

# Design and Synthesis of Mixed Valent Coordination Networks Containing Pyridine Appended Terpyridyl, Halide, and Dicarboxylates

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**(5)** Supporting Information

**ABSTRACT:** The ability of 4'-(4-pyridyl)-2,2':6',2"-terpyridine (L), which contains a chelating center as well as an exodentate center for coordination, to form mixed-valent coordination polymers together with bromide and organic dicarboxylates as bridges has been explored with Cu(I), Cu(II), Co(II), and Ni(II) metal salts using hydrothermal reactions. The mixed-valent complexes containing Cu(I) and Cu(II) with L were formed only when the organic anions are glutarate (GA) or 1,3-dicarboxylate (BDC). The glutarate-containing complex exhibits a double helix in which the opposite handed helices interact with each other via  $\pi$ - $\pi$  interactions between the two L-units. In the case of the BDC-containing complex, the Br<sup>-</sup> joins the two Cu(I) and Cu(II) centers to form a one-dimensional (1D) network containing Cu<sub>2</sub>L<sub>2</sub>Br<sub>2</sub> boxes. The HBDC units, which are connected to the above-mentioned 1D network, extend the



dimensionality of the network to a three-dimensional (3D) network through catemeric -COOH interactions. The presence of succinate (SA) or biphenyl 2,6,2',6'-tetracraboxylate (TCA) produced the complexes containing only Cu(II) but not Cu(I). The SA acts as a bridge between two Cu(II) centers to form one-dimensional chains containing  $Cu_2L_2SA_2$  boxes. On the other hand, the presence of TCA resulted in the formation of a 1D chain of CuL without TCA inclusion in the crystal lattice. The reactions of L in the presence of BDC with Ni(II) and Co(II) resulted in the formation of similar 1D isomeric chains containing ML units. All the six complexes were characterized by single crystal X-ray diffraction, IR, and diffuse reflectance spectroscopy studies. The mixed valence complexes were characterized by cyclic voltammetry.

# INTRODUCTION

Exodentate ligands containing pyridine or -COOH groups are in regular use for the generation of coordination networks or metal-organic frameworks (MOFs).<sup>1</sup> All these networks have gained particular interest due to their fascinating structures, porous nature,<sup>2</sup> guest inclusion phenomenon,<sup>3</sup> selective gas adsorption and desorption,<sup>4</sup> and magnetic properties.<sup>5</sup> On the other hand, the reactions of multidentate chelating ligands with transition metals are traditionally known to form complexes containing discrete assemblies. In several instances, the combination of chelating ligands and exodentate ancillary ligands was shown to produce coordination networks of varied topologies. Despite a plethora of literature, the construction of coordination networks using the ligands containing both exodentate and chelating features are very rare. In the present contribution, we wish to present our studies on one such ligand, namely, 4'-(4-pyridyl) 2,2':6',2"-terpyridine, L.

The interesting feature of L is that it contains a chelating center such as terpyridine<sup>6</sup> and a unidentate coordination center such as pendant pyridine. This type of ligand is expected to coordinate to the metal centers with the varied oxidation states<sup>7</sup> due to the presence of two types of binding centers

(Scheme 1). For example, it was shown that L forms mixed valence rectangular grid complexes with Cu(I) and Cu(II) metal centers via halogen or SCN bridges.<sup>8</sup> Further, it was also shown that the reaction of L and organic anion such as terephthalate with Cu(II) salt resulted in the complex containing only Cu(II) but not Cu(I). The terephthalate units bridge two CuL units to form a discrete species and the 4pyridyl group of L remained uncoordinated. In both cases, the metal salts used for the complexation reactions are Cu(II), but in the case of inorganic anions some of the Cu(II) was reduced to Cu(I), which leads to the formation a mixed valence complex. Given these results, we aim to synthesize the mixed valence networks of L that contain halides or dicarboxylate bridges between the Cu(I) and Cu(II) centers. Three types of bridges (L, inorganic ion, and organic ion) in the same network are expected to result in increased dimensionality of the network, the versatile topologies, cavities, and properties. In anticipation of such versatile functional materials, hydrothermal

