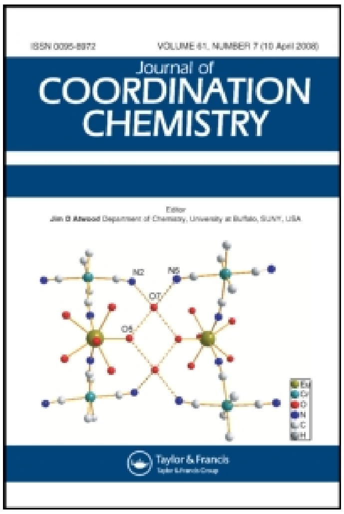

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Monomeric complexes of 1,8-<i>bis</i>(isonicotinyloxy)anthracene-9,10-dione

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Monomeric complexes of 1,8-*bis*(isonicotinyloxy) anthracene-9,10-dione

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Condensation of two equivalents of isonicotinic acid with 1,8-dihydroxyanthraquinone forms 1,8-*bis*(isonicotinyloxy)anthracene-9,10-dione (**1**), a potential bridging diester ligand. Complexation reactions between **1** and Co(II) and Ni(II) perchlorate hexahydrate salts produce 2 : 1 ligand : metal monomeric complexes. One nicotinic nitrogen is bonded to a metal center while the second 'free' isonicotinic nitrogen is hydrogen bonded to water molecules, present from the hydrated salts used in the synthesis, ligated to the same metal center.

Keywords: Anthraquinone; Isonicotinic; Hydrogen bond; Transition metal

1. Introduction

In a previous report we explored the chelating ability of nicotinic derivatives of 1,8-disubstituted anthraquinone [1]. In these complexes, where the nicotinic nitrogen is located in the meta position, the bidentate anthraquinone ligand is ideally suited for chelating with metal cations. Herein we report the complexation chemistry of the isonicotinic derivative, where the new bidentate anthraquinone ligand, with *para* oriented nitrogens, has the potential to act as a bridging ligand (scheme 1). One-dimensional and dimeric metal complexes have previously been shown to be solvatochromic [2] and exhibit cooperative electrochemistry and photophysics due to metal–metal interactions [3]. Ligated anthraquinone ligands are also important in electron transfer reactions between metals and quinones [4–6], as potential DNA intercalators [7], and as selective luminescence sensors when incorporated within macrocycles [8]. In addition, isonicotinic and nicotinic acids play important roles in the metabolism of cells, and metal complexes of these potentially multidentate ligands have been used in drug synthesis [9]. Isonicotinic acid is also a common ligand found in the synthesis of classic molecular/supramolecular metal-organic framework complexes [10]. The synthesis and characterization of complexes in this work shows the formation of monomeric complexes, however, due to formation of an *intramolecular* hydrogen bond between an uncoordinated isonicotinic nitrogen and a coordinated protic solvent molecule.

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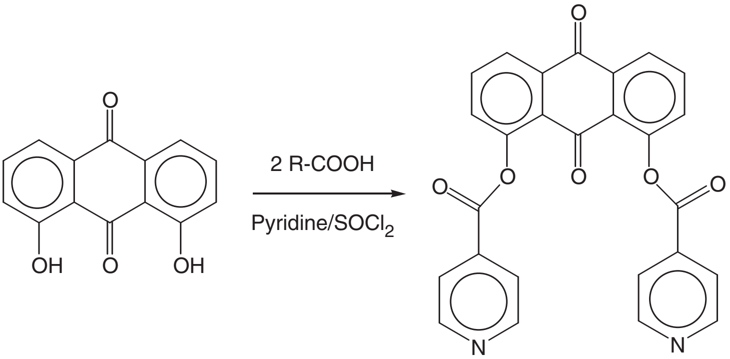


Scheme 1. Synthesis of ligand **1**.

2. Experimental

The metal salts cobalt(II) perchlorate hexahydrate (Aldrich), and nickel(II) perchlorate hexahydrate (Alfa Aesar) were used as purchased. CHN analyses were performed using a CE-440 (Exeter Analytical Inc.) elemental analyzer, and Electrospray Injection-Mass Spectroscopy was conducted using a Varian 500-MS IT mass spectrometer. 200 MHz ^{1}H spectra were obtained at room temperature in $CDCl_3$ using a Varian Mercury 200 spectrometer.

