

Notes

Synthesis, Crystal Structure and Luminescence Property of a New Silver(I) Dimer with Isonicotinic Acid

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Isonicotinic acid (Iso), 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.^{1,2} Furthermore, The isonicotinic acid complexes has raised many interests in fluorescence probing with numerous potential applications for studies of microsecond diffusion and dynamics of membranes.³ Metal centers are potential carriers of electrochemical, magnetic, catalytic, or optical properties that may be introduced into the inorganic-organic hybrid materials.⁴ d¹⁰ metals with rich photophysical and photochemical character have focused attentions to synthesize polynuclear complexes.⁵ Considering the versatile coordination abilities of Iso, we employ the ligand to coordinate with silver nitrate to fabricate a coordination complex with excellent fluorescence property. Herein we report the synthesis, crystal structure and fluorescence property of a new d¹⁰ coordination dimer [Ag₂(Iso)₂(NO₃)₂].

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. Optical diffuse reflectance spectra were measured at room temperature with a Lambda 35 UV-Vis spectrophotometer. The sample was ground into fine powder and pressed onto a thin glass slide holder. The BaSO₄ plate was used as reference. The absorption spectra were calculated from reflection spectra by the Kubelka-Munk function: $\alpha/S = (1-R)^2/2R$, α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the

particle size is larger than 5 μm , and R is the reflectance.

Synthesis of [Ag₂(Iso)₂(NO₃)₂] (1). A solution of Iso (0.025 g, 0.2 mmol) in ethanol (20 mL) was added dropwise to 5 mL stirred aqueous solution of AgNO₃ (0.068 g, 0.4 mmol). After being stirred 4 h, then the obtained suspension was filtered and left to naturally evaporate at ambient temperature in the dim light place. Several weeks later, colorless prismatic crystals suitable for X-ray diffraction could be obtained. Yield: 25%. Anal. Calc. for C₆H₅AgN₂O₅ (%): C, 24.60; H, 1.72; N, 9.56. Found: C, 24.95; H, 1.93; N, 9.28. IR (KBr, cm⁻¹): 3444 (vs), 3188 (m), 2345 (w), 1615 (s), 1547 (w), 1395 (s), 1385 (s), 1128 (m), 1091 (w), 1051 (w), 880 (w), 766 (w), 689 (w), 617 (w).

A colorless prismatic crystal (0.25 × 0.18 × 0.15 mm³) was carefully selected and mounted on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated MoK α ($\lambda = 0.7107 \text{ \AA}$). 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-277467). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, 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.

X-ray single crystal analysis revealed that the crystallographic asymmetric unit in **1** comprises of one silver(I)

Table 1. Crystal and experimental data

Empirical formula	C ₆ H ₅ AgN ₂ O ₅
Fw	292.99
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	13.341(2)
<i>b</i> (Å)	18.337(4)
<i>c</i> (Å)	6.5817(13)
β (°)	102.539(2)
<i>V</i> / Å ³	1571.8(5)
<i>Z</i>	8
<i>D</i> _{calc} (Mgm ⁻³)	2.476
μ (mm ⁻¹)	2.562
<i>F</i> (000)	1136
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ ^a = 0.0493, <i>wR</i> ₂ ^b = 0.1248
Goodness of fit on <i>F</i> ²	1.080
Largest difference peak and hole (e/Å ³)	3.364, -1.162
Largest and Mean Δ/σ	0.004, 0.000

$$^a R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|), \quad ^b wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w|F_o^2|)]^{1/2}$$

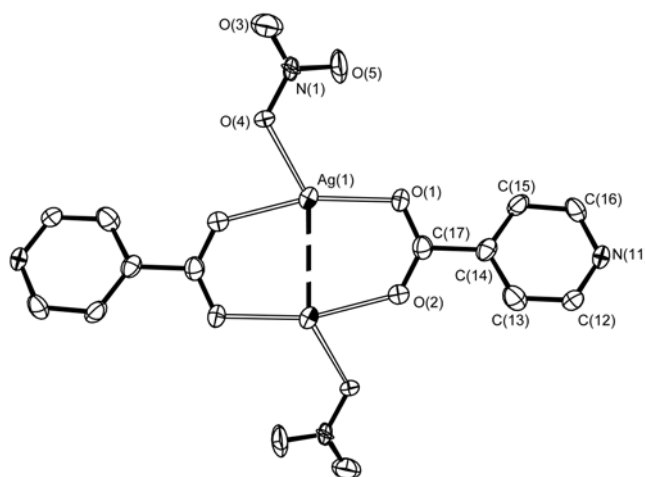
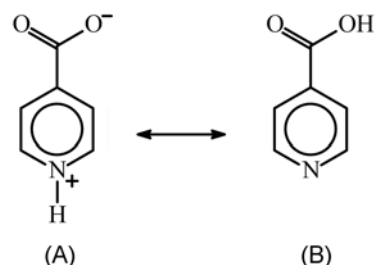
Table 2. Selected Bond Distances (Å) and Angles (°)

