

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

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Received 23 March 2011, revised 28 March 2011, accepted 8 April 2011.

Submitted by invitation to celebrate 2011 the 'International Year of Chemistry'

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.¹ 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).² 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).³ 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.⁴ 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.⁵

2. Experimental

Complex 1: Cd²⁺ 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 Cd²⁺-to-picolinic acid concentration ratio was 1:1) and the solution was further acidified using HNO₃. 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: Cd²⁺ and picolinic acid were dissolved in deionised water in a 1:2 and 1:3 Cd²⁺-to-picolinic acid concentration ratio where the concentration of Cd²⁺ 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.

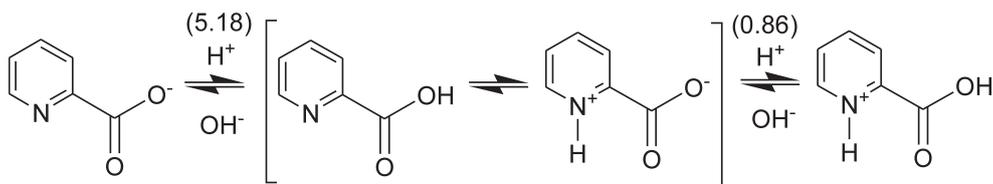
X-ray crystallographic data were collected on a Bruker SMART 1K CCD area detector diffractometer at –100 °C. The collection method and data processing procedures are presented in the supplementary material, together with a summary of the crystallographic data for both structures (Table S1).

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.

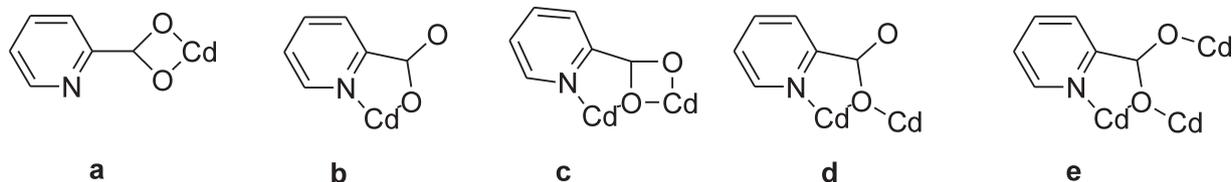
Complex 1, diaquadinitrato-(pyridine-2-carboxylato-O,O)-cadmium(II), Cd(NO₃)₂(C₅H₄NHCO₂)(H₂O)₂, crystallized in the P-1 space group (Z = 2) having one molecule within the asymmetric unit. Picolinic acid bonds bidentately to a single Cd²⁺ ion through the carboxylate group, a coordination not observed in other Cd²⁺-picolinate complexes. The metal centre is also coordinated by two water molecules and two nitrate anions, one of which is bound bidentately. The Cd²⁺ 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

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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 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.^{6,7} 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. 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.⁸ 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 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 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)).⁵ 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

