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Note

Cation exchange, solvent free synthesis and packing patterns of quinolinium nickel(II) dipicolinates

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ABSTRACT

Nickel dipicolinate complexes $(HQ)_2[NiL_2]\cdot5H_2O$ (**1**) and $(H5AQ)_2[NiL_2]\cdot4H_2O$ (**2**) (where L = pyridine-2,6-dicarboxylate anion, Q = quinoline, 5AQ = 5-aminoquinoline) are synthesized in solution and also through solvent free cation exchange reactions of $H_2[NiL_2]\cdot3H_2O$. The crystal structures of the complexes **1** and **2** are determined. The strong π–π interactions between the quinolinium cations disrupt the conventional π-stacking interactions of the nickel–dipicolinate anions. The quinolinium cations of these complexes exchanges with alkali metal cations in basic medium and only at an extreme acidic condition the pyridine-2,6-dicarboxylate can be replaced from these complexes by halide ions.

1. Introduction

Quinolines have the ability to π-stack among themselves that finds interest in supramolecular chemistry [1] and in biology [2,3]. A good number of copper [4], zinc [5] and iron [6] complexes possess quinolinium ions. Metal complexes having methylquinolinium [7] and quinolinium ions with oxalate [8], dipicolinate [9] complexes were studied earlier. The hydroxyquinolines are good metal ion chelators [10,11]. Particularly, 8-hydroxyquinoline [12–16] and 8-aminoquinoline [17–20] are widely studied as chelating ligands. High ability of 8-hydroxyquinoline to form chelate makes the chemistry of 8-hydroxyquinolinium cations [9,21,22] limited. The nickel dipicolinate anion has versatile intercalation chemistry due to its strong tendency to form layered structure through π–π interactions as illustrated in Fig. 1 [23,24]. Since quinolinium ions show strong π-interactions their role to retain π-intercalating anionic assemblies would be of interest [24]. Further, the quinolines being mild base their reactions in solution and solvent free conditions with solid acid such as $H_2[NiL_2]\cdot3H_2O$ (**4**) would provide information on cation exchange reactions.

In this article we present synthesis of $(HQ)_2[NiL_2]\cdot5H_2O$ (**1**), $(H5AQ)_2[NiL_2]\cdot4H_2O$ (**2**) and $(H8HQ)_2[NiL_2]\cdot6H_2O$ (**3**) (where, Q = quinoline, 5AQ = 5-aminoquinoline, 8HQ = 8-hydroxyquinoline and L = pyridine-2,6-dicarboxylato) with or without a solvent. We also demonstrate the utility of $H_2[NiL_2]\cdot3H_2O$ (**4**) as a solid acid in synthesizing the above complexes. The influence of packing patterns of nickel dipicolinate complexes having quinolinium cations are compared with other related structures.

2. Experimental

2.1. Synthesis of complexes in solution

To a solution of dipicolinic acid (0.334 g, 2.00 mmol) in methanol (20 ml), nickel(II) acetate monohydrate (0.224 g, 1.00 mmol) was added. The reaction mixture was stirred for 30 min to obtain a green precipitate. Quinoline (2.00 mmol in 10 ml methanol) was added in small portions to the precipitate and stirred for half an hour. A green solution formed was diluted by Milli Q water (10 ml) and left for crystallization. After 1 week, green crystals of **1** were formed.

The complexes **2** and **3** were prepared in a similar procedure as above by using 5-aminoquinoline and 8-hydroxyquinoline, respectively, instead of quinoline.

*For complex **1**:* Isolated yield, 65%. IR (KBr, cm^{-1}): 3410 (bs), 1621(s), 1590 (w), 1424 (w), 1374 (s), 1277 (w), 1085 (w). Molar conductance: 215.0 $Scm^2\ mol^{-1}$ in water, $\mu_{eff.}$ at 298 K: 2.88 BM. Vis(H_2O) λ_{max}: 606.0 nm; $\varepsilon = 14.0\ M^{-1}\ cm^{-1}$. Thermal analysis: decomposition range: ~70–139 °C (loss of three water molecules of crystallization); further decomposition occurs at ~165 °C.

