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Abstract

The reaction of pyterpy with an excess of cadmium(II) nitrate yields the novel mononuclear complex [Cd(pyterpy)(H$_2$O)(NO$_3$)$_2$]. The crystal structure shows to the Cd(II) centre in a seven-coordinate environment and the molecular units behaving as supramolecular nodes. These neutral nodes are connected through aromatic π-stacking interactions concerted with O–H···N(4-pyridyl) and O–H···O(nitrate) hydrogen bonds to give couples of parallel linear strips assembled in a zipper-like motif. The infinite strips are oriented in the same direction and each one interact weakly with their neighbors by means of C–H···O hydrogen bonds to form the crystal. The supramolecular product is highly insoluble in the most common organic solvents and water, but soluble in dimethyl sulfoxide where the intermolecular interactions are broken.

1. Introduction

In recent years considerable attention has been drawn to the polymetallic coordination architectures maintained by covalent and non-covalent (supramolecular) interactions in the solid-state [1]. This report is concerned with the features of these interactions in the aggregation product formed by reacting cadmium(II) nitrate tetrahydrate with the potentially-bridging pyterpy ligand (Scheme 1). The known reaction products of Cd(NO$_3$)$_2$·4H$_2$O with polypyridyl-bridging ligands are polymeric covalently-linked substances. The N-donors ligands have been either exo-bidentate (divergent) [2–9] or chelating bis-bidentate [10]. The cadmium centre appears as hexa-, hepta- or octa-coordinate and the nitrate anions are usually bonded monodentally or bidentally. The products with divergent ligands exhibit a striking variety of crystalline architectures in their polymeric coordination networks, covering sinusoidal [2,4], zigzag [5], ladder [5,6], brick-wall [6a], helical and non-helical [9], and so forth. The complex [Cd(2,5-bis(2-pyridyl)pyrazine)(NO$_3$)$_2$] is the solitary example of a reaction product between cadmium nitrate with a bis-chelating ligand [10]. The cadmium cations are bridged by the bis(2-pyridyl) ligand leading to the formation of a one dimensional coordination polymer. On the other hand, the known metal complexes containing the pyterpy ligand are those with the cationic homoleptic species [M(pyterpy)$_2$]$^{2+}$ (M = Fe [11,12], Ru [13,14], Os [13]) and the heteroleptic species [M(terpy)(pyterpy)]$^{2+}$ (M = Ru, Os [15]). The homoleptic cations [M(pyterpy)$_2$]$^{2+}$

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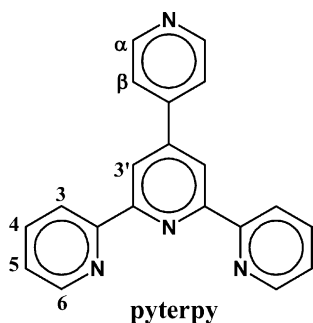
Scheme 1.

have been used as bridging ligands (M = Fe [16], Ru [16–18], Os [16,17]) to generate linear multicomponent systems (M = Ru, Os [17]) and molecular squares (M = Fe, Os [16], Ru [16,18]). The only know X-ray crystallographic study of a complex containing pyterpy is that of the iron(II) [Fe(pyterpy)$_2$](NO$_3$)$_2$ [12], which presents a rectilineal disposition of the two pendant 4-pyridyl groups and π-stacking interactions between the terminal terpy rings belonging to contiguous cations.

Considering that the versatility of the Cd(II) coordination sphere, the bifunctionality of the nitrate anions and the symmetric nature of the bridging-polypyridyl ligands have served consistently as precursors for the self-assembly of coordination polymers, we decided to explore in this field by introducing the asymmetric pyterpy ligand. This is a potentially-bridging species, but with disparity between its two coordinating fragments (mono- and tridentally). Indeed, we inform here that under our experimental conditions, excess of cadmium nitrate, the pyterpy acts unexpectedly as terminal ligand forming neutral monomeric units. The monomers aggregate noncovalently to form a rare case of parallel supramolecular motifs which form an infinite array in the crystal.

2. Experimental

The pyterpy ligand was prepared by a similar method to that described in the literature [11]. Cadmium nitrate tetrahydrate was purchased from Riedel-de Haën.

