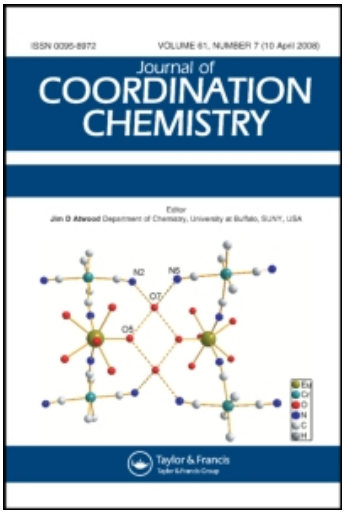


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# Synthesis and Crystal Structure of a Cadmium Complex with Isonicotinate

Liang Shen[a]; Jiageng Liu[a]; Yuanzhi Xu[a]
[a] Department of Chemistry, Hangzhou Teachers College, P.R. China

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# SYNTHESIS AND CRYSTAL STRUCTURE OF A CADMIUM COMPLEX WITH ISONICOTINATE

LIANG SHEN[a,b,*], JIAGENG LIU[b] and YUANZHI XU[b]

[a]*Department of Chemistry, Hangzhou Teachers College, 310012, P.R. China;*
[b]*Department of Chemistry, Zhejiang University, Hangzhou 310027, P.R. China*

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The cadmium(II) complex, $[Cd(iso)_2(H_2O)_4]$ (where iso is the anion of isonicotinic acid), has been synthesized and characterized by element analysis, thermal analysis and IR spectroscopy. An X-ray crystal structure reveals that the cadmium ion is *trans*-octahedral with two pyridyl nitrogens and two aqua oxygens in equational positions and two aqua oxygens in axial positions. The complex forms a three-dimensional network through intermolecular hydrogen bonds.

*Keywords*: Isonicotinate; Cadmium(II); Crystal structure

## INTRODUCTION

Isonicotinic and nicotinic acids play important roles in the metabolism of all living cells and their metal complexes can also be used as drugs [1]. Much interest has been directed towards their metal complexes. Among these, two crystal structures of cadmium(II) complexes, $[Cd(\mu-nic)_2H_2O]$[2] and $[Cd(\mu-nic)(\mu-Br)(H_2O)]$[3] (where nic is the anion of nicotinic acid), have been deternined by X-ray methods, in which the nicotinate anion bridges adjacent metal atoms through the pyridine N atom and the carboxyl O atom to form polymeric chains. Herein we report the synthesis and crystal structure of a cadmium(II) complex with unidentate isonicotinate, $[Cd(iso)_2(H_2O)_4]$. It is interesting that a three-dimensional network of monomers is formed through intermolecular hydrogen bonds.

*Corresponding author.

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## EXPERIMENTAL

### Preparation

A hot, aqueous solution (10 $cm^3$) of $CdCl_2 \cdot 2(1/2)H_2O$ (228 mg, 1 mmol) was added dropwise to a hot, aqueous solution (10 $cm^3$) of isonicotinic acid (246 mg, 2 mmol). The acidity of the mixture was adjusted to pH = 6.5 with ammonia. After refluxing the mixture for 1 h, the resulting colourless precipitate was filtered off and dried under vacuum to give $[Cd(iso)_2(H_2O)_4]$ in 48% yield. Single crystals suitable for X-ray analysis were isolated by slow evaporation of the supernatant at room temperature. Nitrogen, carbon and hydrogen were analyzed with a Carlo Erba 1160 instrument. *Anal.* Calcd. for $C_{12}H_{16}CdN_2O_8$ (%): C, 33.61; N, 6.54; H, 3.73. Found: C, 33.84; N, 6.82; H, 3.47.



### Physical Measurements

Infrared spectra were recorded with a Nicolet 205 spectrophotometer ($4000-400\,cm^{-1}$) using a powdered sample spread on a KBr plate and a Nicolet FTIR 170sx spectrophotometer ($500-100\,cm^{-1}$) employing CsI pellets. Thermogravimetry and differental thermal analysis were recorded on a PCT-2 instrument in air with a heating rate of $10°C\,min^{-1}$.

