing coordination change by solvent [14]. Some hydrogen bond parameters contributing to the assembly of the copper complex are listed in table 2.
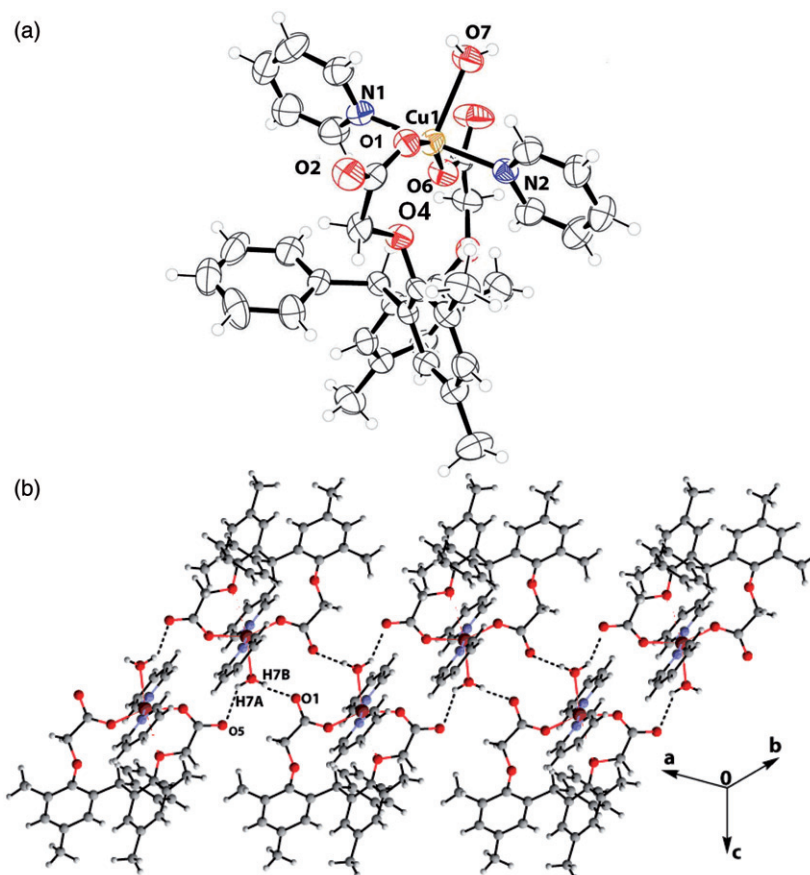
Figure 4. (a) ORTEP diagram of **V** showing the asymmetric unit (drawn with 50% thermal ellipsoids); (b) hydrogen bonding interactions in **V**.

Table 2. Hydrogen bond parameters for **V**.

D–H⋯A	$d_{D–H}$ (Å)	$d_{H⋯A}$ (Å)	$d_{D⋯A}$ (Å)	∠D–H⋯A (°)
O(7)–H(7 A)⋯O(5) [i]	0.82	2.09	2.79(7)	143
O(7)–H(7B)⋯O(1 [ii]	0.81(6)	1.95(6)	2.76(9)	179(9)
C(30)–H(30)⋯O(5) [iii]	0.93	2.52	3.41(10)	160
C(35)–H(35)⋯O(1) [iv]	0.93	2.55	3.29(10)	137

i $=-x$, $1-y$, $1-z$; ii $=1-x$, $-y$, $1-z$; iii $=1+x$, y, z; iv $=-x$, $-y$, $1-z$.

The structure of H-bonded layered structures of **IV** and **V** differ in hydrogen bonds. This difference is attributed to the slight difference in the arrangement of ligands in the coordination sphere of the two complexes. Such variation in orientation provides the difference in projection of the C=O bond of carboxylates in the two complexes and changes the pattern of H-bonds and crystal packing. The hydrogen-bonded layered structure in **V** is devoid of interstitial water molecule and has no room to hold pyridine

Table 3. Comparison of bond angles in **IV** and **V**.

Bond angles	M=Zn	M=Cu
O2–M–N2	87.3(12)	91.6(2)
O6–M–N2	91.9(11)	89.2(2)
O6–M–N1	91.3(12)	88.8(2)
N2–M–N1	176.6(12)	177.8(2)
O6–M–O7	99.9(17)	94.5(2)
N2–M–O7	89.5(14)	91.0(2)
N1–M–O7	89.1(14)	88.1(2)
O6–M–O2	149.8(11)	154.3(19)

in interstices. The bond angles of the coordination spheres of the two complexes are listed in table 3. The extent of distortions from trigonal bipyramidal structure in the two complexes is slightly different, attributed to the difference in ionic size of the two cations.

The presence or absence of pyridine molecules outside the coordination sphere of the two complexes are revealed in the thermogravimetry. The zinc complex shows weight loss at 100–230°C, due to the loss of one coordinated water molecule, one solvated water molecule, one solvated py, and two coordinating pys. Thermogravimetry of the copper complex shows 24% weight loss at 120–240°C, attributed to the loss of one water molecule and two pyridines (theoretical 25%) (please refer to "Supplementary material").