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Scheme 1. Various Possible Networks by the Ligand L with Transition Metals with (b, d-f, and h) or without (a, c, and g) Linking of Anions



Table 1. Crystallographic Parameters for the Crystal Structures of 1-6

compound	1	2	3	4	5	6
formula	$Cu_{3}Br_{2}C_{48}H_{50}N_{8}O_{15}$	Cu3Br3C45H38N8 O6	$Cu_{3}Br_{2}C_{56}H_{42}N_{8}O_{10}$	$CuBr_2C_{20}H_{18}N_4O_2$	$NiC_{28}H_{20}N_4O_5$	$Co_2C_{56}H_{48}N_8O_{14}$
mw	1329.40	1217.18	1337.42	569.74	551.19	1174.88
$T(\mathbf{K})$	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	C2/c	P2/c	$P2_{1}/c$	$P2_1/n$	$P\overline{1}$
a (Å)	16.528(3)	20.984(3)	12.353(3)	8.667(8)	8.796(17)	8.841(4)
b (Å)	8.653(14)	21.858(3)	10.952(2)	10.805(11)	13.421(3)	10.104(5)
c (Å)	18.604(3)	20.929(3)	19.413(4)	21.815(2)	20.615(4)	14.995(7)
$\alpha$ (°)	90.00	90.00	90.00	90.00	90.00	99.32(2)
$\beta$ (°)	104.030(5)	111.872(5)	102.469(6)	99.205(3)	92.277(6)	90.67(2)
γ (°)	90.00	90.00	90.00	90.00	90.00	108.53(1)
vol (Å <sup>3</sup> )	2581.3(8)	8909(2)	2564.4(9)	2016.7(3)	2431.9(9)	1250.4(1)
Ζ	2	8	2	4	4	1
$D_{\rm calc}  ({\rm mg}/{\rm m}^3)$	1.692	1.838	1.682	1.547	1.499	1.863
$R_1 \ (I > 2\sigma(I))$	0.0529	0.0621	0.0657	0.0406	0.0411	0.0906
w $R_2$ (on $F^2$ , all data)	0.1351	0.1519	0.1008	0.1144	0.1141	0.1885

reactions of L and organic dicarboxylates with CuBr and  $CuBr_2$  have been performed. The crystal structures of these materials have been characterized and analyzed in terms of various interactions, coordination geometries of the metal, and network geometries. Further these materials have also been characterized by elemental analysis, IR, diffuse reflectance spectroscopy (DRS), and cyclic voltammetry (CV).

### RESULTS AND DISCUSSION

The ligand **L** was prepared by the modified Kröhnke reaction of 4-pyridine carboxaldehyde with 2-acetyl pyridine in the presence of base.<sup>9</sup> Several aromatic and aliphatic dicarboxylates

were considered as colinkers of metal centers with L. The slow diffusion by layering at room temperature yielded precipitates in all cases. Single crystals suitable for X-ray diffraction were obtained for complexes 1, 2, and 3 in the case of three dicarboxylates, namely, succinate (SA), glutarate (GA), and isophthalate (BDC), respectively, by using hydrothermal methodology. The use of the nonplanar tetracarboxylate such as biphenyl-2,6,2',6'-tetracarboxylic acid resulted in single crystals of complex 4 without inclusion of TCA in the crystal lattice. The reaction of L with Ni(II) and Co(II) salts were tried in the presence of Cu(I) halide and disodium salt of isophthalate to produce mixed metallic complexes. These reactions resulted in



Figure 1. Illustrations for the crystal structure of 1: (a) 1D chain containing the boxes of  $Cu_2(L)_2(SA)_{2r}$  (b) assembling of 1D chains via O-H…Br and weak aromatic C-H…Br interactions.

the single crystals of complexes 5 and 6 with Ni(II) and Co(II) respectively. Pertinent crystallographic information for all these complexes was given in Table 1. The crystal structures of 1-6 were determined and it found that the complexes 2 and 3 have both Cu(I) and Cu(II), while all the other complexes contain bivalent metal centers (1, 4-6).

