

# The Crystal Structures of Two Novel Cadmium-Picolinic Acid Complexes in Relation to the Solution Species

Caren Billing\*, Demetrius C. Levendis and Vanessa L. Vieira

*Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, P.O. WITS, 2050, South Africa.*

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## ABSTRACT

The crystal structures of two novel cadmium-picolinic acid complexes grown in aqueous solutions at selected pH values are reported. The structures are compared to expected solution species under the same conditions. The crystal structure of complex 1 exhibits a seven coordinate structure which contains a protonated picolinic acid ligand that bonds bidentately to the cadmium ion via both carboxylate oxygens. Two nitrates coordinate to the metal centre within the same plane, one monodentately and the other bidentately, and two water molecules are found in the axial positions. The structure of complex 2 shows cadmium bonded to three of N,O-bidentate picolinic acid ligands to produce a distorted octahedron.

## KEYWORDS

Cadmium, picolinic acid, solution species, crystal structures, controlled pH.

## 1. Introduction

Understanding the relationship between species in solution and in the solid state is important in many areas of research; for example in environmental speciation and drug design.<sup>1</sup> Solution studies of metal–ligand equilibria provide information about different complexes that exist and predominate at specific pH values; while crystal structures can be used to study the precise geometry of the complexes formed. Our interest lies in the relationship between species that are found in solution and those crystallized at specific pH values.

The solution species and their stability constants were determined for the cadmium–picolinic acid system using polarography (results to be reported separately).<sup>2</sup> Species distribution diagrams were calculated using these data to indicate the percentage distribution of the cadmium–picolinic acid species as a function of pH. This information was then used to try and target particular species to crystallize by controlling the pH and/or the metal-to-ligand concentration ratios in the liquors for crystal growth.

Picolinic acid can occur as a cation in its fully protonated form, as a picolinate anion in its fully deprotonated form or as a neutral ligand or zwitterion in its singly protonated form (where the zwitterion has been shown to predominate in aqueous solutions).<sup>3</sup> This is represented in Scheme 1 together with the protonation constants.

In literature, various structures have been found where the picolinate anion acts as a bidentate chelating ligand or even as a tridentate chelating bridging ligand, coordinating *via* the ring nitrogen as well as the two carboxylate oxygen atoms.<sup>4</sup> Scheme 2 indicates the potential coordination modes of cadmium to the picolinate anion. Coordination modes (b) to (e) have been found for cadmium and picolinic acid (or substituted picolinic acid) complexes (with various counterions and occasionally in the polymeric form), but to date coordination mode (a) has not been reported.<sup>5</sup>

## 2. Experimental

**Complex 1:** Cd<sup>2+</sup> nitrate tetrahydrate (Fluka, GE99 %) and picolinic acid (Aldrich, 99 %) were dissolved in deionised water to produce 0.5 M of each in the solution (i.e. the Cd<sup>2+</sup>-to-picolinic acid concentration ratio was 1:1) and the solution was further acidified using HNO<sub>3</sub>. Evaporation at room temperature led to the formation of very hard, colourless, block-shaped crystals. The pH of the solution was approximately 0.4 at the time of crystal formation.

**Complex 2:** Cd<sup>2+</sup> and picolinic acid were dissolved in deionised water in a 1:2 and 1:3 Cd<sup>2+</sup>-to-picolinic acid concentration ratio where the concentration of Cd<sup>2+</sup> was 0.125 M in both cases. Evaporation at room temperature led to the formation of colourless, needle-shaped crystals at a pH of 1.0 and 1.3, respectively.

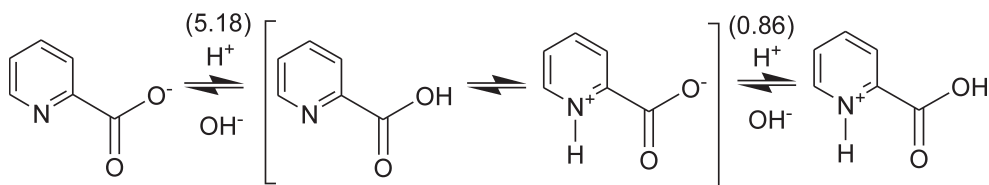
X-ray crystallographic data were collected on a Bruker SMART 1K CCD area detector diffractometer at –100 °C. The collection method and data processing procedures are presented in the supplementary material, together with a summary of the crystallographic data for both structures (Table S1).

## 3. Crystal Structures

The structures of the crystallized complexes 1 and 2, with the atomic numbering schemes, are given in Fig. 1 and Fig. 2, respectively. Selected distances and angles around the metal centre are listed in Table S2.