2.1. Synthesis of [Cd(pyterpy)(H$_2$O)(NO$_3$)$_2$]

Cd(NO$_3$)$_2$ · 4H$_2$O (0.154 g, 0.50 mmol) were added into a flask containing a hot (60 °C) solution of pyterpy (0.016 g, 0.05 mmol) in methanol (10 ml). After 1 h from the palid green solution a crystalline solid start to precipitate. The resultant mixture was cooled and upon standing overnight light yellow crystals were obtained. The solid was washed at room temperature with methanol (4 × 5 ml) and dried in vacuo. The separated crystals were suitable for X-rays structure determination. Yield: 0.025 g (85.9%). Anal. Calc. for C$_{20}$H$_{16}$Cd$_1$N$_6$O$_7$:

C, 42.53; H, 2.86; N, 14.88. Found: C, 42.54; H, 2.84; N, 14.87. ^{1}H NMR ((CD$_3$)$_2$SO): δ 9.09 (s, 2H, H$^{3'}$), 8.95 (d, 2H, H^3), 8.82 (d, 2H, H$^\alpha$), 8.66 (d, 2H, H^6), 8.30 (t, 2H, H^4), 8.18 (d, 2H, H$^\beta$), 7.79 (t, 2H, H^5) (see Scheme 1 for the atom numbering arrange).

2.2. X-ray diffraction

A highly redundant single crystal X-ray diffraction data sets was collected at room temperature up to a max 2θ of ≈58° on a Bruker AXS SMART APEX CCD diffractometer using monochromatic Mo Kα radiation, λ = 0.71069 Å, and a 0.3° separation between frames. Data integration was performed using SAINT and a semi-empirical absorption correction applied using SADABS, both programs in the diffractometer package. The structures was solved by direct methods and difference Fourier, and refined by least squares on F^2 with anisotropic displacement parameters for non-H atoms. Hydrogen atoms attached to carbon were positioned at idealized positions and allowed to ride. Those in the coordinated water molecule were found in the final difference Fourier map and refined with restrained O–H and H···H distances so as to ensure a reasonable geometry. All calculations to solve the structure, to refine the model proposed and to obtain derived results were carried out with the computer programs SHELXS97 and SHELXL97 [19] and SHELXTL/PC [20]. Full use of the CCDC package was also made for searching in the CSD Database [21]. Crystal data for [Cd(pyterpy)(H$_2$O)(NO$_3$)$_2$]: formula, C$_{20}$H$_{16}$Cd$_1$N$_6$O$_7$, Fw 564.78, orthorhombic, Pna2(1) (No. 33), a =16. 4240(13), b = 18.1247(14), c = 7.1092(6) Å, V = 2116.3(3) Å^3, Z = 4, D_c = 1.773 g cm^{-3}, $F(000)$ = 1128. A total of 14 923 (4701 independent, R_{int} = 0.0259). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC_210602. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

2.3. Instruments

^{1}H NMR spectra were performed on a Bruker model Advance DRX 300 spectrometer in (CD$_3$)$_2$SO and were referenced to TMS. The C, H, and N contents of the complexes were determined on a Fisons–Carlo Erba EA 1108 microanalizer (CEPEDEQ Universidad de Chile).

3. Results and discussion

The [Cd(pyterpy)(H$_2$O)(NO$_3$)$_2$] complex was isolated in methanol by treatment of pyterpy with an excess of

Cd(NO$_3$)$_2$·4H$_2$O. The crystals are insoluble in water, chlorinated organic solvents, alcohols, acetonitrile, but they are soluble in dimethyl sulfoxide.