Caution: *Although we have experienced no difficulties with the perchlorate salts, these should be regarded as potentially explosive and handled with care.*

1,8-*Bis*(isonicotinyloxy)anthracene-9,10-dione (1): 2.00 g (16.3 mmol) of isonicotinic acid was added to 15 mL of thionyl chloride to yield a white precipitate. Addition of 15 mL of pyridine gave a clear solution and excess thionyl chloride was removed by passage of air through the mixture. 1.95 g (8.12 mmol) of 1,8-dihydroxyanthraquinone in 30 mL of pyridine was added and stirred for 30 min. The solution was poured into ice water and the product filtered and dried. Purification of the product was conducted by column chromatography using silica gel and CH_2Cl_2. Yield is ~60–70%, m.p. = 263–265°C. ^{1}H NMR ($CDCl_3$, 25°C): 7.50 (d, 2H, 2,7-anthraquinone); 7.78 (d, 4H, 3,5-pyridine rings); 7.85 (t, 2H, 3,6-anthraquinone); 8.28 (d, 2H, 4,5-anthraquinone); 8.71 (d, 2,6-pyridine rings). Elemental analyses calculated for $C_{26}H_{14}N_2O_6$: C, 69.33; H, 3.13; N, 6.22. Found: C, 69.30; H, 2.94; N, 6.25. ESI-MS Calc. for $[\mathbf{1}.H]^+ = 451.4$; Found 451.0.

[(1,8-*Bis*(isonicotinyloxy)anthracene-9,10-dione)$_2$Ni(H$_2$O)$_2$(CH$_3$CN)$_2$](ClO$_4$)$_2$ (2): 0.50 g (1.11 mmol) of **1** and 0.135 g (0.37 mmol) $Ni(ClO_4)_2 \cdot 6H_2O$ were stirred and heated in 60 mL ethanol for 5 h. A pale yellow-green solid was obtained, filtered, and air dried. The dried product was dissolved in CH_3CN and crystallized by vapor diffusion using diethyl ether, m.p. = 279–281°C (dec). Elemental analyses calculated for [(1,8-*bis*(isonicotinyloxy)anthraquinone)$_2$Ni(H$_2$O)$_2$(CH$_3$CN)$_2$](ClO$_4$)$_2$; $C_{56}H_{38}Cl_2N_6O_{22}Ni$: C, 52.69; H, 3.00; N, 6.58. Found: C, 52.06; H, 2.90; N, 6.41. ESI-MS calculated for $\{[Ni(\mathbf{1})_2](ClO_4)\}^+ = 1059.0$; Found 1059.0. ^{1}H NMR ($CDCl_3$, 25°C): 7.82 (d, 2H, 2,7-anthraquinone); 7.77 (d, 4H, 3,5-pyridine rings); 8.01 (t, 2H, 3,6-anthraquinone); 8.20 (d, 2H, 4,5-anthraquinone); 8.66 (d, 2,6-pyridine rings). IR; $\nu(CN) = 2287, 2315\ cm^{-1}$.

[(1,8-*Bis*(isonicotinyloxy)anthracene-9,10-dione)$_2$Co(H$_2$O)$_4$](ClO$_4$)$_2$ (3): 0.50 g (1.11 mmol) of **1** and 0.203 g (0.55 mmol) $Co(ClO_4)_2 \cdot 6H_2O$ were stirred and heated in 60 mL CH_3CN for 4 h. A pale green solid was obtained, filtered, and air dried. The dried product was dissolved in an 80 : 20 $CH_2Cl_2 : CH_3OH$ solution and crystallized by vapor diffusion using diethyl ether, m.p. = >300°C. Elemental analyses of the amorphous pale green solid calculated for [(1,8-*bis*(isonicotinyl)anthraquinone)$_2$ Co(H$_2$O)$_4$](ClO$_4$)$_2 \cdot CH_3CN$ $C_{54}H_{39}CoCl_2N_5O_{24}$: C, 51.00; H, 3.09; N, 5.51. Found: C, 50.91; H, 2.93; N, 5.85. ESI-MS calcd for $\{[Co(\mathbf{1})_2](ClO_4)\}^+ = 1059.2$; Found 1059.0.