*For complex **2**:* Isolated yield: 70%. IR (KBr, cm^{-1}): 3413 (bs), 1624 (s), 1591 (w), 1426 (w), 1377 (s), 1279 (w), 1088 (w). Molar conductance: 206.0 $Scm^2\ mol^{-1}$ in water, $\mu_{eff.}$ at 298 K: 2.85 BM.

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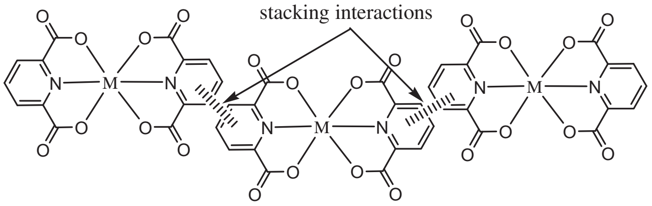
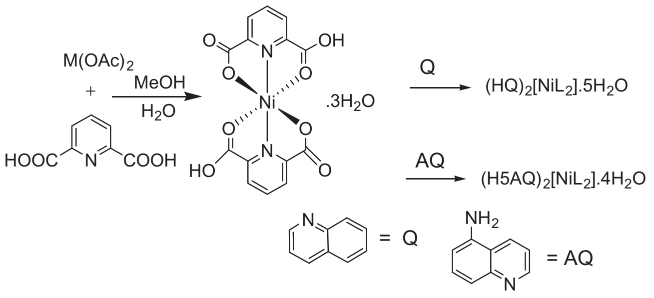


Fig. 1. The π–π stacking generally observed in *bis*-dipicolinate complexes.



Scheme 1. Synthesis of the complexes.

Thermal analysis: decomposition range: ~60–136 °C (loss of three water molecules of crystallization).

For complex **3***:* Isolated yield: 66%. IR (KBr, cm^{-1}): 3412 (bs), 1624 (s), 1588 (w), 1424 (w), 1377 (s), 1279 (w), 1088 (w). Molar conductance: 200.0 $Scm^2\ mol^{-1}$ in water, μ_{eff}. at 298 K: 2.90 BM. Vis(H_2O) λ_{max}: 615.0 nm; ε = 18.2 $M^{-1}\ cm^{-1}$. Thermal analysis: decomposition range: ~60–136 °C (loss of three water molecules of crystallization).

$H_2[NiL_2]\cdot 3H_2O$ (**4**): To a solution of dipicolinic acid (0.167 g, 1.00 mmol) in methanol (20 ml), nickel(II) acetate monohydrate (0.124 g, 0.50 mmol) was added. A green precipitate was obtained after stirring for half an hour at room temperature. The green precipitate formed was dissolved in Milli Q water (10 ml) and left for crystallization in a beaker. After 3–4 days, green colored crystals were collected.

The compound $\{[K_2(H_2O)_7][NiL_2]\}_n$ is isostructural with corresponding copper complex reported earlier [22]. It has IR signals as, IR (KBr, cm^{-1}): 3398 (s), 3071 (m), 2930 (s), 2854 (w), 1620 (s), 1588 (s), 1425 (m), 1364 (s), 1277 (m), 1185 (w), 1083 (m), 774 (m), 725 (m).

2.2. Solid state cation exchange reactions

In a typical solid state synthesis the complex **4** (0.445 g, 1.0 mmol) and quinoline (0.258 g, 2.0 mmol) were mixed together in a mortar. The resulting paste was kept at 80 °C in an oven for half an hour. The paste was cooled to room temperature and was washed with methanol (10 ml). The residue was air dried and characterized. The IR and solid state visible spectra of the solid obtained were compared with the product **1** obtained through solution state synthesis to establish its identity and purity (yield 96%).