Ag(1)–O(1)	2.2032(12)	N(11)–C(12)	1.329(2)
Ag(1)–O(2A)	2.2170(14)	N(11)–C(16)	1.336(2)
Ag(1)–O(4)	2.4466(14)	C(17)–O(1)	1.247(2)
Ag(1)–Ag(1A)	2.8729(5)	C(17)–O(2)	1.259(2)

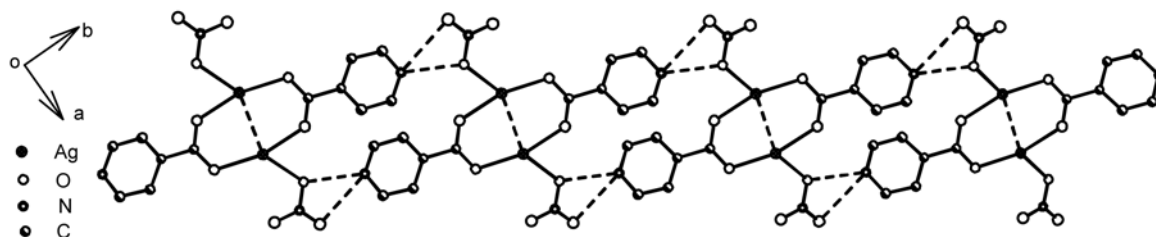
O(1)–Ag(1)–O(2A)	162.94(4)	O(4)–Ag(1)–Ag(1A)	141.83(3)
O(1)–Ag(1)–O(4)	118.63(4)	C(17)–O(1)–Ag(1)	116.05(10)
O(2A)–Ag(1)–O(4)	78.06(4)	C(17)–O(2)–Ag(1A)	131.35(11)
O(1)–Ag(1)–Ag(1A)	88.03(3)	N(1)–O(4)–Ag(1)	118.54(10)
O(2A)–Ag(1)–Ag(1A)	75.57(3)	O(1)–C(17)–O(2)	128.02(15)

Symmetry code: A = -x+1, -y+1, -z+1.

nitrate and one isonicotinate. As shown in Figure 1, the complex is best described as two [Ag(Iso)(NO₃)] subunits with a crystallographic inversion center. Atom Ag(1) lies in a distorted coplanar triangle geometry with the mean deviation of 0.0253 Å, consisting of two oxygen atoms from carboxyl groups of two different isonicotinic moieties and one oxygen atom from a nitrate anion with the Ag(1)⋯Ag(1A) (Symmetry code A: 1-x, 1-y, 1-z) distance of 2.8729(5) Å. The Ag⋯Ag distance is a little shorter than the Ag⋯Ag separation of 2.88 Å in the metallic state and those

**Figure 1.** The molecular structure of **1** with thermal ellipse at the 80% probability level. Hydrogen atoms are omitted for clarity.**Scheme 1.** Two forms of Iso.

found in Iso complexes (2.9–3.23 Å)⁸ or benzene polycarboxylate acids complexes,⁹ showing it is very Ag⋯Ag interaction. However it is longer than the ligand unsupported Ag⋯Ag interaction [2.8031(6) and 2.8118(6)].¹⁰ The distance of Ag(1)–O(1) is 2.2032(12) Å, similar to Ag(1)–O(2A) of 2.2170(14) Å, but much shorter than Ag(1)–O(4) of 2.4466(14) Å. There are two forms of the Iso ligand listed as Scheme 1. In order to keep balance of charge of **1**, the ligand of Iso has to take the form of A, which can be supported by the values of C–O bond distances of carboxyl group and C–N–C angles of isonicotinate. In the isonicotinic acid ligand, the C(17)–O(1) and C(17)–O(2) bond distances, 1.247(2) and 1.259(2) Å respectively, and the O(1)–C(17)–O(2) bond angle, 128.02(15)°, confirm Iso taking the form A compared with those found in complex C₇H₅NO₄.¹¹ The distances of N(11)–C(12) (1.329(2) Å) and N(11)–C(16) (1.336(2) Å) are similar to those found taking the form