 $\{[Cu_{3}L_{2}(SA)_{2}(Br)_{2}(H_{2}O)_{4}]\cdot 3H_{2}O\}_{n}, \mathbf{1} \\ \{[Cu_{3}L_{2}(GA)Br_{3}]\cdot 2H_{2}O\}_{n}, \mathbf{2} \\ \{[Cu_{3}L_{2}(HBDC)_{2}Br_{2}]\cdot 2H_{2}O\}_{n}, \mathbf{3} \\ \{[CuLBr_{2}]\cdot 2H_{2}O\}_{n}, \mathbf{4} \\ [NiL(BDC)(H_{2}O)]_{n}, \mathbf{5} \\ \{[CoL(BDC)]\cdot 3H_{2}O\}_{n}, \mathbf{6} \\ \}$ 

Aliphatic Dicarboxylates as Linkers (1 and 2). Although several aliphatic dicarboxylates have been employed for this purpose, only succinate (SA) and glutarate (GA) have shown such linking ability to give complexes 1 and 2 respectively. The complex 1 crystallizes in the  $P2_1/n$  space group and the asymmetric unit contains two symmetry independent Cu(II) centers (one with full occupancy, Cu<sub>1</sub>, and the other with half occupancy, Cu<sub>2</sub>), one unit each of L, SA, and Br<sup>-</sup>, two units of coordinated water molecules, and 1.5 units of uncoordinated water. Interestingly, the Br<sup>-</sup> ion does not coordinate to metal atoms, but it hydrogen bonds with coordinated water molecules. The metal centers are bridged by succinate such that it forms a linear one-dimensional (1D) chain containing the boxes of  $Cu_2(L)_2(SA)_2$  (Figure 1a). Within the 1D chain, water molecules are hydrogen bonded to axially coordinated Oatom of carboxylate. In this chain, the Cu<sub>1</sub> exhibits a distorted octahedral geometry with three N-atoms of terpyridine and Oatom of carboxylate in the equatorial plane, while the other O atom of carboxylate and coordinated water occupies the axial

positions. On the other hand, the Cu<sub>2</sub> center sits on the inversion symmetry and exhibits elongated octahedral geometry with two each pendant pyridine N-atoms and O-atoms of SA in the equatorial plane. The axial positions of Cu<sub>2</sub> are very weakly coordinated to water with a Cu–O distance of 2.292(4) Å. In the crystal lattice, these 1D chains are assembled via a plethora of O–H…O (2.745(6) and 2.766(5) Å), O–H…Br (3.240(4) Å) and weak aromatic C–H…Br (2.88, 3.03 Å) interactions (Figure 1b). It is interesting to note here that carboxylates of succinate exhibit a diversified nature in the sense that they coordinate as monodentate with Cu<sub>2</sub>, while as bidentate with Cu<sub>1</sub>, and further SA exhibits a gauche conformation with a C–C–C torsion of 72.74°.

The crystal structure analysis of 2 reveals that it contains Cu(I) as well as Cu(II) centers. The asymmetric unit of 2 has two Cu(II) centers, and one Cu(I) center, two units of L, three Br- anions, one unit of GA, and two uncoordinated water molecules. The Cu(II) centers exhibit distorted square pyramid geometry, while the Cu(I) exhibits triangular coordination geometry. The square pyramid geometry was formed by the coordination of three terpyridyl N atoms and carboxylate O atom in equatorial positions and the Br- ion in the axial position. The triangular coordination around Cu(I) is formed by two pendant pyridyl units of L and one Br- anion. It is interesting to note here that, unlike SA in 1, the dicarboxylate links the two Cu(II) centers that are involved in chelation with L to form a 1D network. The GA exhibits gauche-gauche conformation with C-C-C-C torsions of 72.06° and 68.13°. As a result the 1D network exhibits a helicity (Figure 2).<sup>10</sup> Further, two of such opposite handed helices form a double helical chain through aromatic  $\pi \cdots \pi$  interactions between the units of L.

