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Spectroscopic and Structural Study of Ni(II) Dipicolinate Complex with 2-Amino-4-methylpyrimidine

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Nickel(II) dipicolinate complex containing 2-amino-4-methylpyrimidine (2A-4Mpy), [Ni(2A-4Mpy)(dpc)$(H_2O)_2$]$\cdot$ $2H_2O$ was synthesized in solid state and its structural and spectroscopic properties were determined by XRD, IR, and UV-Vis techniques. The crystal data revealed that the Ni complex is in triclinic crystal systems with space group P-1 and $Z = 2$. The Ni(II) ion is bonded to dipicolinate ligand through pyridine N atom together with one O atom of each carboxylate group, 2 aqua ligands, and the N atom of 2-amino-4-methylpyrimidine, forming distorted octahedral geometry. IR and UV-Vis spectra of the complexes all agree with the observed crystal structure.

Key Words: Metal(II)-dipicolinate complexes, X-ray crystal structure, UV-Vis, IR.

Introduction

As an important biological agent, dipicolinic acid (H_2dpc, also known as pyridine-2,6-dicarboxylic acid) is a versatile ligand with N,O-chelator and has diverse coordination modes.[1-4] It has important biological functions in the body metabolism such as enzyme inhibitor,[5] plant preservative,[6] and food sanitizer.[7] During the past few years, these properties have attracted the interest of scientists not only in the field of coordination chemistry but also in both inorganic and bioinorganic chemistry.[8,9]

Dipicolinates commonly coordinate to transition metals by either carboxylate bridges between metal centers, to form polymeric or dimeric complexes[10,11] or tridentate (O, N, O') chelation to one metal ion.[12-14]

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The dipicolinate ligand with Ni(II) ions commonly has 1 or 2 coordination modes. In one coordination mode, a single planar dpc ligand binds in the equatorial plane of a Ni(II) cation and other ligands such as H_2O or pyridine based heterocycles occupy the remaining sites, thereby forming square pyramidal or octahedral coordination geometry,[14,15] or 2 planar dpc molecules coordinate perpendicularly generating distorted octahedral coordination geometry.[16]

In our ongoing research on the determination of spectroscopic and structural properties of biologically important molecules and their interaction with transition metal ions,[17−19] we synthesized a new Ni(II) complex containing dipicolinate anion together with 2-amino-4-methylpyrimidine ligand, namely [Ni(2A-4Mpy)(dpc)$(H_2O)_2$]·$2H_2O$, since it is known that compounds containing pyrimidine are found in the content of various biological systems and play an important role in numerous biological processes.[20] As part of our study on understanding the interactions between pyrimidine derivatives of transition metal complexes and aromatic polycarboxylates, we were interested in preparing and characterizing nickel(II) complexes containing dipicolinate ligands. This compound might also be of interest in pharmacological studies.

Experimental

General method

All chemical reagents were analytical grade commercial products. Solvents were purified by conventional methods. The optical absorption spectra of the complexes were recorded at room temperature in aqueous solution on a CINTRA 20 UV-VIS spectrometer working between 200 and 900 nm. The IR spectra were recorded on a Jasco 430 FT/IR spectrometer using KBr pellets and operating in the 4000-400 cm^{-1} range.

X-ray crystallography

Suitable single crystals were mounted on a glass fiber and data collection were performed on a STOE IPDS(II) image plate detector using Mo K_α radiation (λ = 0.71019 E) at 298 K. Details of the crystal structure are given in Table 1. Data collection: Stoe X-AREA.[20] Cell refinement: Stoe X-AREA.[21] Data reduction: Stoe X-RED.[21] The structure was solved by direct methods using SHELXS-97[22] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97.[22] All carbon hydrogens were positioned geometrically and refined by a riding model with U_{iso} 1.2 times that of attached atoms and remaining hydrogen atoms were found by Fourier difference. Molecular drawings were obtained using ORTEP-III.[23]

Synthesis of [Ni(2A-4Mpy)(dpc)$(H_2O)_2$]·$2H_2O$

2-A-4-Mpy (1 mmol) was added slowly with continuous stirring to an ethanol/water (30 mL, ca. 1:1 *v*/*v*) mixture containing $NiCl_2$· $4H_2O$ (1 mmol) and disodium dipicolinate (1 mmol). The resulting solutions were refluxed for 1 h and then filtered. The green filtrates were left for about 2 weeks at room temperature, and then the green crystals of [Ni(2A-4Mpy)(dpc)$(H_2O)_2$]·$2H_2O$ complex suitable for X-ray diffraction analyses were collected.

Table 1. Crystal data and structure refinement for [Ni(2A-4Mpy)(dpc)(H_2O)$_2$]· $2H_2O$.