**Figure 2.** 1-D ladder-like chain formed by hydrogen bondings along (001) plane.

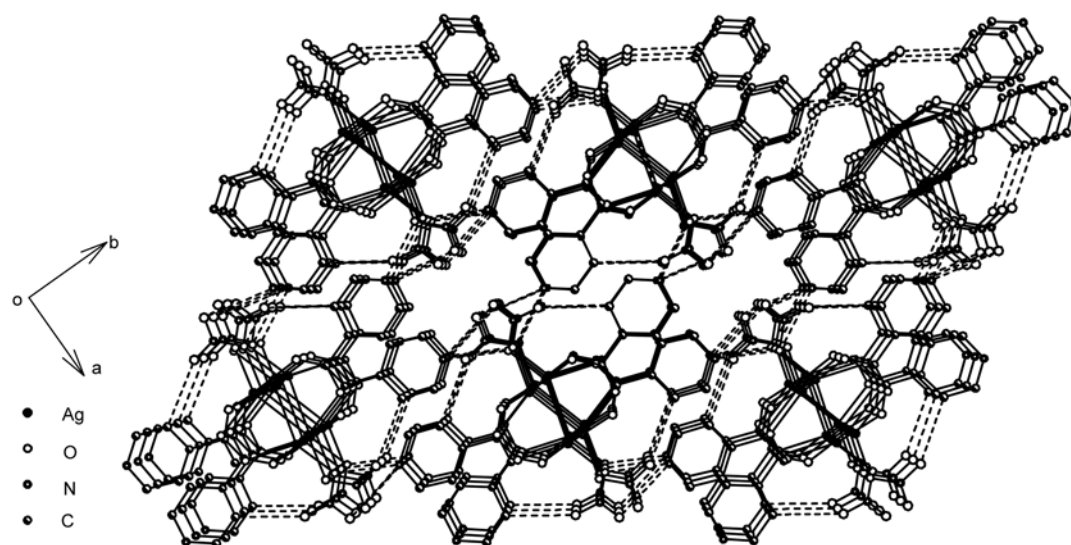


Figure 3. Packing drawing of **1** along (001) plane.

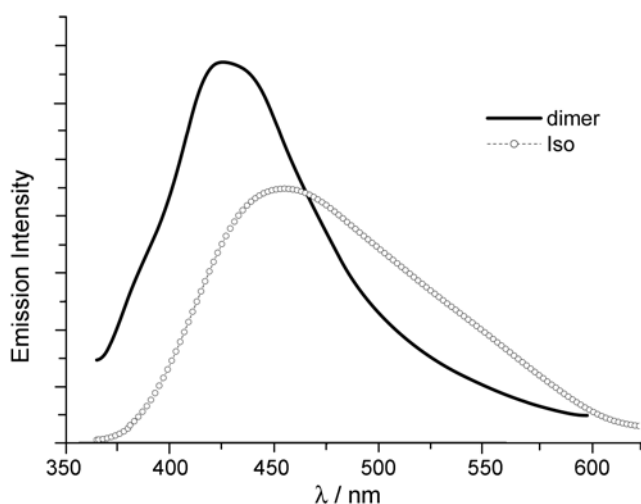


Figure 4. Solid-state emission spectra of dimer ($\lambda_{\text{ex}} = 361$ nm) and Iso ($\lambda_{\text{ex}} = 362$ nm).

A.¹²⁻¹⁴ The IR spectrum of the dimer clearly indicates the absence of characteristic peaks for COOH, the presence of strong peaks at 3444, 1615, 1395 cm^{-1} , suggests the ligand of Iso taking the form A.¹⁵

In **1**, the isolated dimers are further linked into a 1-D ladder-like chain along (001) plane through hydrogen bonds N(11)–H \cdots O(3) (3.145(2) Å, 133.7°), N(11)–H \cdots O(4) (2.7138(19) Å, 167.6°) as shown in Figure 2. The 1-D chains are further linked into 3-D through another type of hydrogen bond of C(13)–H \cdots O(5) (3.180(2) Å, 167.1°) as shown in Figure 3. A minimal centroid-to-centroid distance of 3.968 Å between pyridine rings shows no π - π stacking interactions in the structure.

Optical studies. 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

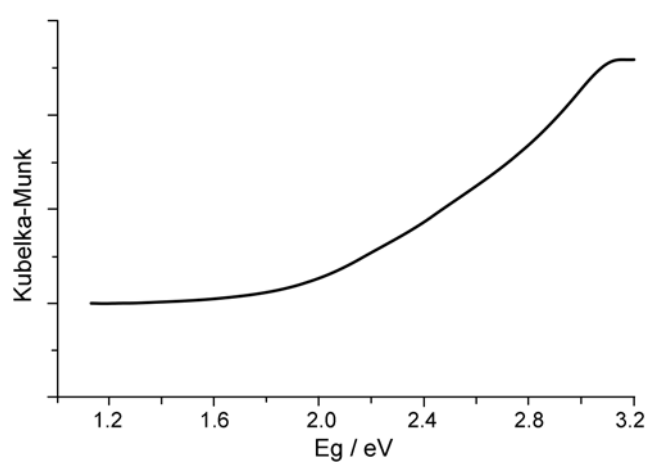


Figure 5. The band gap estimated to be 1.91 eV was assessed by the optical diffuse reflectance data.

and isonicotinic acid N-oxides including data for erbium and europium site distortions from the changes of the photoluminescence and absorption of the rare earth line spectra.¹⁶ Herein, solid state emission spectra of **1** and free ligand Iso show interesting luminescence features at room temperature as given in Figure 4. Excitation of the solid sample of **1** at $\lambda_{\text{ex}} = 361$ nm produces an intense luminescence: a high-energy and broadband at approximately 428 nm. A significant blue shift can be found in the emission wavelength of **1** when compared with that of free ligand Iso (broad peak at about 460 nm, $\lambda_{\text{ex}} = 362$ nm). The emission of **1** is assigned to ligand-to-metal transfer (LMCT) (Iso \rightarrow Ag).

The absorption spectrum was calculated from reflection spectrum by the Kubelka-Munk function (Figure 5).¹⁷ The energy gap of the title compound determined by extrapolation from the linear portion of the absorption edge in a (α/S) versus energy plot is 1.91 eV, which suggests that the title compound behaves as semiconductor.

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