Table 1
Crystal parameters of complexes **1** and **2**.

Compound (No)	$(HQ)_2[NiL_2]\cdot 5H_2O$ (**1**)	$(H5AQ)_2[NiL_2]\cdot 4H_2O$ (**2**)
CCDC No.	874922	874923
Empirical formula	$C_{32}H_{32}N_4NiO_{13}$	$C_{32}H_{32}N_6NiO_{12}$
M_r	739.33	751.35
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.3307(3)	10.2129(3)
b (Å)	18.3048(4)	16.3019(4)
c (Å)	18.2981(3)	20.3817(6)
α (deg)	90.00	90.00
β (deg)	126.6710(10)	103.7910(10)
γ (deg)	90.00	90.00
V ($Å^3$)	3312.65(12)	3295.52(16)
Z	4	4
D_{calc} ($g\ cm^{-3}$)	1.482	1.514
T (K)	296(2)	296(2)
μ (Mo Kα) (mm^{-1})	0.659	0.663
F(000)	1536	1560
Reflections collected	33609	33623
Independent reflections (R_{int})	5836	5768
Range of indices	−14, 14; −21, 21; −21, 21	−12, 11; −19, 19; −24, 23
θ (°)	1.78–25.00	1.62–25.00
Complete to 2θ (%)	100.0	99.6
Data/restraints/parameter	5836/6/499	5768/4/500
Goodness-of-fit (GOF) on F^2	1.108	0.989
R_1, wR_2 [$I > 2\sigma(I)$]	0.0389, 0.1029	0.0391, 0.1241
R_1, wR_2 (all data)	0.0497, 0.1102	0.0495, 0.1352
Largest difference peak/hole ($e\ Å^{-3}$)	1.074/−0.482	0.400/−0.534

Compounds **2** and **3** were prepared in similar procedures by using 5-aminoquinoline or 8-hydroxyquinoline respectively, instead of quinoline. Solid state cation exchange reaction of **1** by 5-aminoquinolinium ion under solvent free condition was similarly done by grinding together **1** (0.739 g, 1.0 mmol) with 5-aminoquinoline (0.288 g, 2.0 mmol) and keeping the reaction mixture at 80 °C for 45 min in an oven. The paste was washed with methanol to obtain **2** in pure form. Isolated yield in every case was found to be above 90% keeping excellent atom economy.

2.3. Structure determination

The X-ray data of **1** and **2** were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 3.0 KW sealed tube, with Mo Kα radiation (λ = 0.71073 Å) at 298 K, with increasing ω (width of 0.5 per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP software. Structures were solved by direct methods using SHELXS-97 and refined with full matrix least-squares on F^2 using SHELXL-97 software. All the non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. The H-atoms, except those attached to nitrogen atoms were placed at their calculated positions and refined in the isotropic approximation; those attached to nitrogen were located in the difference Fourier maps, and refined with isotropic displacement coefficients. The crystal data and details of refinement of **1** and **2** are tabulated in Table 1.

3. Results and discussion

The nickel(II) dipicolinate complexes $(HQ)_2[NiL_2]\cdot 5H_2O$ (**1**) and $(H5AQ)_2[NiL_2]\cdot 4H_2O$ (**2**) were prepared by reacting pyridine-2,6-dicarboxylic acid with nickel(II) acetate monohydrate followed by treatment with the corresponding quinoline derivative (Scheme 1). The compounds **1**–**2** were characterized by determining their crystal structures by X-ray single crystal diffraction technique. Each complex has anionic unit $[NiL_2]^{2-}$, consists of a distorted octahedral nickel(II) center with two meridionally coordinated pyridine- 2,6-dicarboxylate ligands (**L**). The respective protonated quinolines are the cationic units of the complexes. Depending on the cation the complexes **1**–**3** possesses different numbers of water of crystallization molecules. In the crystal lattice of **1** there are five water molecules in symmetry independent positions. These water molecules form discrete pentamers. The water