**1,3-Benzene Dicarboxylate as a Linker (3).** Although several aromatic polycarboxylates such as terphthalate, trimesate, and pyromelitate have been tried for generating the complexes with L and copper metals, only BDC has shown the



**Figure 2.** Illustrations for the crystal structure of 2: (a) One-dimensional helical chain; double helix through aromatic  $\pi \cdots \pi$  interactions between the units of L: (b) cylinder mode and (c) space-filling mode.

ability to give mixed metallic complex 3 and also to bridge 1D clusters of metal, L, and Br<sup>-</sup> into a three-dimensional (3D) network via catemeric O–H···O hydrogen bonds. The crystal structure of 3 reveals that it contains both Cu(I) and Cu(II), and the Br<sup>-</sup> also acts as a bridge between them. The asymmetric unit of 3 contains Cu(I) with full and Cu(II) with half occupancies, one L, one each of HBDC, Br<sup>-</sup> anion, and one water molecule. It is interesting to note here that although disodium salt was used in the reaction one of the carboxylate was protonated during the course of the reaction.

The bridging of Cu(I) and Cu(II) centers by  $Br^-$  leads to the formation of a zigzag chain that contains  $Cu_2L_2Br_2$  boxes (Figure 3). The Cu(I) center exhibits a pseudotetrahedral geometry with the coordination of two pendant pyridyl groups of L and two bridging bromide ions. On the other hand, Cu(II)exhibits distorted square pyramidal geometry with the coordination of three terpyridyl N atoms, one bridging  $Br^-$  ion, and one carboxylate O atom of HBDC. The axial position of Cu(II) is weakly coordinated to the Br<sup>-</sup> anion with the Cu-Br distance of 2.658(4) Å. In Cu<sub>2</sub>L<sub>2</sub>Br<sub>2</sub> boxes, the Cu(I) and Cu(II) centers are connected through the Br<sup>-</sup> bridges such that the two L ligands are in a head-to-tail arrangement leading to the formation of a mixed-valence tetrameric pseudo rectangular grid of size 11.056  $\times$  4.362 Å<sup>2</sup> with the Cu(II)–Cu(I)–Cu(II) angle of 87.29°. The ligand L is somewhat twisted with a torsion angle of 19.92°. Interligand face-to-face  $\pi - \pi$  stacking (centroid-centroid) interactions are observed with a distance of 4.078 Å. The pendant pyridine N atoms from adjacent grids coordinated to the Cu(I) center to extend the rectangular boxes into a 1D zigzag chain. In the crystal lattice two adjacent HBDC units are also assembled via a plethora of O-H···O interactions with a neighboring water molecule (O---O 2.902(5) and 2.787(4) Å). In the crystal lattice, the 1D chains are assembled into an extended hydrogen bonded 3D network



Figure 3. Illustrations for the crystal structure of 3: (a) coordination around Cu(I) and Cu(II) centers, (b) 1D zigzag chain that contains  $Cu_2(L)_2Br_2$  boxes, (c) side view of 1D zigzag chains.

via catemeric O–H···O interactions (O···O: 2.506(4) Å) having huge and continuous channels which are filled by the 4-fold self-interpenetration (Figure 4). Earlier, we have shown in a number of examples that hydrogen bonding can be used to assemble the coordination networks/complexes into higher dimensional aggregates.<sup>11</sup>

Linking of Cu(II) Centers by L Leading to 1D-Chain (4). The asymmetric unit of complex 4 contains one each of L and Cu(II), two each of Br<sup>-</sup> ions and water molecules. The Cu(II) center exhibits square planar geometry with the coordination of four nitrogen atoms, three from terpyridine and one from pendant pyridine (Cu–N<sub>ter</sub> 2.049(3), 1.933(3), 2.047(3) Å and Cu–N(pen) 1.980(3) Å) (Figure 5). The edges of the square N<sub>4</sub> differ largely because three of the nitrogen atoms come from the chelation of terpyridine units. The two N–N edges formed by chelated terpyridyl are shorter (2.561 and 2.553 Å) than the two N–N edges which involve the pendant N-atom (3.075 Å and 3.079 Å). The square contains N–Cu–N bond angles that

range from 79.70° and 99.63°. Overall, the Cu(II) exhibits distorted and elongated octahedral geometry as the epical positions occupied by Br<sup>-</sup> with a Cu(II)–Br distance of 2.726(7) Å. This type of coordination around Cu(II) generates 1D chains that are joined in three dimensions with hydrogen bonds such as C–H···Br (2.99 Å) O–H···O (2.933(11) Å) and O–H···Br (3.340(4) Å) and  $\pi$ ··· $\pi$  interactions (3.723 Å).

