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Mononuclear, dinuclear and polymeric cobalt(II) complexes built on 4-aryl-2,6-bis(2′-pyrazinyl)pyridines

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ABSTRACT

Two new multidentate nitrogen ligands containing a 2,6-bis(2′-pyrazinyl)pyridine (bpp) backbone were synthesized and characterized. The facile Kröhnke condensation procedure allows for efficient synthesis and modification of this class of N-rich ligands. The metal-mediated self-assembly of these ligands along with a previously known derivative with $Co(NCS)_2$ was studied. X-ray structural analysis of the metal assemblies reveals that mononuclear, dinuclear and polymeric structures could be obtained based on the ligands used. Although in most cases including the previously reported results the coordination chemistry of bpp-based ligands involves only inner N_3 cavity, with the outer-N donors remaining uncoordinated, the introduction of a 3-pyridyl group to the 4-position of central pyridine of bpp is found to be critical for the synthesis of new coordination polymers. The thermal properties of these metal complexes have been studied.

1. Introduction

2,2′:6′,2″-Terpyridine (2,2′:6′,2″-tpy) and its derivatives are archetypical convergent N-donating ligands that have been explored as very useful organic building block for coordination and supramolecular chemistry for over 35 years [1]. The facile modification in the 4′-position of tpy allows for the fabrication of a large variety of metal complexes according to strong metal–ligand chelation, and such complexes have found widespread applications as optoelectronic, magnetic, catalytic and nano-materials [2]. However, owing to the presence of only one chelating site in the structure, upon coordinating with metal ions 2,2′:6′,2″-tpy ligands are usually used for the formation of simple small molecular complexes (**A**, Scheme 1). Recent efforts have been made to synthesize more structurally complicated and novel metallosupramolecules by extending metal coordination sites on the 2,2′:6′,2″-tpy backbone, such as introducing extra pyridyl groups in the 4′-position of tpy, or altering 2,2′:6′,2″-tpy to the divergent 4,2′:6′,4″-tpy [3,4]. Both methods proved to be quite successful in the synthesis of complex supramolecular assemblies as well as one-, two- or three-dimensional (1-, 2- or 3-D) coordination polymers and networks [3–5]. Another way to add extra coordination sites is to modify the side-arm pyridines of 2,2′:6′,2″-tpy with pyrazines, which affords a bpp backbone (**B**) as seen in Scheme 1. In structure **B**, two extra N-donors are present, which could potentially bind other metal centers, in addition to the N_3 cavity coordination. Similar to other tpy derivatives, this type of ligands can be readily prepared via the one-pot Kröhnke condensation which facilitates further structural modification on the central pyridine. However, derivatives of bpp have been thus far much less studied, compared to tpys [6–9]. Coordination complexes of bpp derivatives with Cd^{II}, Ni^{II}, Fe^{II} and Ru^{II} have been revealed, where only simple mononuclear structures were observed, with the outer N-donors remaining uncoordinated [6–9]. Furthermore, similar to tpys, the bpp ligands could be modified on the 4-position of the central pyridine with additional coordination sites without difficulties in synthesis (**C**, Scheme 1). Thus, more structurally complicated metallosupramolecular structures are anticipated when using **C** as a ligand.

Recently, we investigated the synthesis of 4-phenyl-bpp and its coordination chemistry with Zn, Cu, Co and Fe [10]. Although in the resultant metal complexes as obtained mononuclear structures utilizing only the N_3 cavity of bpp predominate, a novel bis-ligand trinuclear Cu(II) complex involving the outer-N coordination has been isolated and structurally characterized in our group [10]. Further studies on the Cu(II) complex of a related ligand, 4-(4-hexyloxyphenyl)-bpp, however, revealed a mononuclear complex without the outer-N coordination [11]. The difficulty in predicting

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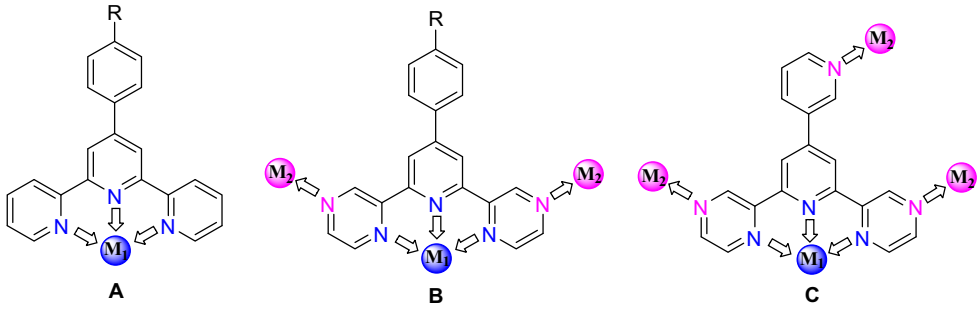


Scheme 1. Plausible evolution of tpy-type ligands with extended metal coordination sites.

the resulting metal assemblies as well as controlling the coordinating modes of such ligands has urged us to further explore the coordination chemistry of related ligands containing the bpp domain.

In this work, we synthesize two new bpp derivatives (L2 and L3, Scheme 2) while varying the 4-substituents of the central pyridine, and report the coordination chemistry of L1-3 with cobalt(II) thiocyanate. It was interesting to find that mononuclear, dinuclear and polymeric cobalt(II) complexes could be obtained using differently 4-substituted bpps and the same metal salt, and the introduction of additional pyridyl group to the 4-position of central pyridine of bpp is crucial for the formation of a 1-D helical coordination polymer.

