



Synthesis, crystal structures, and dye removal properties of a series of discrete and polymeric copper, zinc, cobalt, and cadmium complexes containing bis-pyridyl-bis-amine ligands



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ABSTRACT

Two bis-pyridyl-bis-amine ligands, *trans*-1,2-bis(*m*-picolyamino)cyclohexane (*rac*-*m*-picchxn) and *trans*-1,2-bis(*p*-picolyamino)cyclohexane (*rac*-*p*-picchxn), derived from *trans*-1,2-diaminocyclohexane (*rac*-chxn), were assembled with CuCl₂, ZnCl₂, ZnBr₂, Co(NO₃)₂, and CdCl₂ through reactants slow diffusion to afford corresponding metal complexes. Complexes [Cu(*R,R*-*m*-picchxn)Cl₂] (1) and [Zn(*rac*-*m*-picchxn)Br₂] (3) are mononuclear coordination structures, complex [Zn₂(*rac*-*m*-picchxn)Cl₄]_n (2) adopts a one-dimensional (1D) helical chain, complex {[Co(*R,R*-*p*-picchxn)(NO₃)₂]·THF·2/3H₂O}_n (4) has a two-dimensional (2D) kgm layer structure, complex [Cd(*rac*-*p*-picchxn)Cl₂]_n (5) suits a 1D double-stranded zigzag chain structure, and compound [Cu(*rac*-chxn)₂][CuCl₃] (6) is a Cu(I)-Cu(II) mixed-valence ionic product generated from the hydrolysis of *rac*-*p*-picchxn associated with the reduction of Cu(II) ion. The two bis-pyridyl-bis-amine ligands possess a chelating-bridging mode in forming infinite network and a chelating-only mode in forming discrete complexes. These metal–organic architectures show the influence of metal ion combining with organic ligand and anion on the structure variation. Noteworthy, chain polymers 2 and 5 could be utilized in the removal of methyl orange (MO), acid orange 7 (AO7), and malachite green (MG) from water through adsorptive processes. The adsorption dynamics of MO and AO7 on 2 and MG on both 2 and 5 obeyed a pseudo-second-order kinetics while that of MO and AO7 on 5 followed a pseudo-first-order kinetics.

1. Introduction

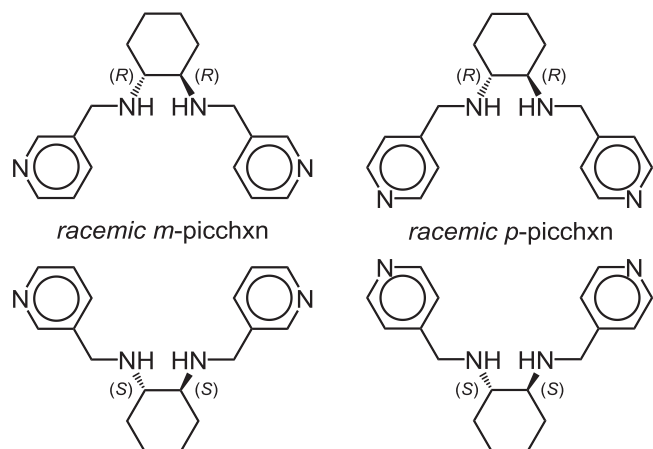
During the past few decades, there has been a constant effort to develop inorganic–organic hybrid materials, due to their unique multi-dimensional network topologies, peculiar structural transformations, various porous frameworks, and interesting optical and magnetic properties as well as their encouraging potentials for use as practically functional materials [1–7]. In recent, inorganic–organic hybrid materials have been explored to behave as liquid-phase adsorbents for adsorbing and separating hazardous dye pollutants from contaminated water [8–24]. A few of low dimensional coordination polymers (CPs) other than three-dimensional (3D) porous CPs and metal–organic frameworks (MOFs) have been found to exhibit remarkable adsorption performance for the adsorptive removal of dye molecules from water though they usually have no or small pores and little surface area [25–27]. This can be attributed to the understanding that the adsorption of dyes on inorganic–organic hybrid materials is most likely dominated by the nature of binding sites and the cooperation of multiple adsorbent–adsorbate interactions, such as electrostatic attractions, hydrogen-bonding interactions, and other mechanisms [28,29].

On the other hand, significant progresses so far have been inspired to get access to the generation of desirable CPs for crystal engineering purposes with the judicious selection of the constituent metal ions and network-forming ligands. 4,4'-Bipyridine and its ingenious bis-pyridyl derivatives with either an innocent (such as alkyl, aryl, -C=C-, -C≡C-, -N=N- etc.) or a non-innocent backbone (such as amide, urea, amine, sulfide, oxadiazole, thiazole) are known to have good coordination ability [30–37], being excellent candidates for building structurally diverse and functionally intriguing CPs. In transition metal complexes, 1,2-diaminocyclohexane is a popular chelating ligand which can be used to modify product dimensionality or decorate a known metal–organic architecture or framework [38–45]. The same ligand recently have also been found to behave as a bridging-only ligand coordinating to two metal centers with mono-coordination of each nitrogen [46–50].

