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1D coordination network formed by a cadmium based pyridyl urea helical monomer

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ABSTRACT

Herein, we report the metal complexation properties of a macrocyclic ligand (L) that contains three pyridines as well as three urea groups. Linear and strand like ligands are typically used to afford helical coordination polymer. Our reported macrocyclic ligand (L) has remarkable flexibility and can twist upon dative bond formation. Two macrocyclic ligands complex with three cadmium atoms to form a helicate monomeric structure $[Cd_3L_2(H_2O)_6(CH_3CN)_2]^{6+}$, which extends to a 1D polymeric structure via hydrogen-bonding. We also investigated the binding property of this new ligand in solution by NMR and UV–Vis spectroscopy. These results together with diffusion NMR studies suggest that in solution this ligand also forms an oligomeric complex with cadmium.

1. Introduction

Design of helical coordination polymers [1] has received tremendous attention due to the potential applications of these polymers in catalysis [2], nonlinear optics [3], luminescence [4] and chiral separation [5]. Two types of ligands are commonly employed to afford helical coordination polymers. One type includes strand like ligands [6] or linear ligands [7] (Fig. 1a) that are preorganized to twist upon dative bond formation to generate helicity. Alternatively, there are bridging ligands that are conformationally restricted into twisted helical structures (Fig. 1b) [8]. Common organic ligands used in coordination polymers include pyridine N-donors and carbonyl O-donors [9]. Pyridines and bipyridines are particularly attractive as they not only can form metal complexes but also associate via aromatic stacking interactions [10]. Macrocyclic ligands are typically less flexible and are not usually amenable for constructing helical polymers [11]. Our group has recently synthesized tripyridyl *tris*-urea macrocycle (Fig. 1c), which has programmed flexibility [12]. Here we report that this macrocyclic ligand is able to twist and bind Cd^{2+} to form a 2:3 complex that further assemble into a 1D helical polymeric structure. These helical polymeric units formed a 2D network by π–π aryl stacking interaction between pyridine π clouds of adjacent chain. We also investigated the binding affinity of this macrocyclic ligand in solution by NMR and UV–Vis titrations. The binding stoichiometry in solution was compared to that of the solid-state structure. Subsequent diffusion NMR data also suggests that in dilute solution this ligand forms an oligomeric complex with cadmium.

In previous work, we reported the synthesis, structure, and binding properties of pyridyl urea macrocycle **1** with alkali metal cations (Li^+, Na^+, and K^+) [12]. This 24 member macrocycle consists of three pyridine units as well as three ureas protected as triazinanone groups. It was crystallized as the dichloromethane solvate (Fig. 2a) [12]. The free ligand was not planar. Three pyridine nitrogens and one of the triazinanone tertiary nitrogens face roughly in the same direction. The three carbonyls point approximately outwards and do not define any binding site. The “hard” alkali cations usually prefer “hard” lewis bases. Thus, we expected that the macrocycle would adjust its conformation to form a binding site for the cation. The low quality crystals of **1**·$NaClO_4$ diffracted sufficiently to establish general structure connectivity [12]. Upon complexation of $NaClO_4$, the macrocycle dramatically flips its conformation, turning all the carbonyl groups inward to coordinate with the Na^+ ions (Fig. 2b). The sodium ion was indeed more oxophilic and preferred to form shorter stronger interactions with the carbonyl oxygens of ligand **1** as well as to the oxygens of the perchlorate ion [12]. Fig. 2b highlights the ligand structure in **1**·$NaClO_4$ with the Na^+, perchlorate and water omitted to accentuate the cavity formed by the inward facing carbonyl oxygens [12]. Ligand **1** is flexible enough to twist and reorient the potential oxygen and pyridine binding sites. The reciprocity among rigidity and flexibility is an important issue in supramolecular chemistry and is an area that we are starting to explore.

The unexpected flexibility of **1** led us to investigate this macrocycle as a ligand for Cd^{2+}. Cadmium (II) has different coordination preferences and a propensity to coordinate with both N and O containing ligands. This tendency has been exploited to generate novel metal-organic frameworks [13], for example $CdCl_2$ formed helical coordination complexes with ligands such as *N*,*N*-bispyridin-4-ylmethylsuccinamide [14]. In addition, Cd(II) can be readily

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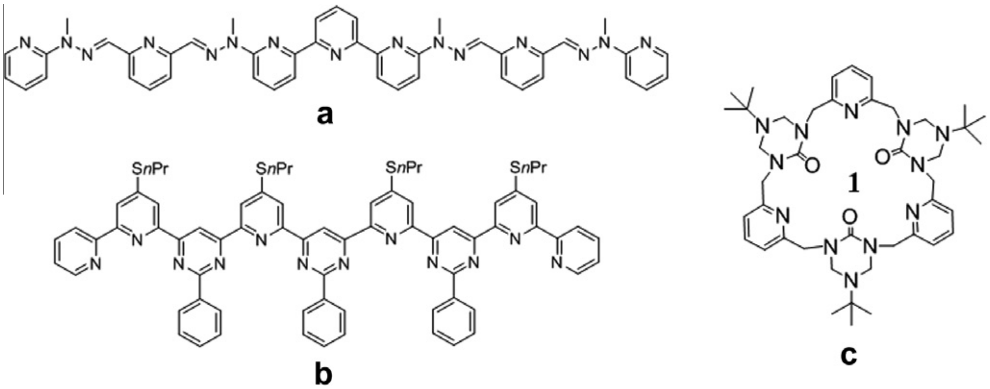

Fig. 1. Comparison of the structure of different types of ligands. (a) Linear strand like ligand that can be preorganized in presence of Pb^{2+} and can generate helicity [7]. (b) Polyheterocyclic strand that is preorganized to helical shape enforced by the pyridine–pyrimidine helicity codon [8]. (c) Macrocyclic ligand **1** that consists of three pyridine units as well as protected urea [12].