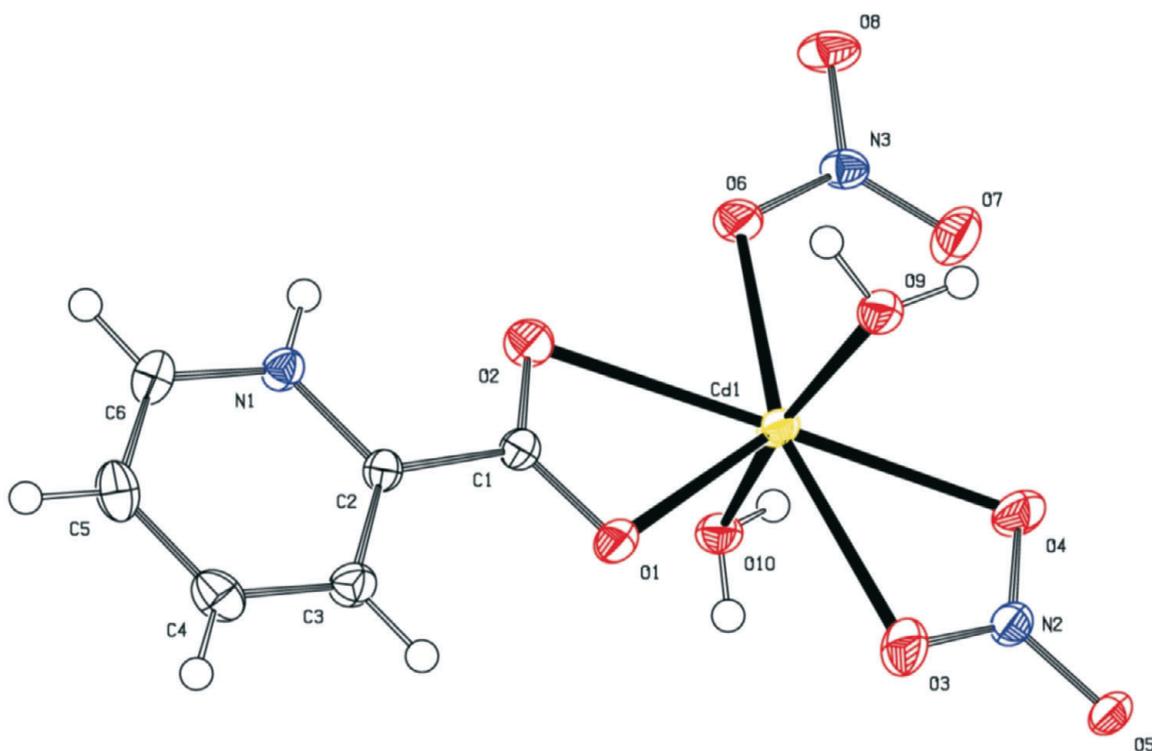


Figure 1 The molecular structure of complex **1**. Displacement ellipsoids are drawn at the 50 % probability level.