Linking of Ni(II)L/Co(II)L Units by BDC (5 and 6). The complex 5 crystallizes in the P2(1)/n space group and asymmetric unit of 5 is constituted by one each of L and Ni(II), BDC ions, and one water molecule. The Ni(II) exhibits perfect octahedral geometry, the three nitrogen atoms from terpyridine (Ni–N<sub>ter</sub> 2.110(3), 1.991(2), 2.108(3) Å) and water molecule occupies an equatorial position and the axial position is occupied by the monocoordination of carboxylates of BDC (Ni–O<sub>BDC</sub> 2.134(19) and 2.040(19) Å and Ni–O<sub>water</sub> 2.027(2) Å) (Figure 6). The resultant network can be described as a 1D chain in which BDC links Ni(L)H<sub>2</sub>O units using the

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Figure 4. Illustrations for the crystal structure of 3: (a) three-dimensional network formed by the linking the 1D chains via a catemer type of -COOH hydrogen bonding; 4-fold interpenetration of the 3D networks: (b) view without hydrogen atoms; (c) line drawing by representing metal atoms and hydrogen bonding synthon as nodes and L and Br atoms as connectors.

inversion symmetry. The 4-pyridyl of L remains uncoordinated and hangs on both sides of the chain and connects the chains into a two-dimensional (2D) layer via O-H...N (O...N2.742(3) Å).

The complex **6** crystallizes in  $P\overline{1}$  space group and its asymmetric unit contains one each of L and Co(II), BDC ions and three uncoordinated water molecules. The Co(II) center exhibits highly distorted square pyramidal geometry with the coordination of three nitrogen atoms from terpyridine (Co–  $N_{ter:}$  2.137(6) Å, 2.149(6) Å, 2.040(6) Å) and two carboxylates in mondentate fashion (Co–O<sub>BDC</sub> 2.061(6) and 2.058(5) Å) (Figure 7). This type of coordination results in the formation of a 1D network that is formed by the linking of Co(L) units by the BDC units. Here it is interesting to note that, unlike in **5**, the 1D chain is propagated using the translational symmetry such that the uncoordinated pyridines of L hang on only one side of the chain. This chain can be regarded as a supramolecular isomer to the one observed in **5**. These chains are interlinked by water molecules via  $O-H\cdots N$ ,  $O-H\cdots O$ ( $O\cdots N$ , 2.993(10) Å and  $O\cdots O$ , 2.998(8), 2.955(10) Å) and  $C-H\cdots O$  interaction ( $C\cdots O$  3.335(12) Å).

Characterization of Cu(I)–Cu(II) Complexes by Cyclic Voltammetric Studies. The CV of the complexes 1–4 were recorded in order to understand the differences in oxidation–reduction behaviors of the complexes containing only Cu(II) (1 and 4) and Cu(II)–Cu(I) (2 and 3) in CH<sub>3</sub>CN. The peaks observed in the cyclic voltammograms for the complexes 1–4 are given in Table S2.

The cyclic voltammograms of complexes 1 and 4 (Figure S1 and S4) exhibit irreversibility and typical behavior of Cu(II) complexes in the forward scans for both 1 and 4. On the other hand, CVs for the mixed valence (Cu(I) and Cu(II)) complexes 2 and 3 exhibit reversibility (Figure S2 and S3). In the forward scans of 2, the close proximity between the two peaks may be attributed to the fact that the SET process<sup>12</sup> from Cu(II) to Cu(I) may be sluggish<sup>13</sup> in nature due to its

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**Figure 5.** Illustrations for the crystal structure of 4: (a) coordination around Cu(II), assembling 1D chains: (b) via O-H…Br and O-H…O and (c) C-H…Br and  $\pi \dots \pi$  interactions.

resistance by the steric effects of the ligand for required structural changes.<sup>14</sup> The CV of **3** contains a single broadened peak both in forward and reverse scans (Figure S3). The broadening of peaks for both **2** and **3** may be attributed to the increase in chain length and the aromatic nature of the dicarboxylate linker which decreases the difference in potential between two adjacent redox states that in turn results in the merging of peaks into a single broad peak.<sup>15</sup> Thus a clear indication from the CV plots that the mixed valence complexes tend to attain reversibility and peaks tend to merge with each other to broaden the voltammogram.