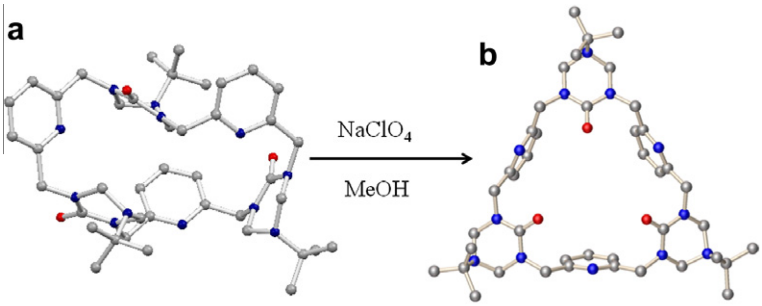

Fig. 2. Comparison of the free ligand **1** versus the conformation it adopted in the **1**·$NaClO_4$ complex. (a) X-ray crystal structure of the free ligand crystallized from dichloromethane. (b) Side view of the ligand **1** from the X-ray crystal structure of ligand **1**· $NaClO_4$ complex. Upon complex formation the macrocycle dramatically flipped its conformation to afford an interior binding cavity.

substituted for Zn^{2+} in metalloproteins and blocks their function, a property that is associated with its toxicity in biological systems [15]. The detection and remediation of cadmium from the environment is of great importance [16]. Given literature precedence, we set out to test the ligating ability of pyridines and ureas in ligand **1** for the transition metal cation Cd^{2+}.

2. Experimental

2.1. Materials

Triazinanone was prepared as previously described [17]. All chemicals were purchased from Aldrich and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Varian Mercury 400. UV–Vis absorption studies were carried out using a Shimadzu UV–Vis spectrophotometer with 50 and 10 mm precision cells made of Quartz Suprasil 300.

2.2. Synthesis

Ligand **1** was prepared as previously described [12]. A suspension of LiH (220 mg, 27.8 mmol) and 5-*tert*-butyltetrahydro-1,3,5-triazin-2(1*H*)-one (720 mg, 4.64 mmol) in THF (200 mL) was heated under reflux for 6 h and then allowed to cool to room temperature. A solution of 2,6-*bis*(bromomethyl)pyridine (1.22 g, 4.64 mmol) in THF (200 mL) was added drop wise over a 60 min period. The resulting mixture was heated under reflux for 80 h and then cooled to 0 °C. Ice-cold water (250 mL) was carefully added to destroy excess LiH, and the organic solvent removed *in vacuo*. The aqueous mixture was extracted with CH_2Cl_2 (3 × 100 mL). The aqueous layer was stirred with 1 N NaOH (100 mL) for 30 min. After 30 min the aqueous layer was re-extracted with CH_2Cl_2 (2 × 150 mL). The combined organic layer was washed with water (2 × 100 mL), dried with $MgSO_4$ and evaporated under reduced pressure. Silica gel chromatography ($CHCl_3$/MeOH 9:1) of the residue afforded ligand **1** (0.29 g, 24.0%).

Synthesis of $[Cd_3L_2(H_2O)_6(CH_3CN)_2]^{6+}$*:* Ligand **1** (15 mg, 0.0192 mM in 3 mL acetonitrile) was stirred with $Cd(ClO_4)_2{\cdot}6H_2O$ (8.06 mg) in a 1:1 ratio overnight. Slow evaporation of this acetonitrile solution of metal ligand complex afforded colorless crystals suitable for X-ray analysis $[Cd_3(C_{42}H_{60}\ N_{12}O_3)_2(CH_3\ CN)_2(H_2O)_6](ClO_4)_6{\cdot}(CH_3CN)_{1.4}(H_2O)_{8.5}$.

2.3. Crystal structure determination

X-ray intensity data from a colorless plate crystal were measured at 150(2) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) [18]. Raw area detector data frame processing was performed with the SAINT+ and SADABS programs [18]. Final unit cell parameters were determined by least-squares refinement of 3353 reflections from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL [19]. The compound crystallizes in the triclinic system. The space group $P\bar{1}$ was confirmed by the successful solution and refinement of the structure. The asymmetric unit consists of half of one $[Cd_3(C_{42}H_{60}N_{12}O_3)_2(CH_3CN)_2(H_2O)_6]^{6+}$ complex located on a crystallographic inversion center, three independent perchlorate anions and several independent included solvent molecules (see below). All non-hydrogen atoms were refined with anisotropic displacement parameters except where noted below. Hydrogen