3.1. Crystal structure of the complex [Cd(pyterpy)(H$_2$O)(NO$_3$)$_2$]

The structure is built up of monomers of [Cd(py-terpy)(H$_2$O)(NO$_3$)$_2$] (Fig. 1), where the cation is hepta-coordinated into the shape of a pentagonal bipyramid. In this polyhedron the base is defined by a tridentate pyterpy and a bidentate anion NO$_3^-$(B), while the two monodentate ligands (O(1W) and NO$_3^-$(A)) occupy the apical sites. This is a "natural" disposition of the ligands, given the restrictions imposed by their particular geometry, and the main departures from ideal values are found in the basal coordination angles, severely conditioned by chelation, viz., the observed value of the O(1B)–Cd(1)–O(2B) angle is 52.42(12)° in comparison with a theoretical value of 72° for a pentagon. Expected right angles subtended from the apical sites to the basal plane are in the range 83.09(15)–95.59(14)°. The monodentate and bidentate nitrate ligands present coordination distances quite usual for cadmium(II) complexes containing nitrogen donor ligands [2–10,22] and
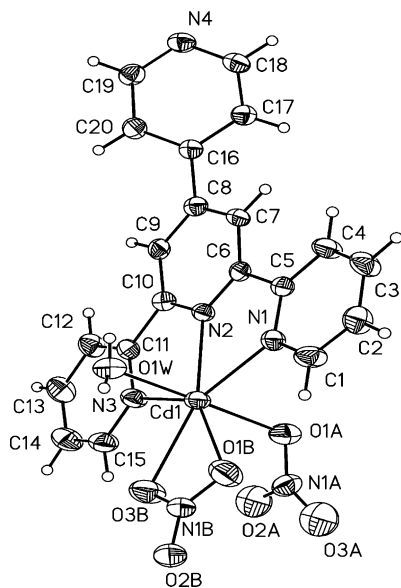
in the same line with the case where both forms are present simultaneously [22], i.e., in the bidentate nitrate ligand the Cd–O distances are unequal (2.470(4) Å; 2.382(4) Å) and longer than that of the monodentate one (2.353(4) Å). The bond length Cd–OH$_2$ (2.338(4) Å) is in the range observed in other Cd(II) complexes containing in their coordination sphere nitrate ions, polypyridyl moieties and water molecules [2,4,5]. The Cd–N bond distances are very similar being that to the central ring (2.317(3) Å) shorter than those to the terminal rings (2.364(3); 2.365(4) Å). This pattern have been attributed in Cd(II) systems to the constrained bite of the terpyridyl-based ligand [23]. The pyterpy molecule does not show any distinctive feature, save perhaps a noticeable rotation about of the interannular bond C(8)–C(16), which gives place to a dihedral angle of 39.5(1)° between the plane of the pendant 4-pyridyl group and that of the central pyridyl ring.

The packing of the monomers in the crystal shows that they are organized in pairs of parallel linear chains (or strips) running along the c-axis, each one internally linked by the O(1W)–H(1WA)···O(2A)#2 hydrogen bond which joins monomers translationally related by one full cell edge (Fig. 2). The individual chains are related by a 2(1) axis and this fact determines that the protruding pyterpy ligands in one of them exactly fit into the interleaving voids in the neighboring one, in a typical "zipper like" fashion. This fitting of the two chains is reinforced by the O(1W)–H(1WB)···N(4)#1 hydrogen bond (Fig. 2), and gives raise to a clear offset face-to-face π–π interaction with the pendant 4-pyridyl group in one column and the central ring of the terpy core of the neighboring one. The two planar moieties are placed in an almost parallel fashion at 4.5(2)° from one another and at a nearly graphitic distances of 3.38(1) Å (centroid–centroid 3.551(1) Å) to the neighbor on one side and 3.46(1) Å (centroid–centroid 3.747(1) Å) to the other, with a slippage of 0.82(2) Å and a parallel overlap of ≈50% of the total ring areas (Fig. 3). These aromatic–aromatic interactions probably, in this case, play an important role in the rotation (39.5(1)°) of the 4-pyridyl substituent as aforementioned. However, rotations of similar magnitude (40.64° and 39.73°) have been observed in the only structurally characterized pyterpy-based complex [Fe(pyterpy)$_2$](NO$_3$)$_2$ [12], but in this species the π–π interactions involving the non-coordinated pyridine are absent. Finally, the resulting strips running along the c-axis are weakly connected with their neighbors through much weaker hydrogen bond interactions of the C–H···O type. In these contacts the O(3A) and O(3B) nitrate oxygens (those not involved either in direct coordination or in the strong hydrogen bonds) act as acceptors.

