

Synthesis, Structure and Green Fluorescence of a Isonicotinic Coordination Polymer Containing a Silver(I) Isonicotinate Array and a Two-coordination Cadmium(II)

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The selection of the metal centers and organic components plays an important role in the structural diversity. Metal centers are potential carriers of electrochemical, magnetic, catalytic, or optical properties that may be introduced into molecular materials.¹ d¹⁰ metals with rich photophysical and photochemical character have focused attentions to synthesize polynuclear complexes.² Three isomers of pyridine carboxylic acid, namely picolinic acid, nicotinic acid and isonicotinic acid, have been extensively investigated.³ Isonicotinic acid (HIso), namely 4-pyridinecarboxylate, a multi-functional chelating and/or bridging ligand, has proved to be very powerful for the construction of multi-dimensional metal-organic coordination networks.⁴ Furthermore, the isonicotinic acid complexes have raised interest in fluorescence probing with numerous potential applications for studies of microsecond diffusion and dynamics of membranes.⁵ Considering the versatile coordination abilities of HIso, we employ the ligand to coordinate with silver nitrate and cadmium acetate to fabricate a coordination complex with excellent fluorescence property. We report the synthesis, crystal structure and fluorescence property of a new silver(I) isonicotinate array {[Ag(Iso)]-[Cd(Iso)₂]_{1/2}]_n.

Experimental Section

Materials and physical measurements. All reagents were obtained from commercial resources and used without further purification. The IR spectrum was recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellets in the range 4000–400 cm⁻¹. Elemental analysis was carried out on a Vario EL III elemental analyzer. The measurements of the solid-state fluorescent excitation and emission spectra were performed on a FluoroMax-3 spectrophotometer at room temperature with excitation and emission slit at 5.0 nm, increment 1.0 nm and integration time 0.1 s.

Synthesis of {[Ag(Iso)]-[Cd(Iso)₂]_{1/2}]_n. A solution of Iso (50 mg, 0.4 mmol) in ethanol (10 mL) was added dropwise to 2 mL stirred aqueous solution of AgNO₃ (34 mg, 0.2 mmol). After being stirred 4 h, then 3 mL aqueous solution of Cd(OAc)₂·2H₂O (46 mg, 0.2 mmol) was added to the resulted suspension. The mixture at 393 K for 72 h resulted pale yellow platelet crystals. Yield: 11%. Anal. Calc. for C₂₄H₁₆Ag₂CdN₄O₈ (%): C, 35.30; H, 1.97; N, 6.86. Found:

Table 1. Crystal and experimental data

Empirical formula	C ₂₄ H ₁₆ Ag ₂ CdN ₄ O ₈
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> (Å)	8.169(4)
<i>b</i> (Å)	19.622(10)
<i>c</i> (Å)	7.416(4)
β (°)	92.884(7)
<i>V</i> / Å ³	1187.1(11)
<i>Z</i>	2
Fw	816.55
<i>D_c</i> (Mgm ⁻³)	2.284
μ (mm ⁻¹)	2.582
<i>F</i> (000)	788
θ (°)	3.25 to 25.02
Independent reflections	2092 (<i>R</i> _{int} = 0.0460)
Observed Reflection [<i>I</i> > 2σ(<i>I</i>)]	1714
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0371, 0.0678
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0532, 0.0736
Goodness of fit on <i>F</i> ²	1.076
Largest difference peak and hole (e/Å ³)	0.001, 0.000
Largest and Mean Δ/σ	0.432, -0.436

^a*R*₁ = (Σ ||*F*_o|| - |*F*_c|| / Σ |*F*_o|), ^b*wR*₂ = [Σ (w(*F*_o² - *F*_c²)) / Σ (w |*F*_o²)]^{1/2}

C, 35.33; H, 1.93; N, 6.88. IR (KBr, cm⁻¹): 3433 (vs), 2973 (s), 2901 (s), 1610 (m), 1549 (w), 1393 (m), 1250 (w), 1230 (w), 1091 (w), 1051 (s), 880 (w), 765 (w), 661 (w).