**DRS Studies for the Complexes.** The DRS studies of the complexes were carried out using a Cary 5000 UV–vis-NIR analyzer. All the complexes were ground into a fine powder, and DRS studies were performed with these powdered samples taking the corresponding metal salts as the reference. The DRS spectra of the complexes showed good agreement with those of the constituent metal salts in the visible region. The peaks observed in the DRS spectra for the complexes are given in the Table S3.

The DRS and absorption spectra in the solid state (null transmittance) of all the copper complexes (1-4) are found to be identical signifying the presence of similar chromophores.<sup>16</sup>

Further in DRS, all the complexes exhibited charge transfer bands in the visible region (600-700 nm) possibly due to LMCT transition from filled orbital of the dicarboxylate to the low lined vacant d-orbital of the transition metals. Among the complexes 1-4, only the complex 2 exhibited distinct LMCT transition in the visible region, which may be attributed to the two distinct coordination environments of copper in 2. Notably, the DRS spectra for the two isomeric complexes (5 and 6) containing Ni(II) or Co(II) did not show distinct LMCT bands in the visible region.

#### CONCLUSIONS

Coordination networks of L with transition metal salts using organic dicarboxylate and  $Br^-$  ions as linkers have been synthesized via hydrothermal methodology, and their crystal structures have been analyzed in terms of network geometry and bridging modes of the linkers. The mixed valent complexes were obtained only in the case of 2 and 3 when the organic linkers are glutarate and isophthalate, both the complexes contain  $Br^-$  in addition to the organic carboxylate anion. In complex 2, the ligand L bridges Cu(I) and Cu(II) centers, while the organic anion bridges two Cu(II) centers to form a helical structure that further assembles into a double helix via



Figure 6. Illustrations for the crystal structure of 5: (a) coordination around Ni(II), (b) linking the Ni(II) centers by the BDC dianion to form a 1D chain; (c) assembling 1D chains into a 2D layer via  $O-H\cdots N$  hydrogen bonds.

aromatic  $\pi - \pi$  interactions. In the case of 3, the inorganic anion, Br<sup>-</sup>, bridges Cu(I) and Cu(II) centers, while HBDC links the 1D chains into a 3d network via catemeric –COOH hydrogen bonds. Complexes 5 and 6 exemplifies the phenomenon of supramolecular isomerism due to the isomeric bridging of dicraboxylate linker in a sense that they have similar network components but not geometries.<sup>17</sup>

# EXPERIMENTAL SECTION

All the chemicals were used as received without further purification. 4-Pyridine carboxaldehyde was purchased from Aldrich Chemicals. Other chemicals were bought from a local chemical company. FTIR spectra were recorded with a Perkin-Elmer Instrument Spectrum Rx serial no. 73713. <sup>1</sup>H NMR (200 MHz) spectra was recorded on a BRUKER-AC 200 MHz spectrometer. Elemental analyses were carried out with a Perkin-Elmer Series II 2400, and melting points were taken using a Fisher Scientific melting point apparatus cat. no. 12-144-1.

**Crystal Structure Determination.** The single crystal X-ray diffraction data for all structures were collected on Bruker-APEX-2 X-ray diffractometer that uses graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using the hemisphere method. The structures were solved by direct methods and refined by least-squares methods on F<sup>2</sup> using SHELX-97.<sup>18</sup> Non-hydrogen atoms were refined anisotropically and hydrogen atoms attached to C-atom and N-atom were fixed at calculated positions and refined using a riding model. The pertinent crystallographic details for the complexes are given in Table 1.