Subsequent to our previous work aimed at controlling the network formation from bis-pyridyl-mono-amine [36,37,51–55], we herein paid our attention to the utilization of two *trans*-1,2-diaminocyclohexane (*rac*-chxn) derived bis-pyridyl-bis-amine ligands, namely *trans*-1,2-bis(*m*-picolyamino)cyclohexane (*rac*-*m*-picchxn) and *trans*-1,2-

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Scheme 1. Structures of racemic *m*-picchxn and *p*-picchxn ligands.

bis(*p*-picolylamino)cyclohexane (*rac-p*-picchxn) (Scheme 1), to attain this end. Six novel metal complexes, [Cu(*R,R*-*m*-picchxn)Cl₂] (1), [Zn₂(*rac-m*-picchxn)Cl₄]_n (2), [Zn(*rac-m*-picchxn)Br₂] (3), {[Co(*R,R*-*p*-picchxn)(NO₃)₂]·THF·2/3H₂O}_n (4), [Cd(*rac-p*-picchxn)Cl₂]_n (5), and [Cu(*rac-chxn*)₂][CuCl₃] (6), are reported. These metal complexes form zero-dimensional mononuclear coordination structures (1 and 3), one-dimensional (1D) helical chain (2), 1D double-stranded zigzag chain structure (5), and two-dimensional (2D) kpm layer (4), as well as Cu(I)-Cu(II) mixed-valence compound (6). The structure diversity among these discrete and polymeric metal–organic architectures significantly refers to the combining influence of metal ion, organic ligand, and anion. Additionally, investigations of dye removal on CPs 2 and 5 indicate that these CP materials are capable of adsorptive removal of methyl orange (MO), acid orange 7 (AO7), and malachite green (MG).

2. Experimental section

2.1. Materials and instrumentation

Ligands *rac-m*-picchxn and *rac-p*-picchxn were synthesized following previously reported procedures [56]. Other chemicals were obtained as received from commercial sources and used without further purification. X-ray powder diffraction (XRPD) measurements were performed on a Shimadzu XRD-7000 diffractometer with graphite monochromatized Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 30 kV, 30 mA with a scan speed of $1.2^\circ \text{ min}^{-1}$. Thermogravimetric (TG) analyses were performed using a Thermo Cahn VersaTherm HS TG analyzer from room temperature to 900 °C with a heating rate of $2^\circ \text{ C min}^{-1}$ under a flux of nitrogen. Infrared (IR) spectra were recorded with a Perkin-Elmer Frontier FT-IR spectrometer using attenuated total reflection (ATR) technique; abbreviations used for the IR bands are s = strong, m = medium, w = weak, br = broad. UV–Vis absorption spectra were recorded on a JASCO V-750 UV/VIS spectrophotometer. Microanalyses (C, H, N) were carried out on an Elementar Vario EL III elemental analyzer. Energy dispersive spectroscopy (EDS) microanalysis was performed using an Oxford model 6111 instrument equipped with a Link data acquisition system and a semiquantitative analysis program.

2.2. Synthesis of [Cu(*R,R*-*m*-picchxn)Cl₂] (1)

A solution of CuCl₂·2H₂O (34.1 mg, 2.0×10^{-1} mmol) in CH₃CN (3 mL) was carefully layered on top of a bilayer solution comprised of a THF solution (3 mL) containing *rac-m*-picchxn (60.3 mg, 2.0×10^{-1} mmol) on the bottom and a buffer solvent of CH₃CN-THF (6 mL, $v/v = 1/1$) on the top at ambient temperature. The solution was allowed to

stand for approximately ten days, resulting in the formation of blue block-shaped crystals. Yield 85% based on the metal (72.9 mg, 1.7×10^{-1} mmol). Anal. Calcd. for C₁₈H₂₄Cl₂CuN₄: C, 50.18; H, 5.61; N, 13.00. Found: C, 50.09; H, 5.87; N, 12.88. IR (ATR, cm⁻¹): 3415br, 2939m, 2854w, 1594w, 1575w, 1484w, 1463w, 1433m, 1222w, 1192w, 1111w, 1056m, 1036m, 990m, 971w, 829m, 784m, 724s, 623m, 557w.