Crystallographic data were collected using Mo-Kα radiation on a Bruker APEXII CCD diffractometer. Final cell constants were calculated from the *xyz* centroids of typically more than 6000 reflections from the data collection after integration [11]. Structures were solved by direct methods using SIR97 [12] and refined using SHELXL-97 [13] and WinGX [14]. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters, with the exception of hydrogen atoms involved in hydrogen bonding which were determined from residual electron density in the difference maps. The perchlorate in $\mathbf{1} \cdot HClO_4 \cdot CH_3CN$ is rotationally disordered around the O(8)–Cl(1) bond in a 75 : 25 ratio. The perchlorate in **2** has complete rotational disorder about the chlorine in a 77 : 23 ratio. Only the major fraction in each case has been treated anisotropically. Table 1 lists additional crystallographic and refinement information.

Table 1. Crystallographic and refinement data for [1,8-*bis*-(isonicotinyloxy)anthraquinoneH](ClO$_4$)·CH$_3$CN, [(1,8-*bis*-(isonicotinyloxy)anthraquinone)$_2$Ni(H$_2$O)$_2 \cdot$ (CH$_3$CN)$_2$](ClO$_4$)$_2$ (**2**), and [(1,8-*bis*-(isonicotinyloxy)-anthraquinone)$_2$Co(H$_2$O)$_4$](ClO$_4$)$_2$ (**3**).

	$\mathbf{1} \cdot HClO_4 \cdot CH_3CN$	**2**	**3**
Empirical formula	$C_{28}H_{18}ClN_3O_{10}$	$C_{56}H_{38}Cl_2N_6NiO_{22}$	$C_{52}H_{36}Cl_2CoN_4O_{24}$
Temperature (K)	295(2)	100(2)	295(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P21/n$	$P21/n$
Unit cells dimensions (Å, °)			
a	8.311(4)	17.900(2)	16.825(1)
b	10.666(6)	8.643(1)	9.487(1)
c	15.840(8)	19.208(2)	16.844(1)
α	91.359(7)		
β	96.981(6)	116.869(1)	105.715(1)
γ	107.532(6)		
Volume (Å^3)	1326.2(1)	2650.7(5)	2588.1(3)
Z	2	2	2
D_{Calcd} (g cm^{-3})	1.48	1.60	1.58
Absorb. coeff. (mm^{-1})	0.210	0.560	0.529
$F(000)$	608	1308	1258
θ range	2.01–25.45	2.10–25.29	2.00–25.40
Index ranges	$h(-10, 10)$, $k(12, 12)$, $l(-19, 19)$	$h(-21, 21)$, $k(10, 10)$, $l(-23, 23)$	$h(-20, 20)$, $k(-11, 11)$, $l(-20, 20)$
Reflections	11152	18711	25464
Indep. reflections	4865	4813	4772
Obser. reflections	3114	3154	3699
Max./Min. trans.	0.949/0.921	0.972/0.845	0.974/0.884
Data/restr/param.	4865/0/397	4813/0/420	4772/0/392
Goodness-of-fit	1.068	1.006	1.021
Final R indices [$I > 2\sigma(I)$]	0.0611	0.0471	0.0394
R indices (all data)	0.1758	0.1025	0.0942
Peak/hole	0.51/−0.40	0.55/−0.35	0.38/−0.40
CCDC number	672248	672246	672247

3. Results and discussion

Synthesis of the *bis*-isonicotinic anthraquinone diester (**1**) proceeds via conversion of isonicotinic acid into the acid chloride followed by combination with 1,8-dihydroxyanthraquinone and purification by column chromatography. Electrochemistry of the new ligand in CH_2Cl_2/0.1M TBAH shows two reversible, one-electron reductions of the quinone at $E^\circ = -0.87$ and –1.55 V *versus* Ag/AgCl, typical for anthraquinones. In the presence of perchloric acid, the ligand forms a protonated salt which has been characterized by X-ray crystallography (figure 1), and includes an acetonitrile solvate. Only one of the isonicotinyl nitrogens is protonated, N(2); and the isonicotinyl groups form hydrogen bonded dimers within the crystal; N(2)–H(99) ··· N1 = 2.751(5) Å; 165(5)° (figure 2). In addition, the anthraquinone moieties form pi-stacks throughout the structure, where interanthraquinone distances range from 3.5–3.7 Å.