2. Experimental

2.1. General

Solvents and reagents were purchased from Fisher Scientific or Sigma–Aldrich in the US. All reactions were performed under ambient conditions (no inert atmosphere). Solution electronic absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer and FT-IR spectra were measured on a Shimadzu 8400S instrument with solid samples using a Golden Gate ATR accessory. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TG-50 analyzer under N_2 atmosphere with a heating rate of 20 °C/min. ^{1}H and ^{13}C NMR spectra were obtained at room temperature on a Bruker III 500 MHz spectrometer with TMS as an internal standard. High resolution mass spectra were recorded on an Agilent 6550 iFunnel ESI-QTOF-LC/MS instrument.

2.2. Synthesis of L2

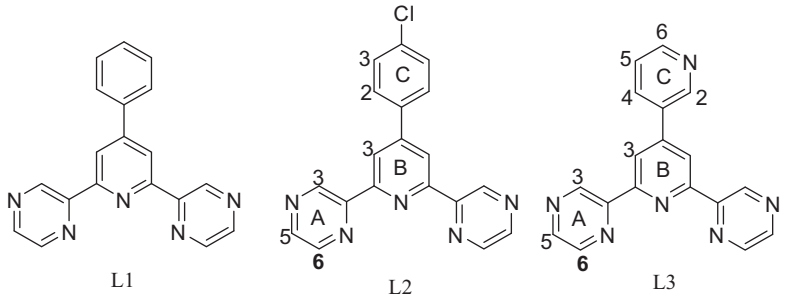
In a 250 mL round-bottom flask, 2-acetylpyrazine (1.22 g, 10.00 mmol) was added to a solution of 4-chlorobenzaldehyde (0.700 g, 5.00 mmol) in EtOH (30 mL) upon stirring. KOH pellets (0.560 g, 10.0 mmol) were then added, and followed by aqueous NH_3 (28%, 25 mL). The resulting brownish solution was stirred at room temperature overnight, during which time gray solid had formed. The solid was collected by filtration, washed with EtOH and dried in vacuo over P_2O_5. L2 was isolated as pure product (1.00 g, 58.0%). UV–Vis λ_{max}/nm (2.5×10^{-5} mol dm^{-3}, CH_2Cl_2-MeOH) 250 ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1} 18.7), 285 (26.1), 320sh (8.1). FT-IR (solid, cm^{-1}): 1603s, 1571w, 1521w, 1496s, 1472m, 1428m, 1372s, 1245w, 1117m, 1050m, 1017s, 852m, 822s, 738w, 690 m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 2 H, H^{A3}), 8.85(dd, J = 6.4, 1.0 Hz, 4 H, H$^{A5/A6}$), 8.72 (s, 2 H, H^{B3}), 8.03(d, J = 8.7 Hz, 2H, H^{C3}), 7.67 (d, J = 7.67 Hz, 2 H, H^{C2}) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.39, 149.58, 148.79, 145.59, 144.10, 143.11, 134.71, 129.44, 128.95, 118.97 ppm. HR-MS: m/z 346.0863 [M + H]$^+$ (calc. 346.0859), 368.0679 [M + Na]$^+$ (calc. 368.0679).

2.3. Synthesis of L3

The procedure is similar that for L2, except that pyridine-3-carbaldehyde (0.535 g, 5.00 mmol) was used. White solid of L3 was collected as pure compound after filtration. Yield: (0.970 g, 62.0%). UV–Vis λ_{max}/nm (2.5×10^{-5} mol dm^{-3}, CH_2Cl_2-MeOH) 245 ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1} 30.4), 284 (31.0), 315sh (12.8). FT-IR (solid, cm^{-1}): 1604s, 1579m, 1520m, 1473m, 1411m, 1373s, 1299w, 1251w, 1149w, 1115s, 1029s, 891w, 855s, 758s, 705s, 650m. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.94 (d, J = 1.0 Hz, 2 H, H^{A3}), 9.16 (d, J = 2.0 Hz, 1 H, H^{C2}), 8.86 (d, J = 1.5 Hz, 2 H H$^{A5/A6}$), 8.84 (d, J = 2.5 Hz, 2 H, H$^{A6/A5}$), 8.77 (s, 2 H, H^{B3}), 8.76 (d, J = 4.5 Hz, 1 H, H^{C6}), 8.41 (dt, J = 8.0, 2.0 Hz, 1 H, H^{C4}), 7.64 (dd, J = 8.0, 4.5 Hz, 1 H, H^{C5}) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 154.43, 150.62, 149.58, 147.89, 147.49, 145.62, 144.13, 143.16, 134.89, 132.78, 124.26, 119.40 ppm. HR-MS: m/z 313.1193 [M + H]$^+$ (calc. 313.1202), 335.1012 [M + Na]$^+$ (calc. 335.1021).

2.4. Synthesis of ***1***

L1 (31.1 mg, 0.100 mmol) was dissolved in MeOH/CH_2Cl_2 (10 mL, 1: 4, v/v) in a 20 mL vial equipped with a magnetic stirrer,



Scheme 2. The molecular structures of ligands L1-3 with atomic labeling for NMR spectroscopic assignments.