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Research Article

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Hydrothermal synthesis, crystal structure and antimicrobial activity of the nicotinate cobalt complex

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ABSTRACT

The title complex$[Co(nic)_2(H_2O)_4]$ (nic: nicotinic acid) wassynthesized by hydrothermal methods and characterized by elemental analysis, IR and X-ray single-crystal structuredetermination. The compound crystallizes in the triclinic system, space groupP1with a=14.1363(12) Å, b=6.8778 (5) Å, c=8.4878(6) nm, β=118.297(5)°, V=726.63 (10)Å^3, Dc=1.715 mg·m^{-3}, Z=2, F(000)=386, μ=1.227mm^{-1}, R=0.0191, wR=0.0539[I>2σ(I)], GOF=1.178. X-ray single crystal diffraction analysis showsthe complex is mononuclearzero dimensional structure and the adjacent chains are held together byhydrogen bonds and$\pi\ldots\pi$interactions, forming three-dimensional network. The complex was valued for its antimicrobial activity by diffusiontest in vitro. It was found to be active against the three test bacterial organisms. CCDC: 945007.

Key words: Nicotinatecobalt complex,Synthesis, Crystal structure,Antimicrobial activity

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INTRODUCTION

Metal-organic frameworks (MOFs) are ultrahigh porous crystal- line materials wherein metal cations are connected with organic ligands through coordination bonding [1]. MOFs assemble the properties of both organic and inorganic compounds.In resent years, MOFs have attracted considerable attentionnot only due totheir fascinating architectures, but also their potential application in heterogeneous catalysis, gasadsorption, magnetism, NLO materials, luminescence,molecular sensing and separation and molecular recognition[2].Employing appropriate bridging ligands and choosing suitable metal ions are of great importance in the syntheses of coordination polymers.

Among the various ligands,pyridine carboxylate is regarded as good building blocks in the design of MOFs thanks to their rich coordination modes.It is because nicotinic acid(pyridine-3-carboxylicacid) possesses two potential donor sites:the pyridine ring nitrogen and the carboxyloxygen, it can produce extended structures and is regarded asmultidentate ligands used to bridge between metal centres to form polymeric structures. Furthermore, higher dimensional architectures may be formed by nicotinic acid as bridging ligand through covalent or hydrogen bonds since the carboxylic groups can form head-to-headO–H…O hydrogenbonds [3].

As an essential vitamin, it is well known that nicotinic acid can promote the absorption of bioactive metals in humans and also acts as coenzyme,taking part invarious oxidation-reduction reactions [4].

On the other hand, cobalt is not only the very important element in life science but also necessary trace element in the body. Cobalt ions are active center of catalase, carbon monoxide dehydrogenase, superoxide dismutase(SOD) and urease.Therefore, study on complex of cobalt and nicotinic acid and their characteristics can provide the basis for exploring the mechanism of action of cobalt in organism[5-6].

Here, we report the syntheses and crystal structure of a novel compound named [Co(nic)$_2$(H$_2$O)$_4$]. Inaddition, the spectroscopic properties and antimicrobial activity of the compound are also investigated.

EXPERIMENTAL SECTION

All chemicals and reagents were obtainedfrom commercial sources and used as received. The IRspectra were recorded as KBr pellets on a Varian 800 FT-IR spectrometerin the 4000–400 cm^{-}1 region.

Synthesis of complex[Co(nic)$_2$(H$_2$O)$_4$] (1)

Complex 1 was prepared by hydrothermal reaction. A mixture of Co(OAc)$_2$·4H$_2$O (249 mg, 1mmol), nicotinic acid(123 mg,1mmol), malic acid(134mg, 1mmol), ethanol (8 mL), water(8 mL)weremixed in 25 mL beaker and the pH of the mixture was adjusted to about 6 by adding NaOH(0.1mol·L^{-1}) solutions.After stirring for 1 h, the mixturewas put into a 25 mL Teflon-lined stainless autoclave andheated at 140℃ for three days, followed by slow cooling (10℃/h)to room temperature. The red brown block crystals of 1 were collectedin a yield of 42%. Anal. Calcd. for $C_{12}H_{16}N_2O_8Co$ (375.20): C,38.38; H, 4.26; N,7.46. Found: C, 38.83; H, 4.12; N, 7.58%. FT-IRdata (cm^{-1}) for 1: 3362 (m), 3275 (m), 1612 (s), 1599 (s), 1567 (s), 1388(m), 1394 (s), 1311 (w), 1253 (w), 1225 (w), 1154(m), 1109(m), 1051(m)，936 (w), 843(m),764(m), 700(m), 684 (m), 538 (w),411 (w) .