The cyclic voltammograms were recorded in an Electrochemical analyzer- CH Instrument 10688. All the solutions were deaerated at



Figure 7. Illustrations for the crystal structure of 6: (a) coordination around central Co(II), (b) linking of CoL units by BDC; compare with Figure 6b, (c) linking of the chains by water molecules via O-H···N and O-H···O hydrogen bonds.

least for 30 min with pure argon. All the potentials were coated against a Ag/AgCl electrode, the counter electrode was selected to be a Pt rod, and all experiments were performed at room temperature. The samples were prepared in CH<sub>3</sub>CN, and NaClO<sub>4</sub> was used as nonaqueous electrolyte. The peaks observed in the voltammograms for the mixed valence complexes are given in Table S2. The cyclic voltammograms for the complexes 1-4 are given in Figures S1–S4.

The thermogravimetric analyses for the complexes were performed using LUXX STA 409PC analyzer in the temperature range of 0-500°C at a scan rate of 5 °C/min. The TGA curves for the complexes are given in Figures S5–S10. The experimental and calculated X-ray powder patterns of the complexes are given in Figures S11–S14.

The DRS studies of the complexes were performed using a Cary 5000 UV-vis-NIR analyzer. All the complexes were ground into fine powder and recorded by taking the corresponding metal salts as the reference. The DRS spectra and the peaks observed in the DRS spectra for all the complexes are given in Figures S15–S20 and Table S3 respectively. The corresponding absorption spectra are given in Figures S21–S26.

**Synthesis of L.** The solution of NaOH (0.075 mM, 3.0 g in 3.0 mL of water) was added to 40 mL of EtOH in a two neck round-bottom flask. To this solution, 5.4 mL of 2-acetyl-pyridine and 2.26 mL of 4-pyridine carboxaldehyde were added and stirred for 10 min. A yellowish color developed immediately after which 15 mL of aqueous NH<sub>3</sub> (28%) was added to the yellow colored solution and stirred for 48 h. The resulting precipitate was filtered and recrystallized from (1:1) v/v hot (EtOH + MeOH) mixture. Yield: 31.2% based on 4-pyridine carboxaldehyde, mp 228.2–228.6 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ H: 7.37 (2H, d of d, <sup>3</sup>*J*<sub>HH</sub> = 4.75 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1 Hz, arom); 7.79 (2H, d, <sup>3</sup>*J*<sub>HH</sub> = 4.5 Hz, arom); 8.09 (2H, d of t, <sup>3</sup>*J*<sub>HH</sub> = 6 Hz, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.75 Hz, arom); 8.82 (2H, s, arom); 8.91 (2H, d, <sup>3</sup>*J*<sub>HH</sub> = 4.5 Hz, arom).

Synthesis of Metal Complexes. Preparation of  $\{[Cu_3L_2(SA)_2(Br)_2(H_2O)_4]\cdot 3H_2O\}_n$  1. Ethanol solution of L (5 mL, 0.016 g., 0.05 mmol) and aqueous solution of Na-succinate (2 mL, 0.0081 g, 0.05 mmol) were mixed with 6 mL of CH<sub>3</sub>CN solution of CuBr (0.007 g, 0.05 mmol) and CuBr<sub>2</sub> (0.011 g, 0.05 mmol) in warm

conditions and to this mixture 0.9 mL of DMA (dimethylacetamide) was added. The resultant solution was sealed in a 15 mL Teflon reactor and was heated up to 100 °C for 3 days and then gradually cooled to room temperature. The dark green crystals were obtained and dried in the air to give 0.0061 g. Yield: 38.13% based on L. Elemental analysis: (%) Calc. for  $C_{48}H_{50}Br_2Cu_3N_8O_{15}$ : C, 59.99; H, 5.49; N, 12.72. Found C, 58.89; H, 5.45; N, 12.22. IR (cm<sup>-1</sup>): 3431.48(m), 3032.46(s), 2365.62(s), 1602.98(s), 1406.96(s), 1247.98(s), 1018.65(s), 837.11(s), 801.39(s), 667.92(m).

Preparation of {[ $Cu_3L_2(GA)Br_3J\cdot 2H_2O$ ]<sub>r</sub>, **2**. Complex **2** was prepared by using a similar procedure as for **1**, except that Na glutarate (0.0088 g, 0.05 mmol) was taken in place of Na-succinate. The dark green crystals were obtained and dried in the air to give 0.0066 g. Yield: 41.25% based on **L**. Elemental analysis: (%) Calc. for  $C_{45}H_{38}Br_3Cu_3N_8O_6$ : C, 68.77; H, 5.40; N, 13.62. Found C, 68.57; H, 5.45; N, 13.66. IR (cm<sup>-1</sup>): 3431.84(m), 3031.59(m), 2362.92(s), 2344.64(s), 1609.76(s), 1408.15(s), 1248.54(s), 1018.37(s), 834.27(s), 801.79(s), 655.76(m).