2.3. Synthesis of [Zn₂(*rac-m*-picchxn)Cl₄]_n (2)

A solution of ZnCl₂ (54.2 mg, 4.0×10^{-1} mmol) in CH₃CN (3 mL) was carefully layered on top of a bilayer solution comprised of a CH₂Cl₂ solution (3 mL) containing *rac-m*-picchxn (60.2 mg, 2.0×10^{-1} mmol) on the bottom and a buffer solvent of CH₃CN-CH₂Cl₂ (6 mL, $v/v = 1/1$) on the top at ambient temperature. The solution was allowed to stand for approximately one week, resulting in the formation of colorless needle-like crystals. Yield 50% based on the metal (57.1 mg, 1.0×10^{-1} mmol). Anal. Calcd. for C₁₈H₂₄Cl₄N₄Zn₂: C, 37.99; H, 4.25; N, 9.85. Found: C, 38.42; H, 4.49; N, 9.55. IR (ATR, cm⁻¹): 3201br, 3050w, 2934 m, 2864w, 1610 m, 1438 s, 1197w, 1036 s, 804 m, 703 s, 653 m.

2.4. Synthesis of [Zn(*rac-m*-picchxn)Br₂] (3)

A solution of ZnBr₂·2H₂O (52.3 mg, 2.0×10^{-1} mmol) in CH₃CN (3 mL) was carefully layered on top of a bilayer solution comprised of a CH₂Cl₂ solution (3 mL) containing *rac-m*-picchxn (60.5 mg, 2.0×10^{-1} mmol) on the bottom and a buffer solvent of CH₃CN-CH₂Cl₂ (6 mL, $v/v = 1/1$) on the top at ambient temperature. The solution was allowed to stand for approximately ten days, resulting in the formation of colorless rod-shaped crystals. Yield 60% based on the metal (61.3 mg, 1.2×10^{-1} mmol). Anal. Calcd. for C₁₈H₂₄Br₂N₄Zn: C, 41.45; H, 4.64; N, 10.74. Found: C, 41.66; H, 4.55; N, 10.75. IR (ATR, cm⁻¹): 3126br, 2939s, 2879m, 1579m, 1479m, 1423m, 1192w, 1102w, 1016s, 799s, 703s, 623m.

2.5. Synthesis of {[Co(*R,R*-*p*-picchxn)(NO₃)₂]·THF·2/3H₂O}_n (4)

A solution of Co(NO₃)₂·6H₂O (58.1 mg, 2.0×10^{-1} mmol) in CH₃OH (3 mL) was carefully layered on top of a bilayer solution comprised of a THF solution (3 mL) containing *rac-p*-picchxn (60.1 mg, 2.0×10^{-1} mmol) on the bottom and a buffer solvent of CH₃OH-THF (6 mL, $v/v = 1/1$) on the top at ambient temperature. The solution was allowed to stand for approximately ten days, resulting in the formation of orange-red rhombic-shaped crystals. Yield 70% based on the metal (64.8 mg, 1.4×10^{-1} mmol). Anal. Calcd. for C₁₈H₂₄CoN₆O₆·2/3H₂O: C, 44.00; H, 5.20; N, 17.10. Found: C, 44.11; H, 5.56; N, 16.92. IR (ATR, cm⁻¹): 3216br, 2934m, 2864w, 1615m, 1303s, 1026m, 799m, 627m.

2.6. Synthesis of [Cd(*rac-p*-picchxn)Cl₂]_n (5)

A solution of *rac-p*-picchxn (60.1 mg, 2.0×10^{-1} mmol) in CH₃OH (3 mL) was carefully layered on top of a bilayer solution comprised of an aqueous solution (3 mL) containing CdCl₂·2.5H₂O (45.6 mg, 2.0×10^{-1} mmol) on the bottom and a buffer solvent of CH₃OH-H₂O (6 mL, $v/v = 1/1$) on the top at ambient temperature. The solution was allowed to stand for approximately two weeks, resulting in the formation of colorless rod-shaped crystals. Yield 40% based on the metal (37.1 mg, 8.0×10^{-2} mmol). Anal. Calcd. for C₁₈H₂₄CdCl₂N₄: C, 45.07; H, 5.04; N, 11.68. Found: C, 44.60; H, 4.87; N, 11.33. IR (ATR, cm⁻¹): 3211m, 2934m, 2889w, 1610m, 1463m, 1429m, 1222m, 1056m, 1005m, 930m, 895m, 794 s, 618w.

2.7. Synthesis of [Cu(*rac-chxn*)₂][CuCl₃] (6)

A solution of CuCl₂·2H₂O (34.3 mg, 2.0×10^{-1} mmol) in CH₃OH (3 mL) was carefully layered on top of a bilayer solution comprised of a

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