Although malic acid was not involved in coordination, the role of it in the synthesis of title compound cannot be ignored. Presumably, it determines the coordination model of nicotinic acid.

Crystallographic Determinations

Data collections for complex**1** was carried out for crystals with dimensions 0.21 x 0.18 x 0.15 mm on a CCD diffractometer with graphite-monochromated Mo*K*α radiation (λ = 0.71073 Å). The crystal structure was solved by direct methods and Fourier synthesis using SHELXS-97 [7] and refined by full-matrix least-squares techniques on F^2 using SHELXL-97 [8]. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added according to theoretical models. A summary of the crystallographic data and refinement parameters is listed in Table 1. Selected bond distances and bond angles for the complex are listed in Table 2.

Table 1 Crystal data and structural refinements for Complex 1

Empirical formula	$C_{12}H_{16}N_2O_8Co$
Formula weight	375.20
Crystal system	Triclinic
Space group	P1
a(Å)	14.1363(12)
b(Å)	6.8778(5)
c(Å)	8.4878(6)
α(°)	90
β(°)	118.297(5)
γ(°)	90
Volume (Å^3)	726.63(10)
Density (calculated) (Mg/m^3)	1.715
Absorption coefficient (mm^{-1})	1.227
F(000)	386
Data/restraints/parameters	699 / 0 / 74
Goodness-of-fit on F^2(GOF)	1.178
Completeness to theta = 24.98°	100%
Final R indices [I＞2σ(I)]	R1 = 0.0191, wR2 = 0.0539
R indices (all data)	R1 = 0.0192, wR2 = 0.0539

Table 2 Selected bond lengths (Å) and angles (°) for 1

Co(1)-O(1)	2.1070(11)	Co(1)-O(1)#1	2.1070(11)
Co(1)-O(1)#2	2.1070(11)	Co(1)-O(1)#3	2.1070(11)
Co(1)-N(1)	2.1489(16)	Co(1)-N(1)#3	2.1489(16)
O(1)-Co(1)-O(1)#1	90.65(7)	O(1)-Co(1)-O(1)#2	89.35(7)
O(1)#1-Co(1)-O(1)#2	180.0	O(1)-Co(1)-O(1)#3	180.0

Symmetry transformations used to generate equivalent atoms:#1 x,-y,z #2 -x+1,y,-z+2 #3 -x+1,-y,-z+2

RESULTS AND DISCUSSION

Crystal structure of[Co(nic)$_2$(H$_2$O)$_4$] (1)

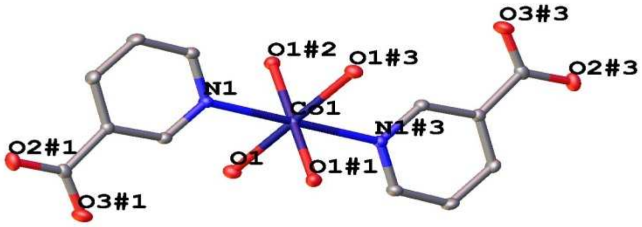

Fig. 1. Structure of the coordination polymer 1 (hydrogen atoms are omitted for clarity)