A pale yellow platelet crystal (0.15 × 0.13 × 0.05 mm³) was carefully selected and mounted on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated MoKα (λ = 0.7107 Å). The intensity data was reduced using CrystalClear program.⁶ The structure was solved by direct methods using SHELXTLTM package of crystallographic software⁷ and refined by full-matrix least-squares technique on *F*². All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were generated geometrically and treated as riding in the final stage of the refinement. Crystallographic data for the title complex are listed in Table 1. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-277468). The data can be obtained free of charge via

Table 2. Selected Bond Distances (Å) and Angles (°)

Ag(1)-O(2)	2.1315(17)	C(17)-O(1)	1.235(2)
Ag(1)-N(11A)	2.1727(18)	C(17)-O(2)	1.262(2)
Cd(1)-N(21)	2.1470(17)		
O(2)-Ag(1)-N(11A)	155.51(6)	C(16)-N(11)-Ag(1C)	119.93(13)
N(21B)-Cd(1)-N(21)	180.00(4)	C(17)-O(2)-Ag(1)	115.54(13)
C(12)-N(11)-C(16)	117.24(16)	C(26)-N(21)-Cd(1)	119.11(13)
C(12)-N(11)-Ag(1C)	122.63(12)	C(22)-N(21)-Cd(1)	123.52(13)

Symmetry code: A = x + 1, -y + 0.5, z - 0.5; B = -x, -y, -z; C = x - 1, -y + 0.5, z + 0.5.

www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1FZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Description of crystal structure. The selected bond distances and bond angles are listed in Table 2. The molecular structure of the title complex is shown in Figure 1.

The crystallographic asymmetric unit in the complex comprises of two neutral parts of [Ag(Iso)] and [Cd_{1.2}(Iso)]. The [Ag(Iso)] subunit contains non-linear two-coordinated geometry on the Ag(I) atom and μ_2 -bidentate bridging Iso anion (with coordinating pyridyl group and a monodentate carboxylic group). In this building block, silver(I) center is two-coordinated to two Iso moieties through one pyridine nitrogen atom and a carboxylic oxygen atom with Ag(1)-

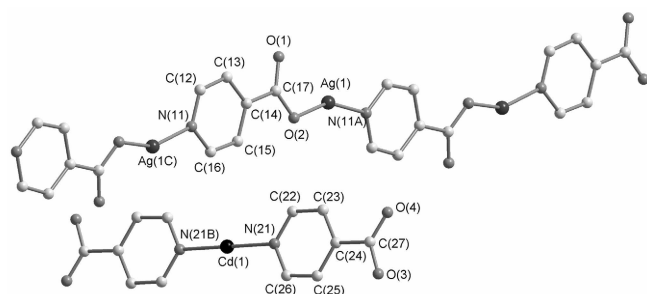


Figure 1. The molecular structure of the title compound. [Hydrogen atoms are omitted for clarity.]

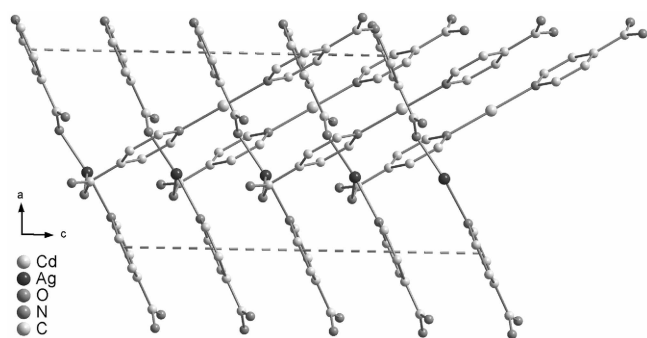


Figure 2. Drawing of hydrogen bonds of the title compound viewed along the *b* axis.

N(11A) = 2.1727(18) (A = x + 1, -y + 0.5, z - 0.5) and Ag1-O(2) = 2.1315(17) Å, forming O(2)-Ag(1)-N(11A) bond angle of 155.51(6)°. The growth of the fundamental repeating unit [Ag(Iso)] results in a 1-D wavy coordination chain along the *a* axis. The deviation from linearity of the silver(I) coordination geometry may make the ligand expand the space of the metal center to form a slight wavy 1-D coordination polymer. The 1-D assembly is same to the coordination chain of [Ag(Iso)]_n in {[Ag(Iso)-(HIso)]_{1.2}[Ag(Iso)]_n}, but unlike to the co-ordination polymer based on silver(I) triangles linked by isonicotinate anions reported by Burrows, A. D.⁸ The monodentate carboxylate group also shows asymmetric C-O bond distances C(17)-O(1) = 1.235(2) and C(17)-O(2) = 1.262(2) Å. The pyridyl ring forms a dihedral angle of 5.43° with neighboring rings and 9.39° with carboxylate group in the same Iso moiety.