For the formation of Ni(II) and Co(II) metal complexes, addition of two equivalents of **1** and one equivalent of a metal perchlorate yields monomeric complexes. Ligand **1** complexes to the metal through only one isonicotinyl nitrogen, while the second, free isonicotinyl nitrogen atom is hydrogen bonded to a protic solvent bound to the metal center. The structure of **2** (figure 3) shows two *trans* isonicotinyl ligands coordinated to a Ni(II) cation. The octahedral coordination sphere is completed by two *trans* acetonitrile molecules and two *trans* water molecules; Ni(1)–N(2) = 2.093(3); Ni(1)–N(3) = 2.079(3); Ni(1)–O(11) = 2.048(3) Å. The anthraquinone plane is bent, 14.7(1)°, and the isonicotinic group bonded to the Ni(II) is almost orthogonal to the anthraquinone plane, 85.6(1)°. The isonicotinic carbonyl groups point in opposite directions from each other. The isonicotinic group that hydrogen bonds to the coordinated water is rotated 76.8(1)° out of the plane of the anthraquinone

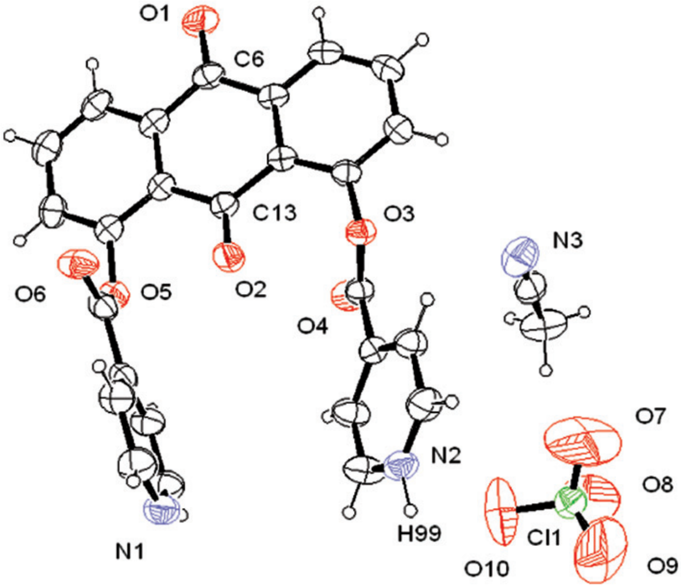


Figure 1. Thermal ellipsoid diagram (30%) of [1,8-*bis*(isonicotinyloxy)-anthraquinoneH](ClO_4) · CH_3CN. N(2)–H(99) ··· N1 = 2.751(5) Å; 165(5)°. C(6)–O(1) = 1.218(5) and C(13)–O(2) = 1.217(4) Å.

and is significantly bent towards the water to form the hydrogen bond, O(11)–H(11B)$\cdots$N(1) = 2.784(4) Å; 175(3)°. In addition, the second hydrogen atom on the O(11) water molecule is hydrogen bonded to a perchlorate, O(11)–H(11A)$\cdots$O(10)$_{\text{perchorate}}$ = 2.802(6) Å; 166(4)°.

