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SYNTHESIS AND CRYSTAL STRUCTURE OF A TRINUCLEAR NICKEL(II) ONO Pincer COMPLEX $[\text{Ni}(\text{Pydc})_2]_2[\text{Ni}(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O} \cdot 2(\text{C}_6\text{H}_{15}\text{N})$ **P. Jerome¹, N.S.P. Bhuvanesh², R. Karvembu¹**¹*Department of Chemistry, National Institute of Technology, Tiruchirappalli, India*

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A novel trinuclear nickel(II) ONO pincer complex $[\text{Ni}(\text{pydc})_2]_2[\text{Ni}(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O} \cdot 2(\text{C}_6\text{H}_{15}\text{N})$ (**1**) (H_2pydc = 2,6-pyridinedicarboxylic acid) is synthesized by the reaction between $\text{Ni}(\text{OAc})_2$ and H_2pydc in acetonitrile in the presence of triethylamine. A detailed study through single crystal XRD reveals that the compound crystallizes in the triclinic space group *P*-1 with cell parameters $a = 11.6646(3)$ Å, $b = 14.0999(4)$ Å, $c = 16.4633(5)$ Å, $\alpha = 80.189(2)^\circ$, $\beta = 75.539(2)^\circ$, $\gamma = 67.017(2)^\circ$. Both terminal Ni(II) centers are coordinated to two ONO pincer ligands (pydc) bridged by the nickel penta aqua unit. Further, triethyl ammonium neutralizes the trinuclear complex.

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Keywords: trinuclear, Ni(II) pincer complex, 2,6-pyridinedicarboxylic acid, crystal structure.**INTRODUCTION**

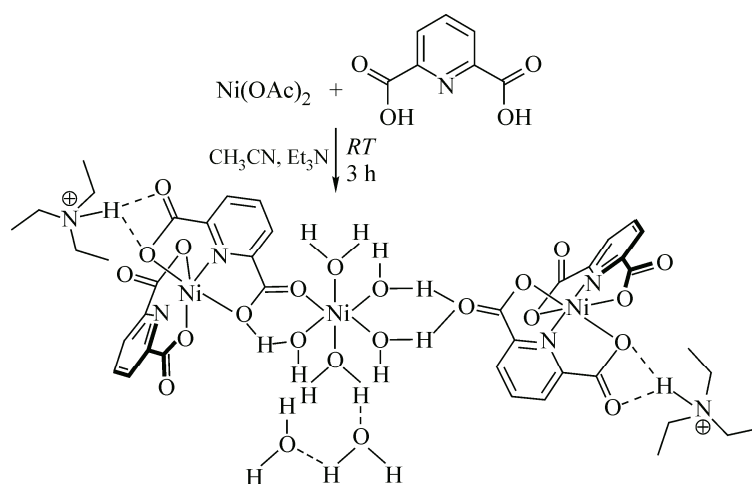
In recent decades, two new branches of coordination chemistry emerged significantly are metal-organic frameworks (MOFs) and supramolecular coordination complexes (SCCs). The former is comprised of infinite networks of metal centers or inorganic clusters bridged by simple organic linkers through metal-ligand coordination bonds. The latter encompasses discrete systems in which carefully selected metal centers undergo self-assembly with ligands containing multiple binding sites oriented with specific angularity to generate a finite supramolecular complex. Supramolecular frameworks can be constructed through two different interactions: (i) coordinate covalent bonds and (ii) noncovalent intermolecular forces such as hydrogen bonding, π – π stacking, and Coulomb interactions. Seldom, pincer complexes were also categorized under SCCs and that, too, after the first demonstration of pincer type ligands by Moulton and Shaw in 1976 [1, 2] Especially in Ni mediated pincer complexes, the arrangement of atoms in the pincer ligand coordinating to the metal is in the meridional fashion, thus the coordination is similar to the arrangement of atoms in supramolecular coordination complexes. In particular, H_2pydc -based pincer complexes find much attention in recent years because it forms rigid tridentate coordination with different transition metals [3, 4]. More importantly, weaker noncovalent interactions (especially hydrogen bonds) associated with Ni-based pincer complexes, played a crucial role in fundamental biological processes, such as the expression and transfer of genetic information. Moreover, it is essential for the molecular recognition between receptors and substrates as well as for the construction of complicated supramolecular arrays through the self-organization of molecules in supramolecular chemistry [5, 6]. Hence, it is paramount important to develop nickel-based pincer complex systems with weaker noncovalent interactions. Herein we report a synthetic route for the tri-