2.3. *Pyridine encapsulation*

From the crystallographic study, it is evident that there are two environments for pyridines, coordination or as guest in the interstices. The process of guest (py) inclusion together with the coordination of py decides the number of py-molecules in each complex. The Cu-complex has two coordinated py molecules, whereas zinc has two coordinated py molecules and one py of crystallization. Thus, the zinc complex formed from **LH$_2$** accepts three py molecules, whereas similar copper complex accepts two (vide GC-MS) py molecules. The process can be used to separate the trace amounts of py in benzene. For example, in a mixture of pyridine in benzene the amount of pyridine can be estimated by GC-MS. When such a solution is treated with a known quantity of solid mass obtained from the reaction of Na$_2$L with zinc acetate, the amount of pyridine taken up can be estimated. A similar experiment by using copper acetate also gives similar qualitative results but the quantitative capability on extracted pyridine differs in two cases. In the former case 1:3 ratio metal:pyridine is absorbed whereas in later it is 1:2 ratio. Thus, the method can be used to separate a mixture of benzene and pyridine at very low concentration. As mentioned, the packing pattern guides the ability to take up extra pyridine molecules to the interstitial spaces of the zinc complex.

3. Experimental

3.1. *General*

^{1}H NMR spectra were recorded on a Varian 400 MHz FT-NMR spectrometer. FT-IR spectra were recorded using a Perkin Elmer Spectrum One spectrometer

Table 4. Crystallographic parameters of **LH$_2$**, **IV** and **V**.

Compound no.	**LH$_2$**	IV	V
Empirical formula	C$_{28}$H$_{31}$O$_8$	C$_{79}$H$_{81}$N$_5$O$_{15}$Zn$_2$	C$_{37}$H$_{38}$CuN$_2$O$_7$
CCDC no.	804435	804437	804436
Formula weight	495.53	1471.23	686.23
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2/c$	$P\bar{1}$
Temperature (K)	296(2)	293(2)	293(2)
Unit cell dimensions (Å, °)			
a	14.9498(13)	20.8706(16)	9.333(5)
b	14.8055(12)	9.7954(8)	10.004(5)
c	12.5249(10)	17.3306(15)	19.333(8)
α	90.00	90.00	79.42(3)
β	97.545(3)	90.857(5)	79.61(3)
γ	90.00	90.00	70.91(3)
Volume (Å^3), Z	2748.3(4), 4	3542.6(5), 2	1662.7(14), 2
Calculated density (Mg m^{-3})	1.198	1.379	1.371
Absorption coefficient (mm^{-1})	0.088	0.749	0.709
Abs. correction	None	None	None
$F(000)$	1052	1540	718
Reflections collected	4960	6595	5881
Reflections, $I > 2\sigma(I)$	2689	4555	2809
Max. 2θ (°)	50.5	51.0	50.5
Limiting indices	$-17 \le h \le 17$; $-17 \le k \le 17$; $-15 \le l \le 14$	$-25 \le h \le 25$; $-11 \le k \le 11$; $-20 \le l \le 20$	$-11 \le h \le 11$; $-12 \le k \le 11$; $-22 \le l \le 23$
Completeness to 2θ (%)	99.7	99.5	98.0
Data/restraints/parameters	4960/5/335	6595/0/466	5881/1/433
Goodness-of-fit on F^2	1.224	1.023	0.999
Final R indices [$I > 2\sigma(I)$]	0.0819	0.0504	0.0727
R indices (all data)	0.1237	0.0818	0.1443

from 4000 to 400 cm^{-1}. UV-Vis spectra were recorded using a Perkin Elmer Lambda 750 spectrometer. X-ray single crystal diffraction data were collected at 296 K with Mo-Kα radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXTL. All non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. The hydrogens, except those attached to oxygen, were placed at their calculated positions and refined in the isotropic approximation; those attached to oxygen were located in the difference Fourier maps and refined with isotropic displacement coefficients. The crystallographic parameters of the compounds are listed in table 4.