### Crystal Structure Determination

A colourless crystal with dimensions $0.44 \times 0.40 \times 0.24$ mm was mounted on a glass fibre and used for the structure determination. Diffraction intensity data were collected on a Siemens P4 diffractometer using the $\omega/2\theta$ scan mode with a variable scan speed of $5.5°-50°\,min^{-1}$ (in $\omega$). Some 2390 reflections (2136 independent, 2123 observed reflections [$Fo > 4\sigma(Fo)$]) were collected in the range $2.28° < \theta < 29.99°$ with $R_{int} = 0.012$. Lp and empirical absorption corrections were applied.

The structure was solved by direct methods followed by Fourier syntheses. The structure was refined on $F^2$ by full-matrix least-squares methods. H atoms were located in a difference Fourier map. Anisotropic refinement including all the non-H atoms converged to agreement factors $R = 0.017$ and $R_w = 0.043$, where $w = 1/[\sigma^2(Fo^2) + (0.027P)^2]$. The highest peak in the final difference Fourier map was $0.334\,eÅ^{-3}$. Atomic scattering factors were taken from International Tables for X-ray Crystallography [4]. All calculations were performed using the SHELXTL software package [5].

## RESULTS AND DISCUSSION

### Crystal Structure

Crystal data: $C_{12}H_{16}CdN_2O_8$, $M = 428.67$, triclinic, space group $P\bar{1}$, $a = 6.4420(10)$, $b = 6.9590(10)$, $c = 9.4150(10)$Å, $\alpha = 94.830(10)$, $\beta = 104.740(10)$, $\gamma = 112.000(10)°$, $V = 370.80(9)$Å$^3$, $Z = 1$, $D_c = 1.920\,\mathrm{gcm}^{-3}$, $F(000) = 214$, $\mu(\mathrm{MoK}\alpha) = 1.518\,\mathrm{mm}^{-1}$.

Fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in Table I. Selected bond distances and angles are given in Table II. The Cd(II) atom has *trans*-octahedral coordination as shown in Figure 1. Angles formed by the ligated atoms around the cadmium atom range from 86.31(5) to 93.69(5)°. The cadmium atom is thus in a slightly distorted octahedral enviroment with two pyridyl nitrogens and two aqua oxygens in equational position and two aqua oxygens in axial positions. The Cd-N distance is 2.312(1)Å, close to similar bonds determined for two cadmium(II) nicotinate complexes [2, 3]. It can be



TABLE I Atomic coordinates and equivalent isotropic displacement parameters (Å)

| | *x/a* | *y/b* | *z/c* | *U(eq)* |
|---|---|---|---|---|
| Cd | −0.5000 | 0.5000 | −0.5000 | 0.027(1) |
| O(1) | 0.1094(2) | 0.8078(2) | 0.2974(1) | 0.041(1) |
| O(2) | 0.4272(2) | 0.9215(2) | 0.2211(1) | 0.038(1) |
| O(3) | −0.3298(2) | 0.2756(2) | −0.5473(1) | 0.033(1) |
| O(4) | −0.2719(2) | 0.7634(2) | −0.6028(2) | 0.043(1) |
| N | −0.2413(2) | 0.6395(2) | −0.2595(1) | 0.028(1) |
| C(1) | −0.3292(2) | 0.6431(2) | −0.1456(2) | 0.029(1) |
| C(2) | −0.1901(3) | 0.7087(2) | 0.0030(2) | 0.028(1) |
| C(3) | 0.0514(3) | 0.7746(2) | 0.0368(1) | 0.024(1) |
| C(4) | 0.1439(3) | 0.7767(2) | −0.0809(2) | 0.030(1) |
| C(4) | −0.0074(3) | 0.7070(3) | −0.2269(2) | 0.032(1) |
| C(6) | 0.2091(3) | 0.8406(2) | 0.1984(2) | 0.028(1) |

*U*(eq) is defined as one third of the trace of the orthogonalized $u_{ij}$ tensor.