As shown in Fig. 1,Co(II) sites lie in distorted octahedral geometry: the coordinationsphere around Co1 atom is defined by two nitrogen atoms from two differentnicotinic acid ligands and four water molecules, resulting in mononuclearzero dimensional structure.Intriguingly,as long as four Co-O bond length, is 2.1070(11) Å and two Co-N bond is the same length of2.1489 (16) Å. In addition, the O1, O1#1,O1#2 and O1#3 atoms comprise the baseplane, whereas N1and N1#3 occupy the axial positionsof the octahedron [O(1)-Co(1)-O(1)#1=90.65(7)Å,O(1)-Co(1)-O(1)#2=89.35(7)Å,O(1)#2-Co(1)-O(1)#3=90.65(7)Å,and O(1)#1-Co(1)-O(1)#3=89.35(7) Å; total = 360.02(8) Å].It is seen from Fig.2a, each simpleunit linked with six adjacent units through hydrogen bonding interactionsof $R_2^1(6)$ patterns. On one hand, the four O-atoms of the coordinated water in each chain are engaged in eight hydrogen bondings with the non-coordinating carboxylate groups of nicotinic acid ligands of the six adjacent units ,on the other hand, in each unit, the four O-atoms of the two nicotinic acid ligands are also engaged in eight hydrogen bondings with six O-atoms of the coordinated water in the same six adjacent units. For example, Co2 and Co5 units are connected to the center Co unit through four O-H…O hydrogen bondsrespectively ; while the other four cobalt units (Co1, Co3, Co4 and Co6 units) are also linked with center Co unit with two O-H…O hydrogen bonds respectively. In this way, the adjacent molecules recognize eachother to generate a 2D supramolecular chain between the uncoordinated carboxylate oxygen atoms (O2, O3) and aquae oxygen atoms (O1)[O(1)-H(1A)...O(2)^{vi},2.7099(15)Å;O(1)-H(2A)...O(3)^{vii}, 2.6936(19)Å; symmetry code (vi): x+1/2,y+1/2,z+1; (vii):-x+1,-y,-z+1](Fig. 2b). Such strong hydrogen bonds in the crystal lattice of 1 make the crystals more stable. It is worthwhile to note that a 3D hydrogen bonding network were formed if thehydrogen bonding interactions between O1 atoms of carboxylate groups and H atoms of the pyridyl group with C3 and C4 [C3–H3…O1, 3.585 Å; C4-H4…O1, 3.983Å] are all taken into account, which contributes to the additional stability of thestructure (Fig. 3a). Need to add that in the solid state, $\pi\ldots\pi$ interactions are observed as illustrated in Fig. 3b. and the two coordinated pyridyl rings of nicotinic acid ligands in one molecule unit are interact with other pyridyl rings from adjacent units (3.744 Å for centroid-centroid distance), which consolidate the 3D network structure of the supramolecular.

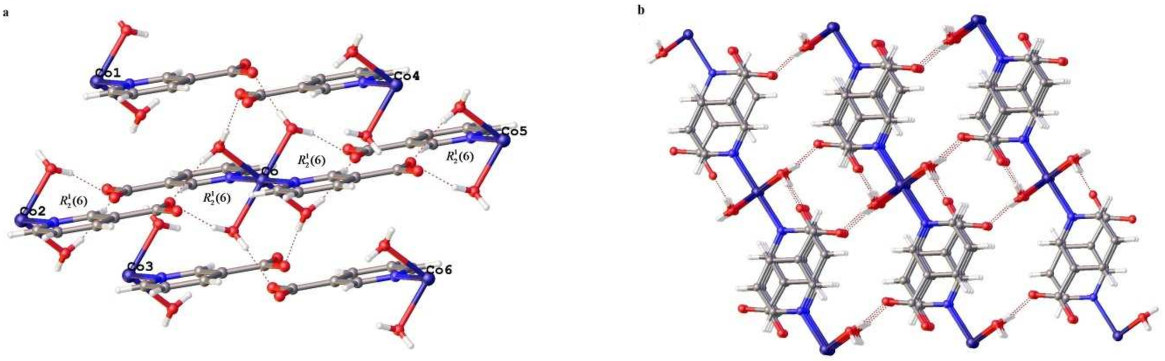

Fig.2 a Each simpleunit linked with six adjacent units through hydrogen bonding interactions; b The 2D packing framework of complex 1 through O–H…O hydrogen-bonding