3.2. *Synthesis of LH$_2$*

The 2-[(2-hydroxy-3,5-dimethylphenyl)(phenyl)methyl]-4,6-dimethylphenol [29] (**I**) (1.62 g, 5 mmol) was dissolved in dry acetone (30 mL). To the reaction mixture, K$_2$CO$_3$ (1.38 g, 10 mmol) was added and stirred for 20 min. Then methyl bromoacetate (0.95 mL, 10 mmol) was added and refluxed at 60°C for 22 h (progress of the reaction was monitored at regular intervals using TLC). After completion of the reaction, the reaction mixture was filtered; the solvent from the filtrate was removed under reduced

pressure to obtain the crude product which was further purified by thin-layer chromatography (silica gel; hexane/ethyl acetate) to obtain pure **II**. Isolated yield: 78%. Compound **II** (2.38 g, 5 mmol) and sodium hydroxide (0.48 g, 12 mmol) were dissolved in mixed methanol:water (4:1, 20 mL) and refluxed for 1 h at 60°C. After completion of the reaction, the solvent was removed under reduced pressure, then 10 mL of water was added and the solution was acidified with dilute hydrochloric acid (20 mL, 10%) solution. A white solid **LH$_2$** was obtained on acidification. The solid was filtered and washed with water until it was free from the acid. The product was isolated as a white solid and was further purified by recrystallizing from methanol. Isolated yield: 59% based on diester. IR (KBr, cm^{-1}): 3440 (bs), 2926 (s), 2857 (w), 1742 (s), 1720 (s), 1602 (s), 1493 (m), 1473 (m), 1404 (w), 1300 (w), 1207 (s), 1138 (s), 1094 (s), 1063 (s), 872 (w), 824 (s), 803 (w), 702 (w), 685 (w), 605 (w). ^{1}H NMR (DMSO-d$_6$, 400 MHz): 7.27 (t, $J = 7.2$ Hz, 2H); 7.19 (t, $J = 7.6$ Hz, 1H); 7.04 (d, $J = 7.2$ Hz, 2H); 6.89 (s, $J = 8.8$ Hz, 2H); 6.43 (s, $J = 8.8$ Hz, 2H); 6.23 (s,1H); 3.99 (s, 4H); 2.16 (s, 3H); 2.12 (s, 3H). ^{13}C NMR (DMSO-d$_6$): 170.3, 152.5, 143.6 136.4, 132.4, 130.4, 130.3, 129.2, 128.2, 126.2, 69.3, 43.1, 20.7, 15.9. LCMS (*m/e*) [M − 1]: 447.09.

3.3. *Typical procedure for synthesis of complex*

To a well-stirred solution of **LH$_2$** (0.196 g, 0.5 mmol) and NaOH (0.02 g) dissolved in methanol (20 mL), Cu(O$_2$CCH$_3$)$_2$·H$_2$O (0.1 g, 0.5 mmol) was added. The blue precipitate obtained was dissolved by the addition of pyridine (2 mL). The reaction mixture was refluxed, filtered, and the liquid was kept for crystallization. After 1 week, blue needle-like crystals of **V** were obtained. Isolated yield: 50% (based on copper). IR (KBr, cm^{-1}): 3430 (bs), 2925 (w), 1631(s), 1611(s), 1603(s), 1454 (w), 1397 (s), 1300 (w), 1253 (m), 1210 (m), 1143 (m), 1044 (m), 1031 (m), 923 (w), 764 (w), 716 (m), 705 (m). Magnetic moment (RT) 1.99 BM. Visible (χ_{max}) = 729 nm ($\varepsilon = 142.5$ mol^{-1} cm^{-1}). % copper (iodometry) Calcd: 9.25%; found: 9.27%. Complex **IV** was synthesized by a similar procedure as **V** where Zn(O$_2$CCH$_3$)$_2$·4H$_2$O was used instead of Cu(O$_2$CCH$_3$)$_2$·H$_2$O. Yield: 72% (based on zinc). IR (KBr, cm^{-1}): 3419 (b), 2922 (m), 1599 (s), 1473 (m), 1449(m), 1439 (m), 1416 (s), 1327 (m), 1246 (m), 1209 (m), 1138 (m), 1068 (w), 1039 (s), 1013 (w), 936 (w), 857 (w), 814 (w), 763 (w), 751 (w), 705 (s), 627 (w), 576 (w). ^{1}H NMR (CD$_3$OD): 2.0 (s, 6H), 2.5 (s, 6H), 3.99 (m, 2H), 3.8 (m, 2H), 6.45 (s, 2H), 6.55 (s, 1H), 6.8 (s, 2H), 7.0 (m, 2H), 7.25 (m, 1H), 7.35 (m, 2H), 7.4 (s, 6H) 7.8 (m, 3H), 8.6 (s, 6H).

3.4. *Separation of pyridine from benzene*

IV was added to an equimolar mixture (1.5 mmol each) of benzene and pyridine in methanol. After the addition of the solid to the pyridine/benzene solution, the solution was distilled and distillate was analyzed by GCMS and found to be free from pyridine.

4. Conclusions

Two five-coordinate complexes of copper (2+) and zinc (2+) of a new ligand are synthesized and characterized. The geometrical constraints arising from the

coordination of **L** to metal ions guide the orientation of carbonyl groups of the carboxylate complexes and controls the packing pattern. The weak interactions of water molecules in the interstices discriminates encapsulation of pyridine molecules in these two complexes.

Supplementary material

The TG of the complexes, ESR of the copper complex, NMR of the ligand and zinc complexes, and the CIFs of the compounds are available.

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