Preparation of {[ $Cu_3L_2(HBDC)_2Br_2$ ]·2 $H_2O$ }<sub>n</sub>, **3**. Complex **3** was prepared by using a similar procedure as for **1**, except that Na-BDC (0.011 g, 0.05 mmol) was used in place of Na-succinate. The dark green crystals were obtained and dried in the air to give 0.0075 g. Yield: 46.88% based on L. Elemental analysis: (%) Calc.for  $C_{56}H_{42}Br_2Cu_3N_8O_{10}$ : C, 68.29; H, 4.03; N, 11.78. Found C, 68.30; H, 4.10; N, 11.50. IR (cm<sup>-1</sup>): 3422.43(m), 3032.09(s), 2365.15(s), 1609.71(s), 1413.57(s), 1248.20(s), 1018.83(s), 838.01(s), 802.01(s), 667.64(m).

**Preparation** {[CuLBr<sub>2</sub>]·2H<sub>2</sub>O}<sub>n</sub>, **4.** Complex **4** was prepared by following a similar procedure as for **1** except bipyridine 2,6,2',6'-tetracarboxylic acid (0.017 g, 0.05 mmol), and a calculated amount of Et<sub>3</sub>N was taken in place of Na-succinate. The dark green crystals were obtained and dried in the air to give 0.0048 g. Yield 30% based on L. Elemental analysis: (%) Calc. for  $C_{20}H_{18}Br_2$  CuN<sub>4</sub>O<sub>2</sub>: C, 64.29; H, 3.60; N, 8.33. Found C, 69.35; H, 5.24; N, 16.17. IR (cm<sup>-1</sup>): 3422.19(m), 3032.06(s), 2365.40(s), 1560.28(m), 1405.99(s), 1248.30(s), 970.27(s), 841.10(s), 802.01(s), 667.80(s).

Preparation of  $[NiL(BDC)(H_2O)]_{rv}$  5. Complex 5 was prepared by following a similar procedure as for 1 except that Na-BDC (0.011 g, 0.05 mmol) and NiCl<sub>2</sub> (0.024 g, 0.1 mmol) were used in place of Nasuccinate and CuBr<sub>2</sub>. Light green crystals were obtained and dried in the air to give 0.0087 g. Yield: 54.38% based on L. Elemental analysis: (%) Calc. for C<sub>28</sub>H<sub>20</sub>N<sub>4</sub>NiO<sub>5</sub>: C, 68.29; H, 4.09; N, 11.38. Found C, 68.22; H, 4.10; N, 10.68. IR (cm<sup>-1</sup>): 3055.88(m), 1611.55(s), 1545.25(m), 1361.68(s), 1013.90(s), 794.02(s), 748.72(s), 708.02(m).

Preparation of {[CoL(BDC)]· $3H_2O$ }<sub>n</sub>, **6**. Complex **6** was prepared following a similar procedure as for **1** except for Na-BDC (0.011 g, 0.05 mmol) and CoCl<sub>2</sub> (0.028 g, 0.1 mmol) was used in place of Na-succinate and CuBr<sub>2</sub>. Dark red crystals were obtained and dried in the air to give 0.0143 g. Yield: 89.375% based on L. Elemental analysis: (%) Calc. for  $C_{56}H_{48}Co_2N_8O_{14}$ : C, 63.63; H, 4.58; N, 10.60. Found C, 63.65; H, 4.45; N, 10.50. IR (cm<sup>-1</sup>): 3055.12(s), 1610.07(s), 1542.81(m), 1361.90(s), 794.19(s), 744.16(m), 709.38(s).

# ASSOCIATED CONTENT

#### **Supporting Information**

<sup>1</sup>H NMR of L, XRPD-patterns, IR, TGA, CV, DRS spectra, and crystallographic information for the complexes 1-6 (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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