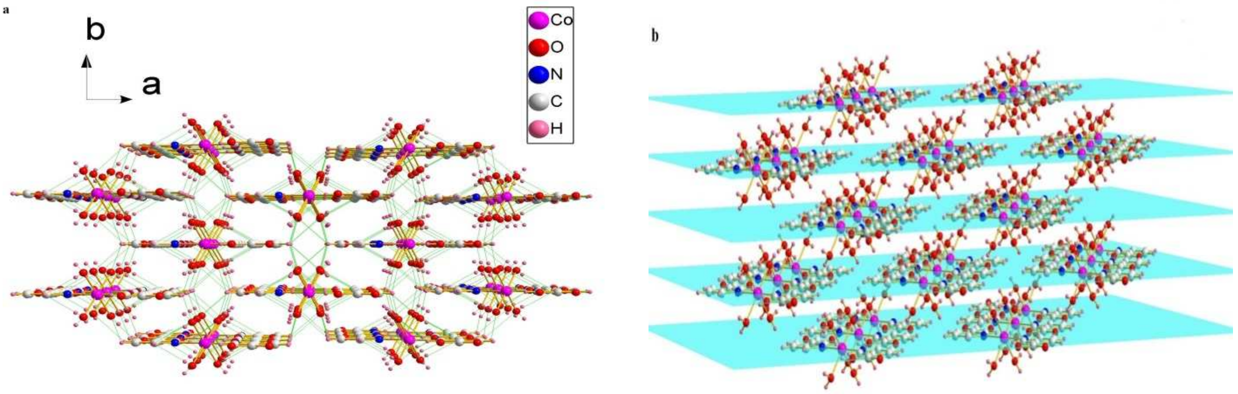

Fig. 3 aThe 3Danions architecture on the basis of via hydrogen bonds in 1; b π…π interactions of complex 1

Determination of antibacterial activity

The synthesized compound 1 and metal salts were screened for their antibacterial activity against three different organisims like Staphylococcus aureus, Bacillus subtilis and Escherichia coli by AGAR diffusion method. Beer extract protein agar medium, laboratory bench and Oxford cups were sterilized for 30 minutes under 129 ℃. The medium first melt and was cooled to about 50 ℃, and then it was put into culture dishes to be condensed into flat according to aseptic manipulation. After that, the culture mediums were inoculated with the test strains. The compounds were dissolved in DMSO and were injected into the Oxford cups, which were put on the bacterial culture medium. Subsequently, the Oxford cups were incubated at 37℃ for 24h and then the antibacterial activities were determined by measuring the diameter of the zone of growth inhibition (mm).

Table 3 Antibacterial activity data of the metal salt and the title complex

Compound	Concentration (mmol·L^{-1})	Bacterial species		
		Staphylococcus aureus	*Bacillus subtilis*	*Escherichia coli*
$Co(OAc)_2·4H_2O$	1	9.3	11.4	11.6
	0.75	8.6	10.5	9.1
	0.5	8.3	10.1	8.8
$Co(nic)_2(H_2O)_4$	1	15.4	12.7	13.1
	0.75	13.9	12.4	11.3
	0.5	11.8	11.3	10.7
DMSO	AR	7.9	8.0	8.1

The antibacterial screening data is presented in Table 3. As results show metal salts and synthesized complex 1 exhibited activity against the test strains. In general, antibacterial activity of complex 1 is stronger than metal salt and with the increase of concentration, the complex of bacteriostatic effect also increase.

CONCLUSION

Cobalt (II) nicotinic acid single crystals have been successfully grown by hydrothermal methods and apH of about 6 producedgoodqualitycrystals.Thecrystalbelongs tothe triclinic system.Thecrystalstructure analysis revealsthatitisanovel3D polymerstabilizedby extended hydrogenbonding andπ…π interactionsconsolidate the 3D network structure of the supramolecular.The synthesized compound 1 and metal salts were screened for their antibacterial activity against three different organisms. The results show metal salts and synthesized complex 1 exhibited activity against the test strains and antibacterial activity of complex 1 is stronger than metal salt. In addition, with the increase of concentration, the complex of bacteriostatic effect also increase.The present complex can serve as lead for further structural modifications in the search for new drug molecules.

Supporting Information

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos.CCDC945007. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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