Compound **3**, using Co(II) instead of Ni(II), is almost a duplicate of **2** except the coordination sphere is completed by four water molecules (figure 4), as crystals were grown from 80 : 20 CH_2Cl_2 : CH_3OH instead of acetonitrile. Bond distances within the coordination sphere are Co(1)–N(2) = 2.153(2); Co(1)–O(11) = 2.096(3); Co(1)–O(12) = 2.082(2) Å. One major difference between **2** and **3** is the isonicotinic carbonyl groups in **3** are located on the same side of the anthraquinone plane, with the anthraquinone plane bent slightly out of planarity, 6.0(1)°. The isonicotic groups are rotated 82.5(1) and 75.3(1)° out of the anthraquinone plane and accommodate an

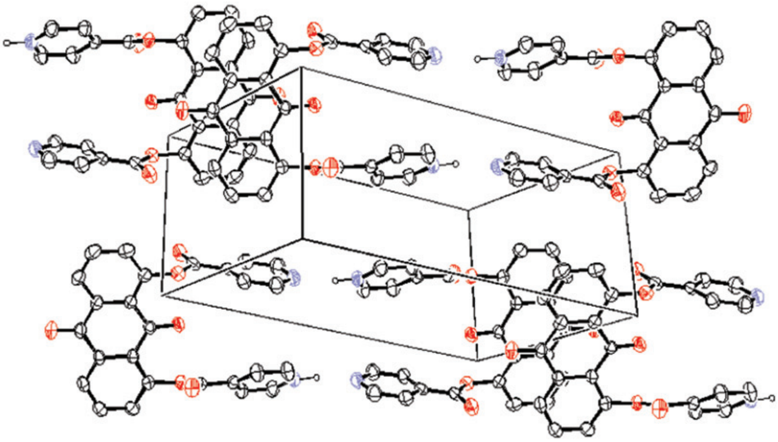


Figure 2. Packing diagram (30%) of $[\mathbf{1}\cdot H]^+$, showing alternating hydrogen-bonded N–H$\cdots$N isonicotinyl dimers and anthraquinone pi-stacks that form chains in the horizontal direction (running diagonally within the cell). The perchlorate and acetonitrile molecules have been excluded for clarity.

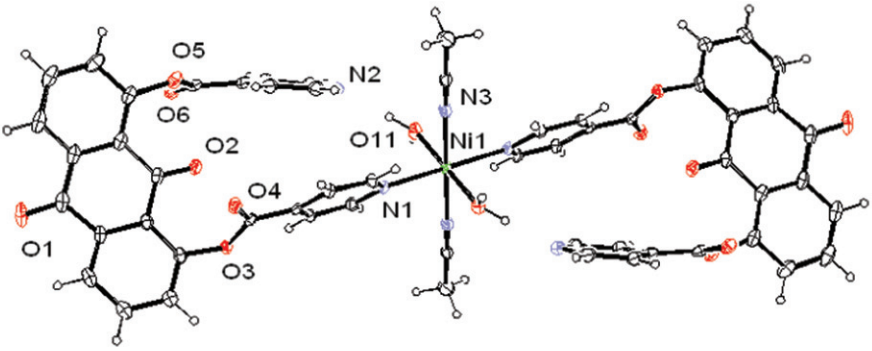


Figure 3. Thermal ellipsoid diagram (30%) of **2**. The non-coordinating perchlorates have been omitted. O(11)–H(11B)$\cdots$N(2) = 2.784(4) Å; 175(3)°; O(11)–H(11A)$\cdots$O(10)$_{\text{perchorate}}$ = 2.802(6) Å; 166(4)°. C(6)–O(1) = 1.223(6) and C(13)–O(2) = 1.223(5) Å.

isonicotinyl nitrogen-coordinated H_2O hydrogen bond, O(12)–H(12B) $\cdots$ N(1) = 2.728(4) Å; 166(5)°. The second coordinated water forms an additional hydrogen bond with perchlorate, O(11)–H(11A) $\cdots$ $O(6)_{perchlorate}$ = 2.636(4) Å; 165(3)°.

Addition of two equivalents of bidentate **1** to one equivalent of a metal(II) salt has the proper stoichiometry to potentially form *tetrakis* bridging complexes, A, as shown in scheme 2. However, we have isolated only 2 : 1 monomeric complexes, B, where the free isonicotinic nitrogen is hydrogen bonded to water bound to the same metal center, water present from the original metal hydrate salts used in synthesis. The anthraquinone spacer and the isonicotinic groups are also confined to essentially a single degree of rotation about the ester bond, which may not be flexible enough to