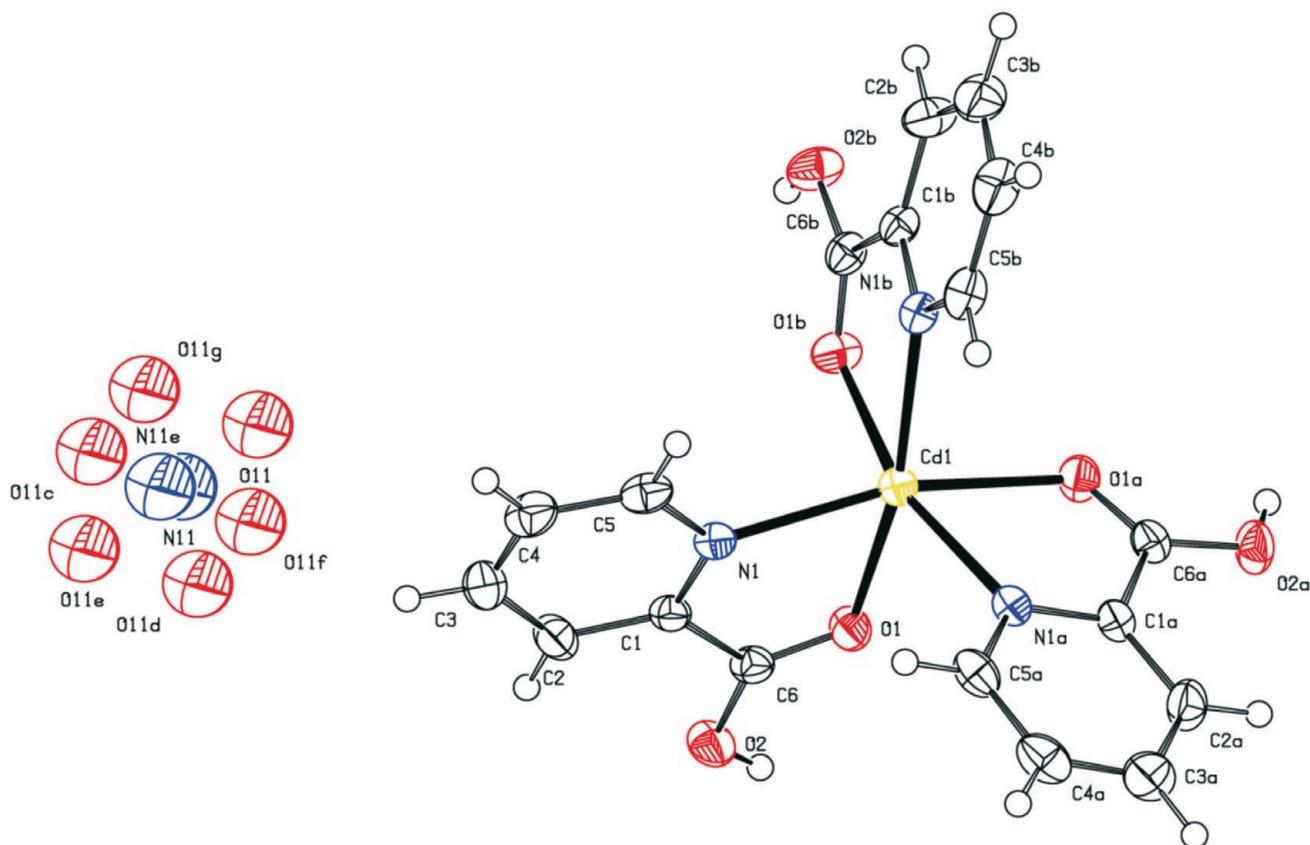


Figure 2 The molecular structure of complex 2. Displacement ellipsoids are drawn at the 50 % probability level.

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 Cd^{2+} is bound to a protonated picolinate ligand), but it was difficult to confirm this.² 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 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.

Acknowledgements

The financial assistance of the National Research Foundation (NRF) towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at are those of the author and are not attributed to the NRF. The authors also thank Dr M.A. Fernandes for assistance in data collection and advice.

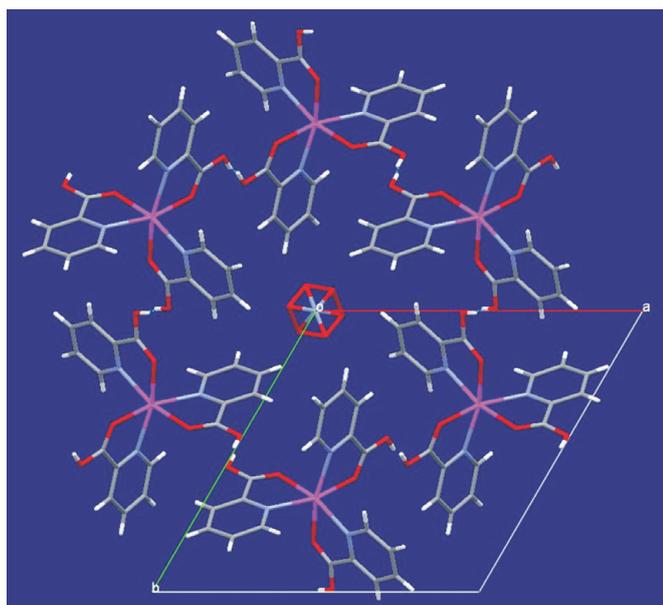


Figure 3 Packing diagram as seen down the *c*-axis showing the disordered nitrate ions down the channels of the hydrogen bonded cadmium complexes (created in *Mercury*).

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SUPPLEMENTARY INFORMATION

**THE CRYSTAL STRUCTURES OF TWO NOVEL CADMIUM-PICOLINIC
ACID COMPLEXES IN RELATION TO THE SOLUTION SPECIES**

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X-ray crystallography

Intensity data were collected on a Bruker SMART 1K CCD area detector diffractometer with graphite monochromated Mo K_{α} radiation (50kV, 30mA, $\lambda = 71073 \text{ \AA}$). The collection method involved ω -scans of width 0.5° and 512×512 bit data frames. Data reduction was carried out using the program *SAINT+*, version 6.02⁹ and for complex **1** face empirical absorption corrections were made using the program *SADABS*. Both crystals were studied at $-100 \text{ }^{\circ}\text{C}$ (173 K) by the aid of a *CRYOSTREAM* which is designed for operation over a wide temperature range. The crystal structures were solved by direct methods using *SHELX-97*.¹⁰ Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using *SHELX-97*.¹⁰ All hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms, except those of O9 and O10 in complex **1** which were placed according to electron density and refined freely. Absorption corrections were made for complex **1**, but it was unnecessary to do so for complex **2** as no changes in the refinement were observed when applied. Diagrams and publication material were generated using *WinGX*,¹¹ *SHELX-97*,¹⁰ *PLATON*,¹² *ORTEP-3*,¹³ and *Mercury*.¹⁴

See article for references.

Table S1 Crystal data and structure refinement for complexes **1** and **2**.