The other subunit of [Cd_{1.2}(Iso)] has not formed a 1-D form as [Ag(Iso)], but just a isolated [Cd(Iso)₂] unit. In this unit, it is noteworthy that the cadmium(II) center is rare two coordination geometry through one pyridine nitrogen atom and its symmetry-related atom with Cd(1)-N(21) = 2.1470(17) Å. The ligands usually are some inorganic components like NH₃, Cl, NCS, Si(tBu)₃, Si(SiMe₃)₃ in the examples of two-coordination cadmium(II) center,⁹ while organic components are rare, the examples only being Ph, pentafluorobenzene, bis(Triphenylsilyl) phosphine, ethylenediamine, allylthiourea-S, bis(Trimethylsilyl)dimethyl(methoxy)silyl)methane, bis(Trimethylsilyl)(vinyl dimethylsilyl)methane and Tartrato.¹⁰

In the crystal structure it is possible to observed some hydrogen bonds. The subunits of [Ag(Iso)(HIso)] interlink into 2-D layer through π - π stacking interactions of pyridine rings (centroid-to-centroid distance of 3.801 Å).

Optical studies. Significant absorption bands in the IR of free ligand HIso are observed at 3550(m), 1656(m) cm⁻¹ assigned to ν (OH) and ν (CO). The absorption band in the infrared spectrum of the present compound is observed at 1610 cm⁻¹, due to the carboxyl group (ν (CO)). The

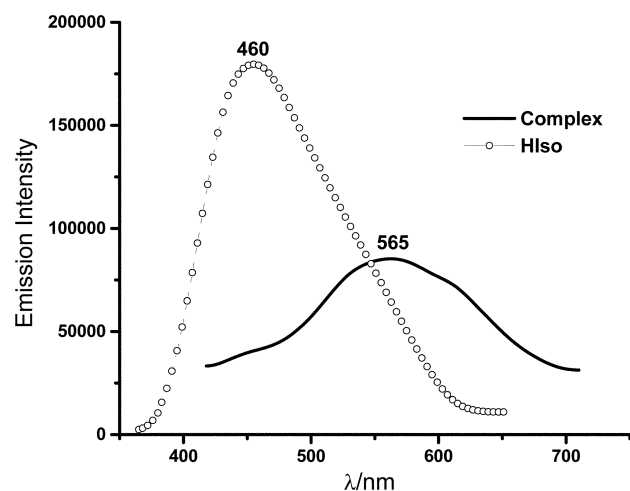


Figure 3. Solid-state emission spectra of the title compound (λ_{ex} = 370 nm) and HIso (λ_{ex} = 362 nm).

significant blue shifts of the carboxyl group take place because of the coordination through the carboxyl oxygen. This situation indicates that coordination of Iso take place via the carboxyl oxygen to the metal ions.¹¹

In contrast to the rich structural chemistry of isonicotinic acid coordination complexes, to our knowledge, the luminescence data were quite limited, but there are the related rare earth complexes with nicotinic and isonicotinic acid N-oxides that included data for erbium and europium site distortions from the changes of the photoluminescence and absorption of the rare earth line spectra.¹² Herein, solid state emission spectra of the d^{10} complex and Hiso show interesting luminescence features at room temperature as given in Figure 3. Excitation of the solid sample of **1** at $\lambda_{\text{ex}} = 370$ nm produces green fluorescence with a broad emission at 565 nm. A significant red shift can be found in the emission wavelength of the title compound when compared with that of free ligand Hiso (broad peak at about 460 nm, $\lambda_{\text{ex}} = 362$ nm). The emission is assigned to ligand-to-metal transfer (LMCT). The compound is yellow in color and showed green fluorescence under UV in the solid state, indicating the compounds are good candidate as electron-transporting materials with fluorescent properties.

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