TABLE II Selected bond distance (Å) and angles (°)

| | | | |
|---|---|---|---|
| Cd–O(3) | 2.2922(12) | Cd–O(3) #1 | 2.2922(12) |
| Cd–N | 2.3120(12) | Cd–N #1 | 2.3120(12) |
| Cd–O(4) | 2.3365(13) | Cd–O(4) #1 | 2.3365(13) |
| O(3) #1–Cd–O(3) | 180.0 | O(3) #1–Cd–N | 87.51(4) |
| O(3)–Cd–N | 92.49(4) | O(3) #1–Cd–N #1 | 92.49(4) |
| O(3)–Cd–N #1 | 87.51(4) | N–Cd–N #1 | 180.00(4) |
| O(3) #1–Cd–O(4) #1 | 93.59(5) | O(3)–Cd–O(4) #1 | 86.41(5) |
| N–Cd–O(4) #1 | 86.31(5) | N #1–Cd–O(4) #1 | 93.69(5) |
| O(3) #1–Cd–O(4) | 86.41(5) | O(3)–Cd–O(4) | 93.59(5) |
| N–Cd–O(4) | 93.69(5) | N #1–Cd–O(4) | 86.31(5) |
| O(4) #1–Cd–O(4) | 180.0 | | |

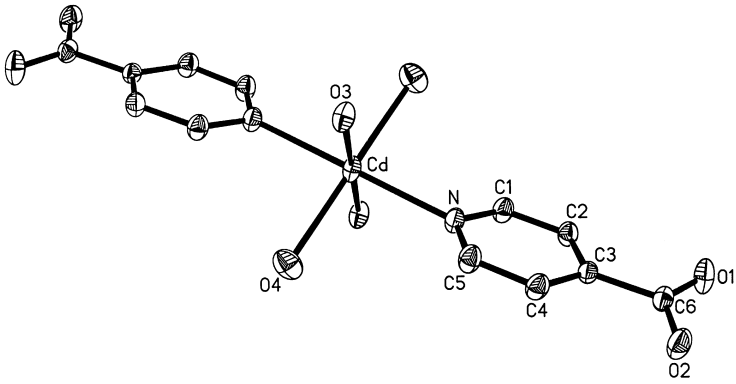


FIGURE 1 Crystal structure of the complex $[Cd(iso)_2(H_2O)_4]$ showing the atom numbering scheme.



seen that isonicotinate coordinates to Cd(II) atom as a unidentate through pyridyl N unlike the bridging mode of nicotinate found in $[Cd(\mu-nic)_2H_2O]^2$ and $[Cd(\mu-nic)(\mu-Br)(H_2O)]^3$. The O atom of carboxyls form strong hydrogen bonds with the coordinated water molecule. It is obvious that the coordinated water molecule hinders the carboxyl group from bridging another Cd(II) atom.

Within the crystal, molecules are bound together by bonds between the oxygen of the carboxyls and the water molecules attached to adjacent cadmium ions. Typical hydrogen bond distances and angles are listed in Table III. The complex forms a three-dimenisonal network of monomers linked through intermolecular hydrogen bonds.

## Infrared Spectrum

The infrared spectrum of free isonicotinic acid was recorded along with the title complex for comparision. In the complex there was a intense new band at $1604\,cm^{-1}$ and the quartet of peaks which occurs between 800 and $650\,cm^{-1}$ in free isonicotinic acid was altered by a large increase in the intensity of the two innermost bands. This indicates that the isonicotinic

TABLE III Typical hydrogen bond distances (Å) and angles (°) (D = donor, A = acceptor)

| *Donor-H* | *d(D-H)* | *d(H···A)* | *∠DHA* | *d(D···A)* | *A* |
|---|---|---|---|---|---|
| O(3)–H(3A) | 0.810 | 1.843 | 178 | 2.653 | O(1) |
| O(4)–H(4A) | 0.825 | 1.950 | 172 | 2.769 | O(1) |
| O(3)–H(3B) | 0.816 | 1.977 | 170 | 2.783 | O(2) |
| O(4)–H(4B) | 0.817 | 2.013 | 174 | 2.826 | O(2) |

acid is coordinated to the metal [6]. One new band at $305\,cm^{-1}$ was observed and assigned to a zinc-nitrogen stretch. This is in agreement with the value of $310\,cm^{-1}$ reported for a Cr(II) nicotinate complex [6].

## Thermal Analysis

The complex loses 15.5% weight from 121° C to 156° C, approximately corresponding to the loss of four water molecules (calcd. 16.8%). The higher temperature of water loss simply indicates that water is coordinated to cadmium(II), as confirmed by the crystal structure of the complex. At 395°C, the complex decomposes exothermically to 476° C, losing 58.1% weight, approximately corresponding to the loss of two isonicotinate ligands (calcd. 57.0%).



## *Supplementary Data*

Full lists of crystallographic data are available from the authors upon request.

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