Complex	1	2
CCDC entry no.		
Empirical formula	C ₆ H ₉ Cd N ₃ O ₁₀	C ₁₈ H _{13.5} Cd N ₄ O ₉
Formula weight / g.mol ⁻¹	395.56	1022.45
Temperature	173(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Trigonal
Space group	P -1	P-3
a	8.4374(8) Å	14.0290(5) Å
b	9.2353(7) Å	14.0290(5) Å
c	9.5588(8) Å	5.6564(2) Å
α	111.409(5)°	90°
β	116.156(5)°	90°
γ	94.582(6)°	120°
Volume	596.03(9) Å ³	964.10(6) Å ³
Z	2	2
Density (calculated)	2.204 Mg/m ³	1.761 Mg/m ³
Absorption coefficient	1.892 mm ⁻¹	1.184 mm ⁻¹
F(000)	388	508
Crystal size	0.46 x 0.36 x 0.28 mm ³	0.499 x 0.152 x 0.121 mm ³
Theta range for data collection	2.47 to 27.99°	1.68 to 27.97°
Index ranges	-11 ≤ h ≤ 10, -12 ≤ k ≤ 12, -12 ≤ l ≤ 12	-9 ≤ h ≤ 18, -18 ≤ k ≤ 15, -7 ≤ l ≤ 7
Reflections collected	11730	7838
Independent reflections	2863 [R(int) = 0.0223]	1556 [R(int) = 0.0453]
Completeness to theta	99.80%	99.90%
Absorption correction	Semi-empirical from equivalents	None
Max. and min. transmission	0.6194 and 0.3273	
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	2863 / 0 / 197	1556 / 1 / 91
Goodness-of-fit on F ²	1.184	1.104
Final R indices [I>2σ(I)]	R ₁ = 0.0166, wR ₂ = 0.0440	R ₁ = 0.0293, wR ₂ = 0.0762
R indices (all data)	R ₁ = 0.0171, wR ₂ = 0.0442	R ₁ = 0.0333, wR ₂ = 0.0782
Largest diff. peak and hole	0.294 and -0.857 e.Å ⁻³	0.772 and -0.984 e.Å ⁻³

Table S2 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**.

<i>Complex 1</i>			
O(1)-Cd(1)	2.3540(12)	O(10)-Cd(1)-O(4)	82.15(5)
O(2)-Cd(1)	2.5509(13)	O(6)-Cd(1)-O(4)	107.82(4)
O(3)-Cd(1)	2.5217(14)	O(1)-Cd(1)-O(4)	126.12(4)
O(4)-Cd(1)	2.4802(14)	O(9)-Cd(1)-O(3)	88.74(5)
O(6)-Cd(1)	2.3157(12)	O(10)-Cd(1)-O(3)	90.51(5)
O(9)-Cd(1)	2.2438(13)	O(6)-Cd(1)-O(3)	159.02(4)
		O(1)-Cd(1)-O(3)	74.90(4)
O(9)-Cd(1)-O(10)	167.51(5)	O(4)-Cd(1)-O(3)	51.22(4)
O(9)-Cd(1)-O(6)	91.38(5)	O(9)-Cd(1)-O(2)	93.34(5)
O(10)-Cd(1)-O(6)	84.88(5)	O(10)-Cd(1)-O(2)	96.85(4)
O(9)-Cd(1)-O(1)	92.27(5)	O(6)-Cd(1)-O(2)	72.32(4)
O(10)-Cd(1)-O(1)	99.57(4)	O(1)-Cd(1)-O(2)	53.72(4)
O(6)-Cd(1)-O(1)	126.04(4)	O(4)-Cd(1)-O(2)	178.96(4)
O(9)-Cd(1)-O(4)	87.68(5)	O(3)-Cd(1)-O(2)	128.62(4)
<i>Complex 2</i>			
O(1)-Cd(1)	2.3209(16)	N(1)#1-Cd(1)-O(1)#1	72.15(6)
N(1)-Cd(1)	2.2949(19)	N(1)-Cd(1)-O(1)#1	162.19(7)
		N(1)#2-Cd(1)-O(1)#1	91.75(7)
N(1)#1-Cd(1)-N(1)	105.68(5)	O(1)-Cd(1)-O(1)#1	90.15(6)
N(1)#1-Cd(1)-N(1)#2	105.68(5)	N(1)#1-Cd(1)-O(1)#2	162.19(7)
N(1)-Cd(1)-N(1)#2	105.68(5)	N(1)-Cd(1)-O(1)#2	91.75(7)
N(1)#1-Cd(1)-O(1)	91.75(7)	N(1)#2-Cd(1)-O(1)#2	72.15(6)
N(1)-Cd(1)-O(1)	72.15(6)	O(1)-Cd(1)-O(1)#2	90.15(6)
N(1)#2-Cd(1)-O(1)	162.19(7)	O(1)#1-Cd(1)-O(1)#2	90.15(6)