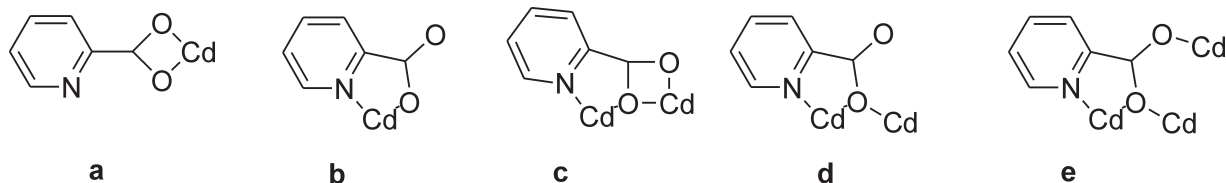
Complex 1, diaquadinitrato-(pyridine-2-carboxylato-O,O)-cadmium(II), Cd(NO<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>NHCO<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>, crystallized in the P-1 space group (Z = 2) having one molecule within the asymmetric unit. Picolinic acid bonds bidentately to a single Cd<sup>2+</sup> ion through the carboxylate group, a coordination not observed in other Cd<sup>2+</sup>-picolinate complexes. The metal centre is also coordinated by two water molecules and two nitrate anions, one of which is bound bidentately. The Cd<sup>2+</sup> ion is thus seven coordinate where both nitrate groups and water molecules are arranged *trans* from each other. However, the intraligand O3···O4 distance of the bidentate nitrate is smaller than 2.2 Å

\* To whom correspondence should be addressed. E-mail: [caren.billing@wits.ac.za](mailto:caren.billing@wits.ac.za)



Scheme 1

Protonation equilibria of picolinic acid (L) with stepwise protonation constants given in brackets (quoted as log K values).



Scheme 2

Coordination modes of  $\text{Cd}^{2+}$  to picolinate.

(2.162(2) Å), and therefore the average of the two chemically equivalent atoms can be considered to lie at the vertex of a common coordination polyhedron.<sup>6,7</sup> As a consequence, the coordination number is reduced from seven to six and the resulting geometry can be described as a distorted octahedron. The water molecules are axial ligands and the remaining groups all lie within the equatorial plane.

Crystals of complex **2**, tri(pyridine-2-carboxylato-*N,O*)-cadmium(II) dinitrate,  $[\text{Cd}(\text{C}_5\text{H}_4\text{NCO}_2\text{H})_3] 2\text{NO}_3$ , belong to the trigonal crystal system and crystallize in the *P*-3 space group.  $\text{Cd}^{2+}$  is coordinated bidentately through a carboxylate oxygen atom and the pyridine nitrogen atom of three picolinate ligands. The geometry is distorted octahedral with an average bite angle (O–Cd–N) of 72.14(2)°. Since picolinic acid is an unsymmetrical, bidentate ligand, it can have two isomeric forms, namely facial and meridional.<sup>8</sup> In this structure the facial isomer is present as the three pyridine nitrogens are adjacent and occupy the cor-

ners of one triangular face of the octahedron. There are two  $\text{Cd}^{2+}$ -picolinate complexes per unit cell centred on a 3-fold axis, with a disordered carboxylate hydrogen of half occupancy near the centre of inversion. There is thus a hydrogen bond between the two molecules with a O2–H3...O2 distance of 1.644(2) Å. The packing diagram (Fig. 3), viewed down the *c*-axis, shows the hydrogen bonded pairs of  $\text{Cd}^{2+}$ -picolinate complexes and the channels containing the disordered nitrate ions.

In most of the structures found in the Cambridge Structural Database (CSD) cadmium ions are bound to picolinate-related ligands *via* both oxygen atoms and the nitrogen of the pyridine ring, as indicated by structure (c) in Scheme 2 (e.g. YILBIF and QUFKUY (see supplementary material for the CSD search)).<sup>5</sup> The coordination modes shown by structures (b), (d) and (e) in Scheme 2 are less common for the picolinate ligand and can be seen in only NELNIB, CDPICO and REXHUX, respectively. Complex **2** is thus only the second example where cadmium