nuclear Ni(II) ONO pincer complex and its complete structural characterization by single crystal X-ray crystallography.

EXPERIMENTAL

Materials and measurements. All the chemicals and solvents used were of analytical grade. Nickel acetate, 2,6-pyridinedicarboxylic acid (Alfa Aesar), and triethylamine (Merck) were used as received. The FT-IR spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} on a Thermo Scientific–Nicolet iS5 spectrophotometer.

Synthesis of $[\text{Ni}(\text{pydc})_2]_2[\text{Ni}(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O} \cdot 2(\text{C}_6\text{H}_{15}\text{N})$ [1]. 2,6-Pyridinedicarboxylic acid (0.189 g, 1.1313 mmol) was added to a solution of nickel acetate (0.1 g, 0.5656 mmol) in acetonitrile. The reaction mixture was allowed to stir for 3 h at room temperature. Triethylamine was added dropwise until it raised the solution pH to 8.0. The green precipitate formed was filtered, washed, dried, and recrystallized from an acetonitrile-ethanol mixture. Yield: 0.183 g (28%) (Scheme 1).



Scheme 1. Synthesis of 1

X-ray crystal structure determination. Single crystal X-ray structural study of 1 was performed on a BRUKER GADDS X-ray (three-circle) diffractometer. Data were collected at 110 K from a Cu sealed X-ray tube ($K_{\alpha} = 1.5418 \text{ \AA}$ with a potential of 40 kV and a current of 40 mA) fitted with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes). The goniometer was controlled using the FRAMBO software, v.4.1.05 [7]. The data were collected by φ and ω scans and were scaled and reduced using the APEX2 software [8]. SADABS was employed to correct the data for absorption effects [9]. The structure was solved by direct methods using SHELXTL (SHELXS) and refined by full matrix least squares with SHELXTL (SHELXS) [10]. Hydrogen atoms were placed in idealized positions and refined using the riding model. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined (weighted least squares refinement on F^2) to convergence. PLATON was used to verify the absence of additional symmetry and voids. OLEX2 was employed for the thermal ellipsoidal plot (Fig. 1) [11]. Supplemental data for this article can be accessed on the publisher's website. CCDC NO. 1043431 contains the supplementary crystallographic data for 1. These data can be downloaded free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/datarequest.cif.

RESULTS AND DISCUSSION

FT-IR spectroscopy. The IR spectrum of 1 presents two distinguishable regions. In the high energy bands ranging from 3400 cm^{-1} to 2900 cm^{-1} there are three absorption peaks at 3376 cm^{-1} , 3090 cm^{-1} , and 3001 cm^{-1} due to $\nu(\text{O}-\text{H})$ of coordinated and free water molecules. At low energy,