The above results reveal a supramolecular motif for the [Cd(pyterpy)(H$_2$O)(NO$_3$)$_2$] complex without the mediation of the pyterpy as a bridging ligand. This fact can most likely be ascribed to an enhancement of the capacity of the
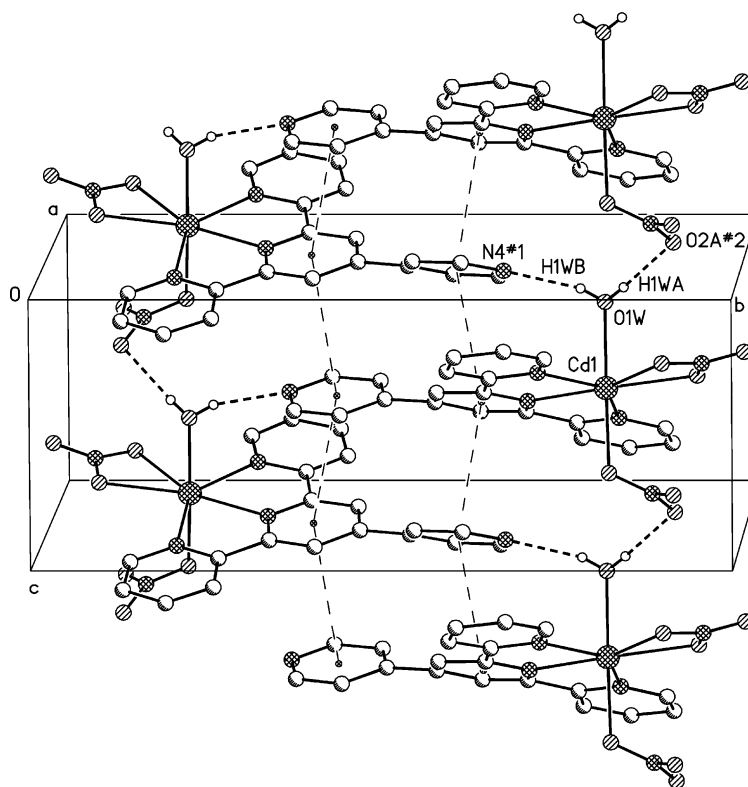

Fig. 1. Molecular diagram for [Cd(pyterpy)(H$_2$O)(NO$_3$)$_2$] showing the atom-labeling scheme (50% thermal ellipsoids). Selected bonds lengths (Å) and angles (°): Cd(1)–N(2) 2.317(3), Cd(1)–O(1W) 2.338(4), Cd(1)–O(1A) 2.353(4), Cd(1)–N(1) 2.364(3), Cd(1)–N(3) 2.365(4), Cd(1)–O(2B) 2.382(4), Cd(1)–O(1B) 2.470(4), N(2)–Cd(1)–O(1W) 90.60(13), N(2)–Cd(1)–O(1A) 92.12(13), O(1W)–Cd(1)–O(1A) 176.25(16), N(2)–Cd(1)–N(1) 69.76(12), O(1W)–Cd(1)–N(1) 90.01(13), O(1A)–Cd(1)–N(1) 88.53(14), N(2)–Cd(1)–N(3) 69.73(12), O(1W)–Cd(1)–N(3) 93.89(14), O(1A)–Cd(1)–N(3) 89.46(16), O(1W)–Cd(1)–O(2B) 83.09(15), O(1A)–Cd(1)–O(2B) 95.59(14), N(3)–Cd(1)–O(2B) 84.51(12), O(1W)–Cd(1)–O(1B) 88.00(16), O(1A)–Cd(1)–O(1B) 88.42(16), N(1)–Cd(1)–O(1B) 84.17(13), O(2B)–Cd(1)–O(1B) 52.42(12).