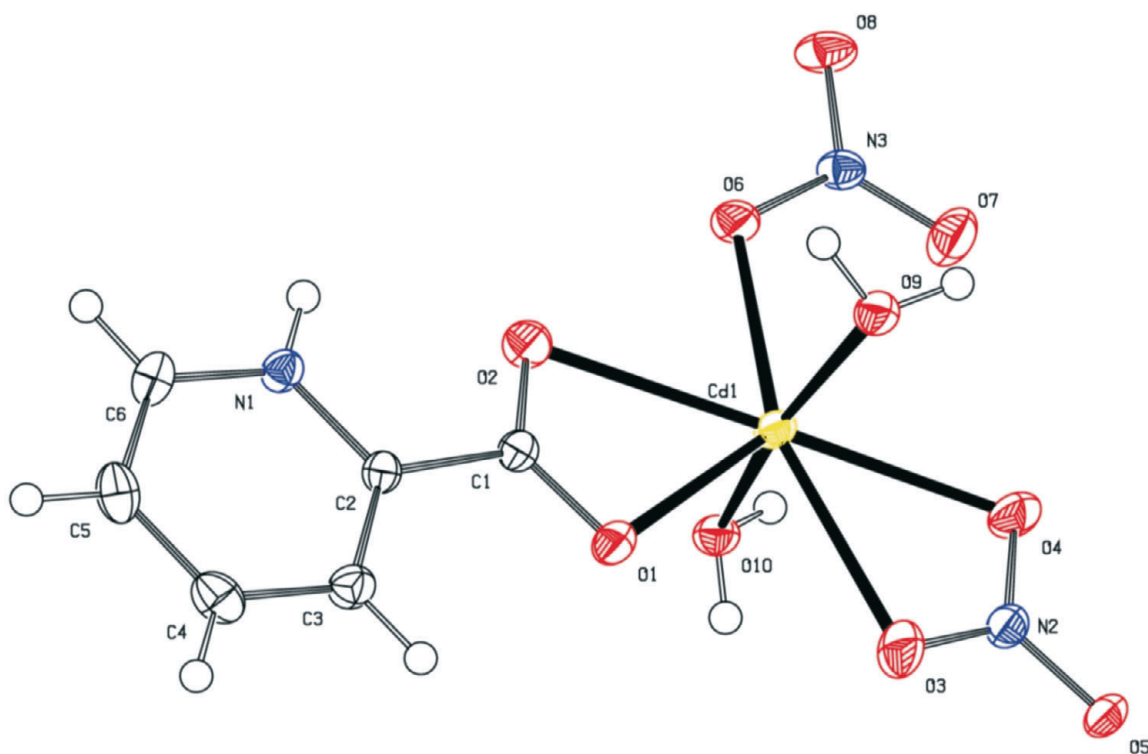
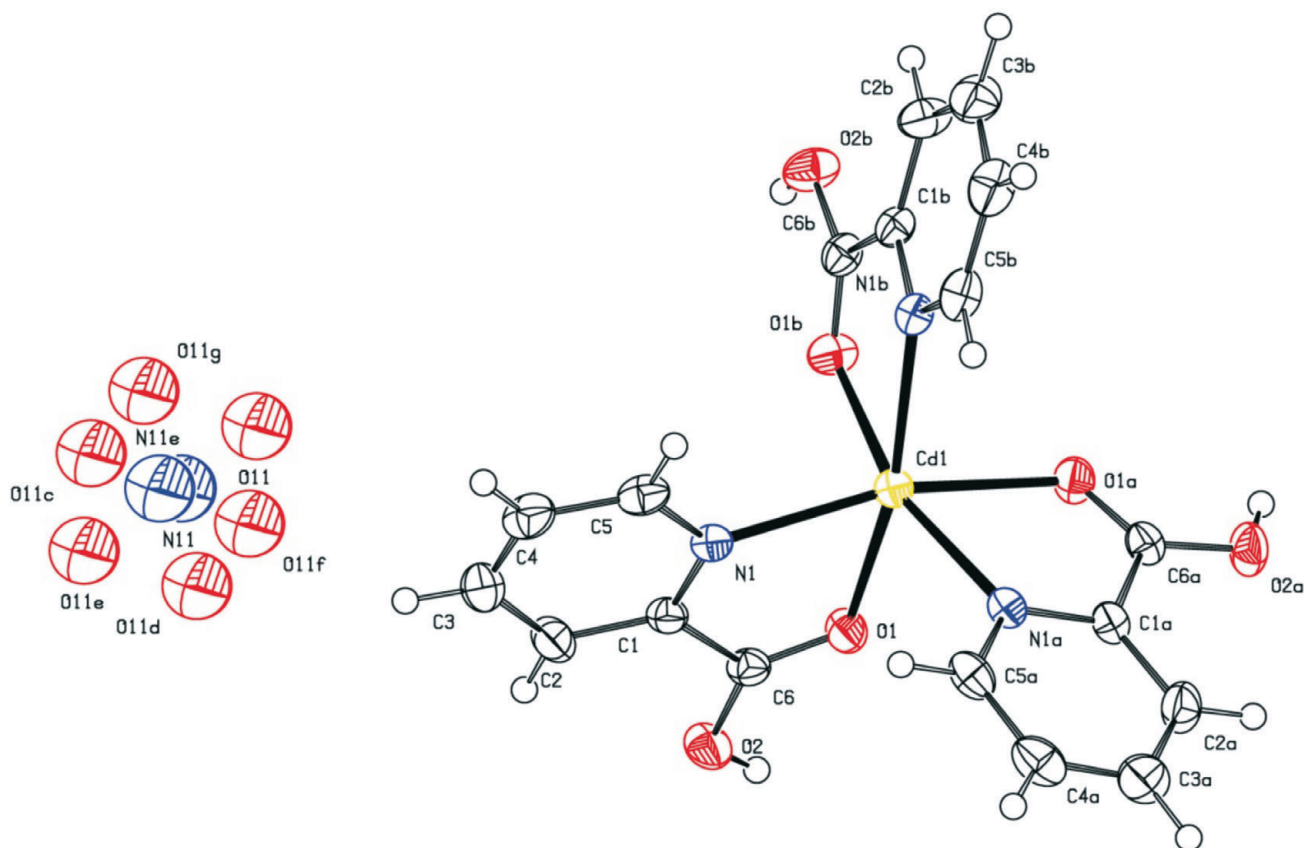