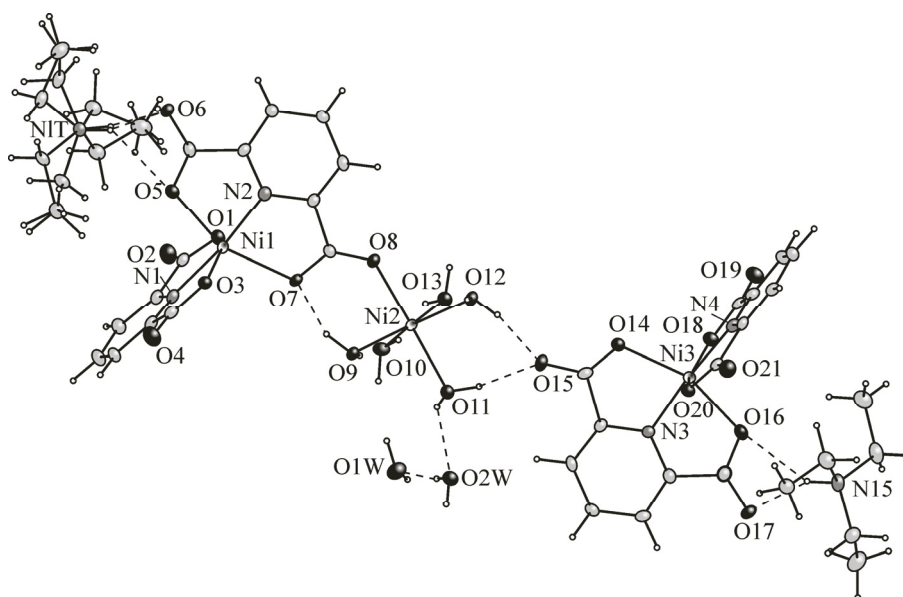


Fig. 1. The crystal structure of $[\text{Ni}(\text{pydc})_2]_2[\text{Ni}(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O} \cdot 2(\text{C}_6\text{H}_{15}\text{N})$ **1**

Table 1

Crystal data and structure refinement details for **1**

Compound	$[\text{Ni}(\text{pydc})_2]_2[\text{Ni}(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O} \cdot 2(\text{C}_6\text{H}_{15}\text{N})$
Empirical formula	$\text{C}_{40}\text{H}_{58}\text{N}_6\text{Ni}_3\text{O}_{23}$
Formula weight	1167.05
Temperature, K	110.15
Wavelength, Å	1.54178
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> , Å	11.6646(3), 14.0999(4), 16.4633(5)
α , β , γ , deg.	80.189(2), 75.539(2), 67.017(2)
Volume, Å ³	2405.72(12)
<i>Z</i>	2
Density (calculated), g/cm ³	1.611
Absorption coefficient, mm ⁻¹	2.157
<i>F</i> (000)	1216
Crystal size, mm	0.18×0.03×0.01
θ range for data collection, deg.	2.781 to 60.821
Index ranges	$-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-18 \leq l \leq 18$
Reflections collected / independent	40930 / 7140 [<i>R</i> (int) = 0.0542]
Completeness to $\theta = 67.679^\circ$, %	82.2
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7471 and 0.6304
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	7140 / 30 / 673
Goodness-of-fit on <i>F</i> ²	1.073
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0457, <i>wR</i> ₂ = 0.1400
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0563, <i>wR</i> ₂ = 0.1498
Extinction coefficient	n/a
Largest diff. peak and hole, e/Å ³	0.702 and -0.759

a series of absorption peaks is observed, including $\nu(\text{C—O})$ at 1686 cm^{-1} , $\nu(\text{pyridine ring})$ at 1618 cm^{-1} and 1577 cm^{-1} , $\nu(\text{O—H})$ at 914 cm^{-1} , and $\nu(\text{C—H})$ at 1376 cm^{-1} and 812 cm^{-1} . The $\nu(\text{O—C—O})$ in-plane deformation vibration, which occurs as a strong sharp band at 687 cm^{-1} in the free H_2pydc ligand, shifts to 729 cm^{-1} in the complex [6].