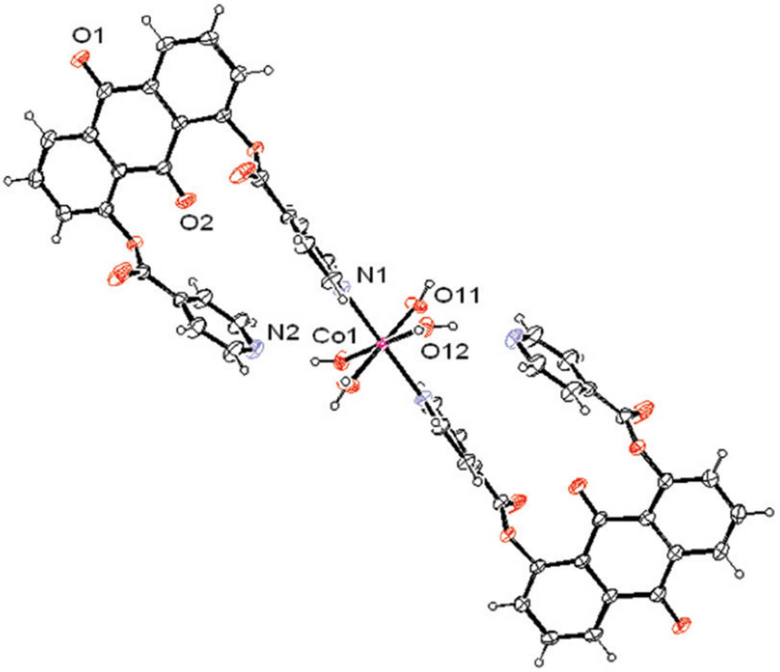
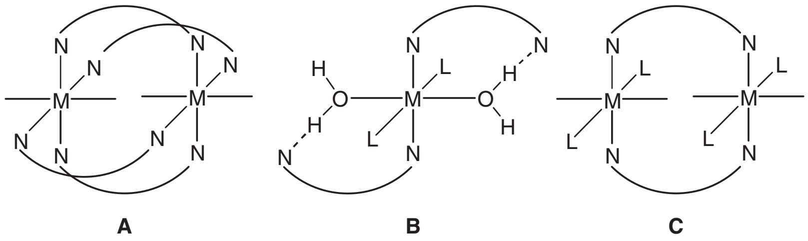


Figure 4. Thermal ellipsoid diagram (30%) of **3**. The non-coordinating perchlorates have been omitted. O(11)–H(11A) $\cdots$ $O(6)_{perchlorate}$ = 2.636(4) Å; 165(3)°; O(12)–H(12B) $\cdots$ N(2) = 2.728(4) Å; 166(5)°. O(1)–C(6) = 1.218(3); O(2)–C(13) = 1.217(3).



Scheme 2. Potential binding modes of ligand **1**: (a) bridging-tetrakis, (b) monomeric, (c) bridging-*bis*.

accommodate a bridging geometry if other solvates are coordinated to octahedral Co(II) and Ni(II). Formation of the *bis* 1 : 1 complex, as in C, could possibly prevent this; however, our attempts to isolate complexes different from **2** or **3** have been unsuccessful, indicating B may act as the thermodynamic sink.

Heating of the nickel complex **2** (~200°C) produces a change from green ($\lambda_{\max} = 650\,\mathrm{nm}$) to red ($\lambda_{\max} = 540\,\mathrm{nm}$). The color change is accompanied by complete loss of the IR stretching frequencies for coordinated acetonitrile observed at $\nu(\mathrm{CN}) = 2287, 2315\,\mathrm{cm}^{-1}$. In addition, the elemental analyses of the dried red product show a significant reduction in the percentage of nitrogen. It is possible that the uncoordinated isonicotinic nitrogen fills the coordination site of a vacating acetonitrile molecule to make a bridging complex, but poor solubility in nonpolar solvents prevented recrystallization. Addition of the red product to polar solvents such as acetonitrile, DMF and DMSO only returned the original green color of **2**. We are currently investigating the complexation chemistry of this ligand with transition metal cations that do not contain waters of hydration, specifically $[\mathrm{M(NCCH_3)}_x]^{n+}$.

Supplementary material

X-ray structure data can also be obtained free of charge from the Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/conts/retrieving.html

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