Formula	$C_{12}H_{18}N_4O_8Ni$
Formula weight	404.99
Temperature (K)	297(2)
Radiation, λ, (MoKα)	0.7107
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	
a, b, c (Å)	7.6812(7), 9.7659(9), 11.4235(10)
α, β, γ (°)	97.257(7), 98.239(7), 103.652(7)
Volume (Å^3)	812.62(13)
Z	2
Calculated density (g cm^{-3})	1.655
μ (mm^{-1})	1.245
F(000)	420.0
Crystal size (mm)	0.42 × 0.27 × 0.15
θ range (°)	1.83-27.07
Index ranges	$-9 \leq h \leq 9$
	$-12 \leq k \leq 12$
	$-14 \leq l \leq 14$
Reflections collected	11428
Independent reflections	3510 [$R_{int} = 0.138$]
Reflections observed [$I \geq 2\sigma(I)$]	2742
Absorption correction	integration
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameters	3510 / 12 / 268
Goodness-of-fit on F^2	1.059
Final R indices [$I \geq 2\sigma(I)$]	0.037
R indices (all data)	0.049
Largest diff. peak and hole (eÅ^{-3})	0.45, -0.53

Results and discussion

Crystal Structure

The structure of nickel(II) complex consists of an isolated neutral [Ni(2A-4Mpy)(dpc)(H_2O)$_2$] unit and 2 crystal lattice water molecules. The ORTEP(III)[23] view of the complex with atom labeling is shown in Figure 1. The H_2dpc is deprotoned during the reaction and acts as a tridentate ligand. The Ni(II) ion is hexa-coordinated by 2 oxygens together with 1 nitrogen atom from dpc dianion and 2A-4Mpy composing the basal plane, and 2 aqua ligands occupying the axial sites, adopting a distorted octahedral sphere (Figure 1). The fact that the

Ni1-N_{dpc} [1.969(2) Å] length is significantly shorter than $\text{Ni1-N}_{2A-4Mpy}$ [2.053(2)] bond length indicates that atom N1 is the strongest site, because 2 carboxylate groups in ortho positions enhance the basicity of this atom.

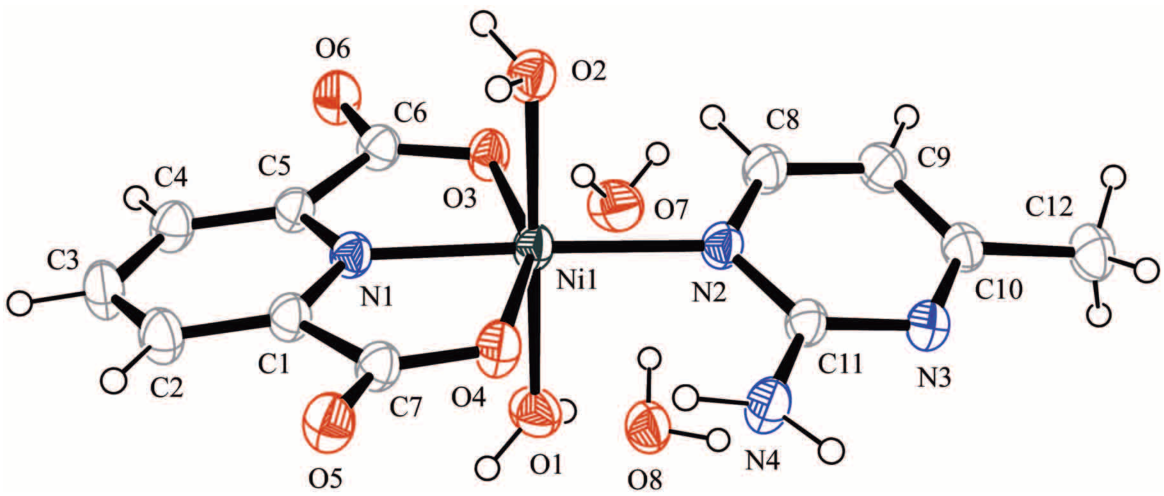

Figure 1. The molecular structure of nickel(II) complex, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