X-ray crystallography. The single crystal X-ray analysis confirms the trinuclear structure of **1** which crystallizes in the triclinic $P-1$ space group. Crystal data and structure refinement details are presented in Table 1. The formula unit of **1** consists of one $[\text{Ni}(\text{H}_2\text{O})_5]$ acting as a bridge between Ni(1) and Ni(3). The Ni(2) unit bridges Ni(1) and Ni(3) through hydrogen bonding and the O(8) atom. The bridging Ni(2) center shows a distorted octahedral coordination geometry [O(8)—Ni(2)—O(11) 177.83° ; O(9)—Ni(2)—O(12) 177.10° , and O(10)—Ni(2)—O(13) 175.67°] with five terminal water molecules and one carbonyl oxygen atom (Fig. 1). Ni(1) and Ni(3) also exhibit a distorted octahedral geometry [O(1)—Ni(1)—O(3) 155.16° ; O(5)—Ni(1)—O(7) 155.12° ; N(1)—Ni(1)—N(2) 172.35° ; O(14)—Ni(3)—O(16) 156.66° ; O(18)—Ni(3)—O(20) 155.30° , and N(3)—Ni(3)—N(4) 175.58°] and each coordinated to two ONO pincer (pydc) ligands. Each pincer ligand acts in a tridentate fashion, binding the metal center at O, N and O forming two five-membered chelate rings with bite angles of 78.63° [O(5)—Ni(1)—N(2)], 76.60° [O(7)—Ni(1)—N(2)], 78.10° [O(1)—Ni(1)—N(1)], 77.16° [O(3)—Ni(1)—N(1)], 77.97° [O(14)—Ni(3)—N(3)], 78.72° [O(16)—Ni(3)—N(3)], 77.04° [O(18)—Ni(3)—N(4)], and 78.26° [O(20)—Ni(3)—N(4)]. The equatorial plane of Ni(1) and Ni(3) constitutes two nitrogen and two carboxylate oxygen atoms together with Ni while axial sites are occupied by remaining two carboxylate oxygen atoms. The bond distances between the central Ni atoms and coordinated atoms are in the usual range (Table 2) [6]. Two triethyl ammonium ($\text{C}_6\text{H}_{15}\text{N}$) molecules and two uncoordinated water molecules are also present in the structure. Packing diagram and hydrogen bonding interactions are depicted in Fig. 2. Hydrogen bond parameters are provided in Table 3.

Table 2

Selected bond lengths (Å) and angles (deg.)

Bond lengths		Angles		Angles	
Ni(1)—O(1)	2.118(2)	O(1)—Ni(1)—O(3)	155.16(9)	Ni(2)—O(9)—H(9A)	111.3
Ni(1)—O(3)	2.180(2)	O(1)—Ni(1)—O(7)	94.99(9)	Ni(2)—O(9)—H(9B)	111.0
Ni(1)—O(5)	2.087(2)	O(3)—Ni(1)—O(7)	91.68(9)	H(9A)—O(9)—H(9B)	107.6
Ni(1)—O(7)	2.202(2)	O(5)—Ni(1)—O(1)	88.40(9)	Ni(2)—O(10)—H(10A)	111.0
Ni(1)—N(1)	1.972(3)	O(5)—Ni(1)—O(3)	95.51(9)	Ni(2)—O(10)—H(10B)	110.8
Ni(1)—N(2)	1.978(3)	O(5)—Ni(1)—O(7)	155.12(9)	H(10A)—O(10)—H(10B)	107.8
Ni(2)—O(8)	2.072(2)	N(1)—Ni(1)—O(1)	78.10(10)	Ni(2)—O(11)—H(11A)	110.4
Ni(2)—O(9)	2.051(2)	N(1)—Ni(1)—O(3)	77.16(10)	Ni(2)—O(11)—H(11B)	110.2
Ni(2)—O(10)	2.072(2)	N(1)—Ni(1)—O(5)	93.93(11)	H(11A)—O(11)—H(11B)	108.4
Ni(2)—O(11)	2.077(2)	N(1)—Ni(1)—O(7)	110.90(10)	Ni(2)—O(12)—H(12A)	110.6
Ni(2)—O(12)	2.040(2)	N(1)—Ni(1)—N(2)	172.35(12)	Ni(2)—O(12)—H(12B)	110.6
Ni(2)—O(13)	2.080(2)	N(2)—Ni(1)—O(1)	103.24(10)	H(12A)—O(12)—H(12B)	108.1
		N(2)—Ni(1)—O(3)	101.58(10)	Ni(2)—O(13)—H(13A)	110.6
		N(2)—Ni(1)—O(5)	78.63(10)	Ni(2)—O(13)—H(13B)	110.4
		N(2)—Ni(1)—O(7)	76.60(10)	H(13A)—O(13)—H(13B)	108.2
		C(1)—O(1)—Ni(1)	114.5(2)	C(2)—N(1)—Ni(1)	118.4(2)
		C(7)—O(3)—Ni(1)	113.9(2)	C(2)—N(1)—C(6)	121.4(3)
		C(8)—O(5)—Ni(1)	114.9(2)	C(6)—N(1)—Ni(1)	119.8(2)
		C(14)—O(7)—Ni(1)	113.8(2)	C(9)—N(2)—Ni(1)	117.9(2)
		C(14)—O(8)—Ni(2)	130.0(2)	C(9)—N(2)—C(13)	121.6(3)
				C(13)—N(2)—Ni(1)	120.6(2)