Fig. 2. Packing diagram for [Cd(pyterpy)(H$_2$O)(NO$_3$)$_2$] showing the hydrogen-bonding and π–π interactions. Non-interacting hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, z-1/2$, #2 $x, y, z-1$. Hydrogen bonds: O(1W)–H(1WB)···N(4)#1: 0.73(5) Å, 2.10(4) Å, 2.795(5) Å, 161(5)°; O(1W)–H(1WA)···O(2A)#2: 0.73(5) Å, 2.11(5) Å, 2.839(6) Å, 176(8)°.
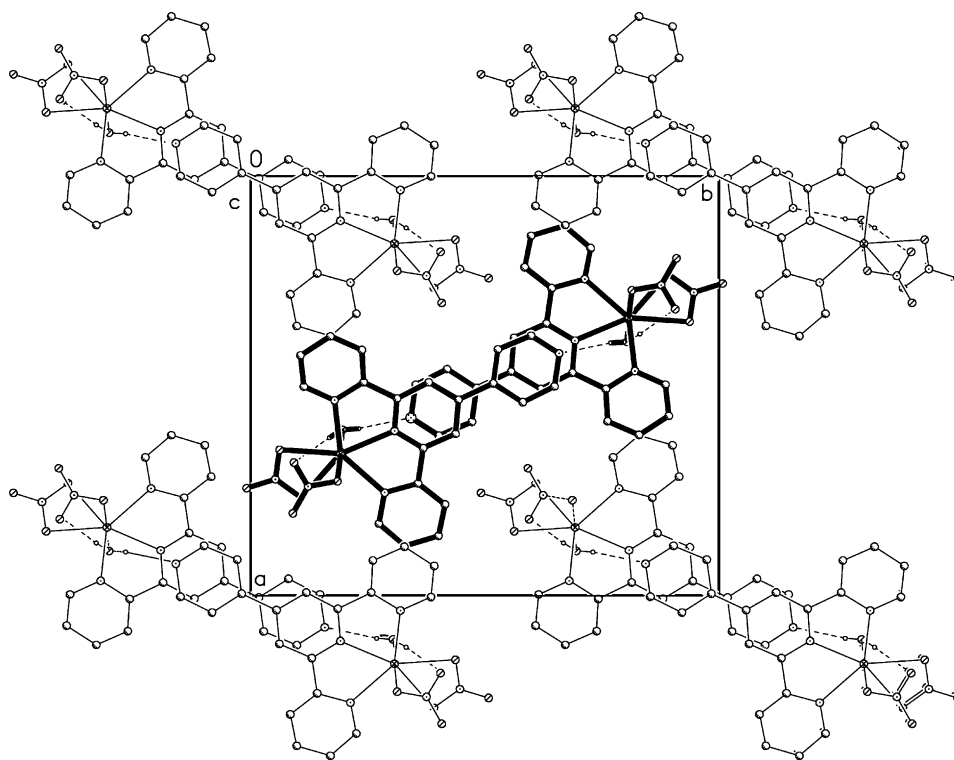
Fig. 3. Packing diagram for [Cd(pyterpy)(H$_2$O)(NO$_3$)$_2$] along the c-axis, showing the disposition of the supramolecular chains. Note the overlap of the pyridine groups. Non-interacting hydrogen atoms are omitted for clarity.

4-pyridyl tail for π–π interactions in the assembled structure. Certainly, it is expected an strengthening of the π-stacking if in the interacting entities the electron-withdrawing nitrogen atoms are present; they reduce the π-electron density in the rings and consequently the π-electron repulsion [24]. In the same sense must be considered the contribution of the hydrogen bonding between a protic hydrogen atom of the pivotal water molecule with the nitrogen atom of the tail portion, which introduce an extra electron withdrawing effect on the pertinent ring. Hence, these effects predispose to the tail part for a competition between its coordinating N-donor potentiality versus its non-covalent interactions, and in this particular case the latest appear as predominant.

3.2. ^1H NMR spectra of [Cd(pyterpy)(H$_2$O)(NO$_3$)$_2$]

The ^{1}H NMR spectra of (CD$_3$)$_2$SO solutions of the complex [Cd(pyterpy)(H$_2$O)(NO$_3$)$_2$] was assigned with the aid of COSY spectra in the aromatic region. The proton resonances indicate that the polypyridyl ligand is symmetrical on the NMR time scale. Furthermore, the expected seven resonances [11] are not sensitive to the concentration changes, indicating that the solid-state aggregation is not effective in solution. Indeed, it could be expected this result due to the presence of a competitive solvent such as dimethyl sulfoxide with respect to the weak coordinating capacity of the water molecule and of the nitrate ion.

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