Figure 1 The molecular structure of complex **1**. Displacement ellipsoids are drawn at the 50 % probability level.



**Figure 2** The molecular structure of complex 2. Displacement ellipsoids are drawn at the 50 % probability level.

bonds bidentately as described by structure (b), Scheme 2. In complex 1, the nitrogen is protonated and hence not involved in bonding to the metal ion. This is the first time the coordination mode (a) in Scheme 2 has been witnessed for a cadmium-picolinate complex.

#### 4. Relating the Crystal Structures to Solution Chemistry

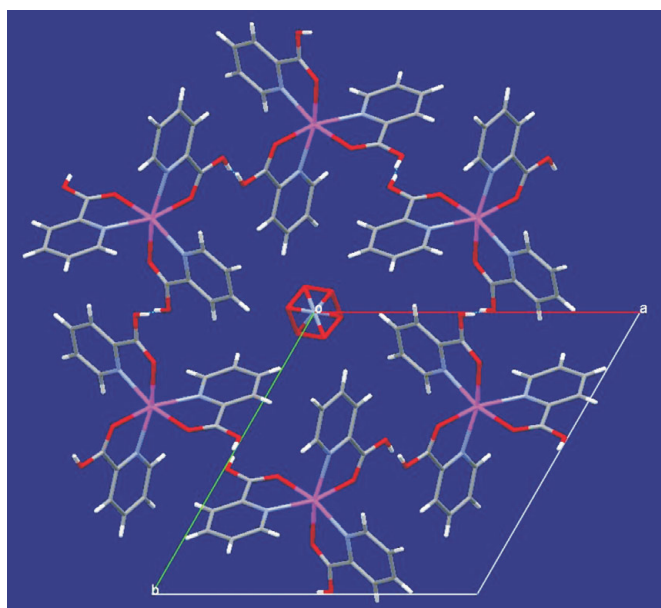
Solution studies of the cadmium-picolinic acid system under very acidic conditions pointed to the presence of a CdLH species

(i.e. where  $\text{Cd}^{2+}$  is bound to a protonated picolinate ligand), but it was difficult to confirm this.<sup>2</sup> Complex 1, having the nitrogen atom protonated, supports the presence of this solution species. The species distribution diagram (Fig. S1) indicates that CdLH is the dominant species in solution at pH 0.4 to 0.5, where complex 1 was produced.

Complex 2 was formed at two slightly different metal-ligand concentration ratios and pHs. Three ligands were bound to a single  $\text{Cd}^{2+}$  centre, but in this case the carboxylate group was protonated on each ligand, giving the species  $\text{Cd}(\text{LH})_3$ . This has never been reported in solution studies before, probably because it is not a major species under the conditions studied. When revisiting the data used to calculate the formation constants, it was possible to include this  $\text{Cd}(\text{LH})_3$  species in the model, but the standard deviation for its formation constant was large ( $\log \beta = 20 \pm 3$ ) and the overall fit did not change. This is typical for minor species. Species distribution diagrams were plotted for this system including  $\log \beta$  values ranging from 17 to 23 for  $\text{Cd}(\text{LH})_3$  using the solution conditions under which the crystals were grown. The percentage distribution of this species ranged between 6–97%. Of interest here, however, was that this species was found to exist below pH 4 in solution which correlates to the pH values at which the crystals were obtained. This research clearly indicates how solution studies and crystal structure studies complement each other.

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**Figure 3** Packing diagram as seen down the *c*-axis showing the disordered nitrate ions down the channels of the hydrogen bonded cadmium complexes (created in *Mercury*).

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