The Cambridge Crystallographic Data Centre deposition numbers are CCDC 821168 & 821169 for Complex **1** and **2** respectively.

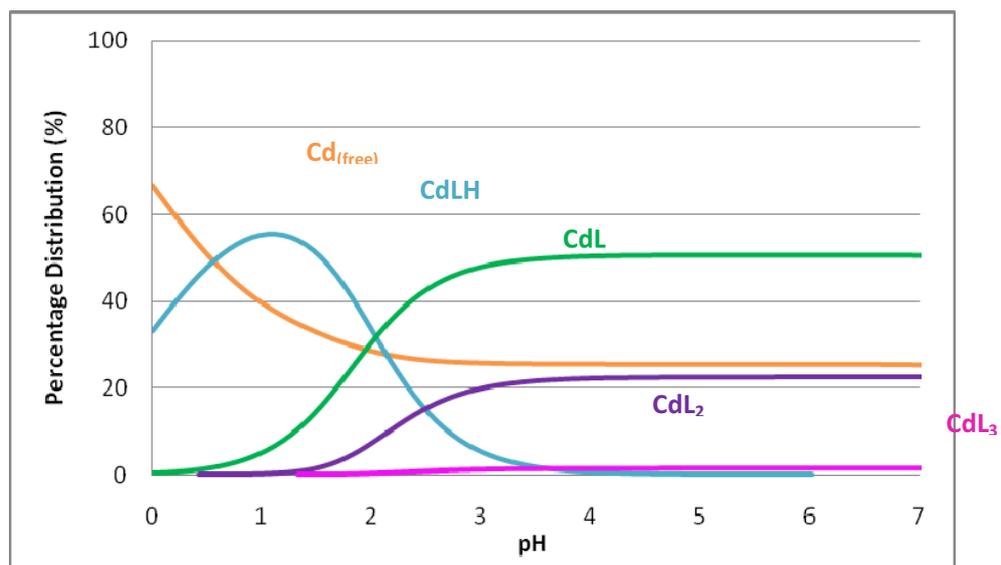


Figure S1 Species distribution diagram for the cadmium-picolinic acid system using formation constant values as follows: $\log \beta(\text{CdLH}) = 6.27 \pm 0.07$, $\log \beta(\text{CdL}) = 4.23 \pm 0.01$, $\log \beta(\text{CdL}_2) = 7.81 \pm 0.09$ and $\log \beta(\text{CdL}_3) = 10.53 \pm 0.08$ at 25 °C and 0.25 – 0.5 M H/NaNO₃ ionic strength.² $[\text{Cd}^{2+}] = [\text{L}] = 0.5 \text{ M}$.