The Ni1-N_{dpc} [1.969(2) Å] and Ni1-O_{dpc} [2.101(2) -2.142(2) Å] bond lengths in the title complex are slightly different from the corresponding lengths reported for [Ni(Hdpc)$_2$]· 3H$_2$O [Ni-N = 1.966(3) Å; Ni-O = 2.098(2)-2.099(2)Å],[24] [Ni(dpc) (H$_2$O)$_2$] [Ni-N = 1.903(3) Å; Ni-O = 2.005(2)-2.006(2) Å],[15] [Ni(nit2Py)(dpc)(H$_2$O)]· (MeOH)· (H$_2$O) [Cu-N = 1.965(4) Å; Cu-O = 2.083(3)-2.113(3) Å][2] [nit2Py: 2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, MeOH: methanol], [Ni(bta)$_3$(dpc)] [Ni-N = 1.992(5) Å; Ni-O = 2.112(1)-2.180(1) Å][25] [bta: benzo-trizole], [Ni(cyclam)(H$_2$O)$_2$][Ni(dpc)$_2$]· 2.5H$_2$O [Ni-N = 1.931(3) Å; Ni-O = 2.132(2)-2.146(2) Å][26] [cyclam: 1,4,8,11-tetraazacyclotetradecane]. The Ni–O_{aqua} [2.098(2)- 2.089(2)] bond lengths are slightly different from those found in [Ni(dpc)(H$_2$O)$_2$] [Ni-O = 1.971(2)-2.150(3) Å] and [Ni(nit2Py)(dpc)(H$_2$O)]· (MeOH)· (H$_2$O) [Ni-O = 2.080(3) Å]. This is most probably due to the hydrogen bonding interactions between the aqua and acceptor groups. The dpc chelate angles are 78.72(8)° and 77.68(8)°, which are comparable to those found in other dipicolinate-metal complexes.[27,28] The pyridine ring of the dpc anion in the title complex is essentially planar and the 2 carboxylate groups are not significantly displaced from the mean planes of this ring [torsion angle is 172.5(2) for C4/C5/C6/O3° and 172.6(2) for C2/C1/C7/O4]. The dihedral angle between the mean pyridine and pyrimidine planes of dpc and 2A-4Mpy is 23.59(13)°.

In the crystal structure of the title compound, the neutral [Cu(2A-4Mpy)(dpc)(H$_2$O)$_2$] · 2H$_2$O units are connected by hydrogen bonds involving all the H atoms of the crystal water molecules and aqua ligands. Additionally, it can be seen from Figure 2 that the 2 dipicolinate molecules are joined by 2 N-H$\cdots$O intermolecular hydrogen bonds, which lead to the formation of a centrosymmetric dimer of the title compound in the unit cell (Table 2). Extended monomeric moieties produce a 3D supramolecular array in the crystal network. The arbicular hydrogen-bonded synthons consisting of 2 and 3 monomeric units, notated as $R_4^4(12)$ and $R_3^2(8)$,[29] are observed as the basal building block of this 3D pattern (Figure 2).

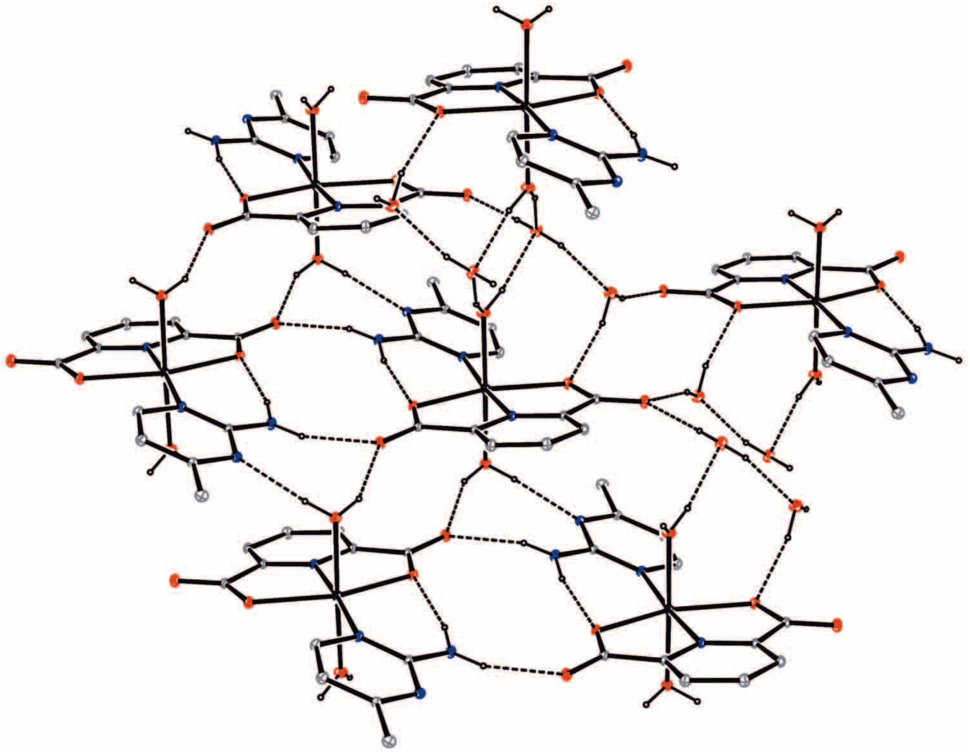

Figure 2. 3D supramolecular network of nickel(II) complex, showing hydrogen-bond interactions.