Search Overview

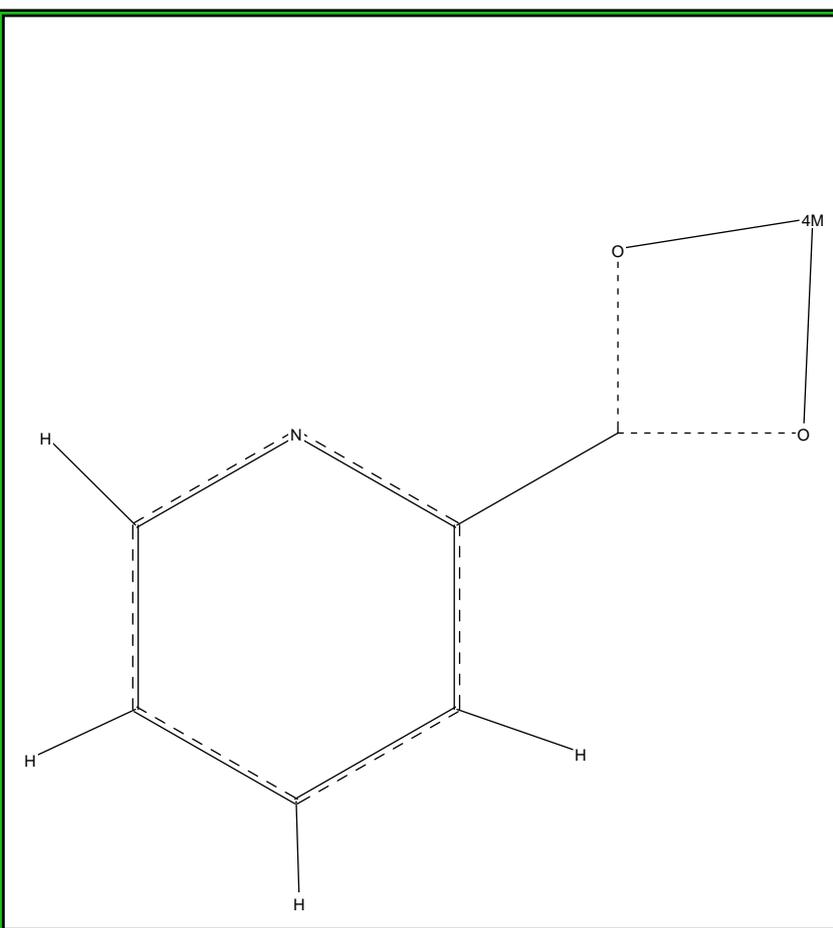
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Restriction Info: No refcode restrictions applied
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Single query used. Search found structures that:

match

Query 1

Query 1



Search: search2 (Tue Dec 7 15:35:25 2010): Hits 1-2

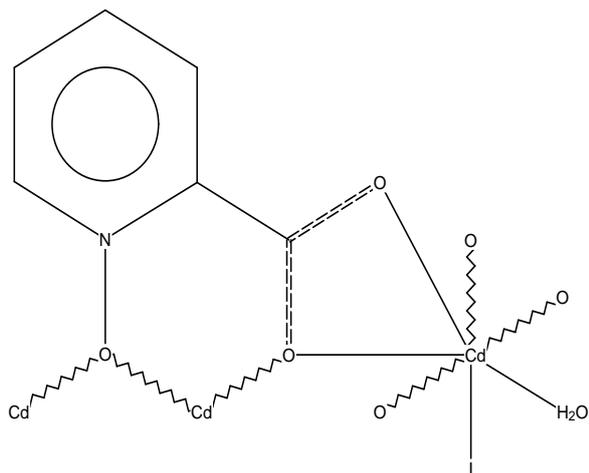
TEQTAK

Reference: E.Bermejo, A.Castineiras, R.Dominguez, J.Strahle, C.Maichle-Mossmer (1996) *Polyhedron* ,15,1923

Formula: (C₆H₆Cd₁I₁N₁O₄)_n

Compound Name: catena-(μ₂-Pyridine-1-oxide-2-carboxylato)-aqua-iodo-cadmium(ii)

Space Group: P21/c **Cell:** a 10.848(4) b 8.488(1) c 10.604(4)
Space Group No.: 14 **(Å,°)** α 90.00 β 90.77(2) γ 90.00
R-Factor (%): 4.60 **Temperature(K):** 295 **Density(g/cm³):** 2.690



YILBIF

Reference: C.Papatriantafyllopoulou, C.P.Raptopoulou, A.Terzis, J.F.Janssens, E.Manessi-Zoupa, S.P.Perlepes, J.C.Plakatouras (2007) *Polyhedron* ,26,4053

Formula: (C₁₂H₁₄Cd₂N₂O₁₁S₁)_n.n(H₂O)₁

Compound Name: catena-(μ₂-Picolinato-N,O,O)-μ₂-picolinato-N,O,O,O)-(μ₂-aqua)-(μ₂-sulfato-O,O')-diaqua-di-cadmium(ii) monohydrate

Space Group: P21/c **Cell:** a 11.200(5) b 13.231(6) c 13.650(6)
Space Group No.: 14 **(Å,°)** α 90.00 β 110.36(1) γ 90.00
R-Factor (%): 5.93 **Temperature(K):** 298 **Density(g/cm³):** 2.232