Optical absorption and FT-IR investigation

The electronic absorption spectra of nickel(II) complex were recorded in aqueous solution. In the UV-range 2 strong absorption peaks were observed at near 240 and 285 nm, which can be assigned to intraligand transitions of dpc and 2A-4Mpy ligands. In the visible range, 3 broad peaks were observed at 402, 657, and 841 nm, which can be assigned to spin-allowed $d-d$ transition bands of $^3A_{2g} \rightarrow {}^3T_{1g}(P),^3A_{2g} \rightarrow {}^3T_{1g}$, and $^3A_{2g} \rightarrow {}^3T_{2g}$.

The IR spectra of dipicolinate-containing complexes have quite characteristic absorption bands. The IR spectrum of the title complex presents 2 distinguishable regions. In the high energy band (3500-3100 cm^{-1}), significant ν(NH) absorption bands due to the amine group in pyrimidine appeared. This region of the NH$_2$ stretching vibrations is relatively broadened by partial superposition of the OH vibrations of the crystal water molecules. The relatively weak absorption bands between 3000 and 2800 cm^{-1} are assigned to the ν(CH) vibrations. In the low energy region, the strong bonds 1658 and 1631 cm^{-1} are assigned to ν(C=O)$_{dpc}$, and another strong absorption at 1371 cm^{-1} is due to ν(C-O) vibration. The difference between ν(C=O) and ν(C-O) of dpc is at near 300 cm^{-1}, indicating that the carboxyl groups are monodentate-coordinated,[30] consistent with the XRD structural results. The weak intensity band centered at 1295 cm^{-1} is attributed to the C-N stretching vibrations.[31] The ring wagging vibration of the pyridine group is also observed at 759 cm^{-1}. The δ_{O-C-O} in-plane deformation vibration, which occurs as a strong sharp band at 701 cm^{-1} in the free H$_2$dpc, shifts to 688 cm^{-1} in the title complex, as is also found in the literature.[32]

Table 2. Interatomic bond distances (Å) and angles (°) around the Ni1(II) ion.

(a) Bond lengths, bond angles

Bond lengths (A)

O1–Ni1: 2.096(2)   O2–Ni1: 2.089(2)   O3–Ni1: 2.142(2)
O4–Ni1: 2.101(2)   N1–Ni1: 1.969(2)   N2–Ni1: 2.053(2)

Bond angles (°)

O2–Ni1–O1: 178.63(9)   O2–Ni1–N1: 91.45(8)   O1–Ni1–N1: 88.50(9)
O1–Ni1–N2: 87.67(9)   O2–Ni1–N2: 92.44(8)   N1–Ni1–N2: 175.23(8)
N2–Ni1–O4: 104.09(8)   O1–Ni1–O4: 89.55(9)   O2–Ni1–O4: 89.09(9)
N2– Ni1–O3: 99.49(8)   O1–Ni1–O3: 90.28(9)   O4–Ni1–O3: 156.40(7)

(b) Hydrogen-bonding interactions (A, °)

D—H··A	D—A	H··A	D··A	D—H··A
O1–H1A··O8$^{\mathrm{i}}$	0.82(2)	2.04(2)	2.845(3)	168(3)
O1–H1B··O8	0.82(3)	1.99(3)	2.804(4)	172(4)
O2–H2A··N3$^{\mathrm{ii}}$	0.84(2)	2.07(2)	2.906(4)	171(3)
O2–H2B··O5$^{\mathrm{iii}}$	0.82(3)	2.00(3)	2.753(3)	152(3)
N4–H4A··O4	0.90(3)	2.02(3)	2.899(3)	166(3)
N4–H4B··O5$^{\mathrm{iv}}$	0.88(3)	2.04(3)	2.900(3)	164(3)
O7–H7A··O6$^{\mathrm{v}}$	0.85(2)	2.02(2)	2.838(3)	161(4)
O7–H7B··O3	0.84(3)	2.06(3)	2.871(3)	161(3)
O8–H8A··O7	0.86(3)	1.89(3)	2.721(4)	162(3)
O8–H8B··O6$^{\mathrm{vi}}$	0.85(3)	1.92(4)	2.768(4)	172(4)

Symmetry codes: (i) -x+2, -y+1, -z+2; (ii) x-1, y, z; (iii) -x+1, -y+1, -z+1; (iv) -x+2, -y+1, -z+1; (v) -x+1, -y, -z+2; (vi) x+1, y,

Supplementary Data

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. CCDC 642006. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB12 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web http://www.ccdc.cam.ac.uk

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