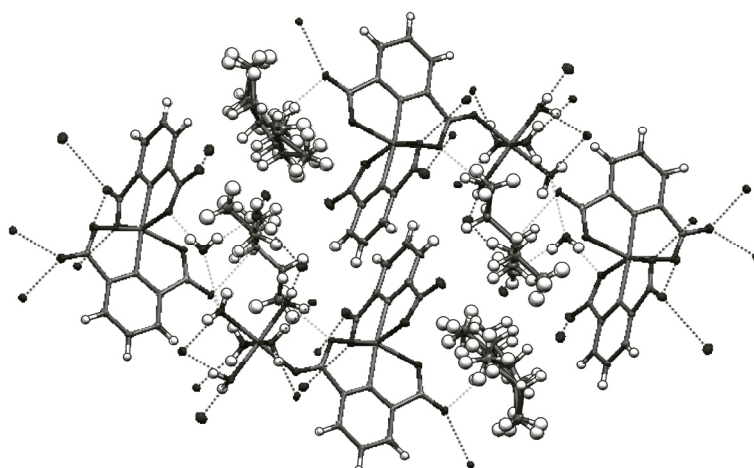
Fig. 2. Hydrogen bonding in **1**

Table 3

Hydrogen bond parameters (Å and deg.)

D—H...A	<i>d</i> (D—H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
O(9)—H(9A)...O(19)#1	0.88	1.85	2.723(3)	171.9
O(9)—H(9B)...O(7)	0.88	1.86	2.666(3)	150.9
O(10)—H(10A)...O(3)#2	0.87	2.11	2.935(3)	156.9
O(10)—H(10B)...O(17)#3	0.87	1.85	2.711(3)	166.2
O(11)—H(11A)...O(15)	0.87	1.90	2.710(3)	156.2
O(11)—H(11B)...O(2W)	0.87	2.09	2.735(3)	131.0
O(12)—H(12A)...O(15)	0.87	1.85	2.700(3)	166.4
O(12)—H(12B)...O(4)#2	0.87	1.83	2.660(3)	159.0
O(13)—H(13A)...O(6)#4	0.87	1.99	2.825(3)	159.8
O(13)—H(13B)...O(18)#1	0.87	1.97	2.774(3)	153.5
O(1W)—H(1WA)...O(19)#1	0.85	2.04	2.885(4)	169.9
O(1W)—H(1WB)...O(21)#5	0.85	2.03	2.829(3)	156.5
O(2W)—H(2WA)...O(20)#3	0.85	1.96	2.804(3)	172.7
O(2W)—H(2WB)...O(1W)	0.85	1.95	2.792(3)	169.7
N(1S)—H(1S)...O(16)	1.00	2.28	3.112(4)	140.0
N(1S)—H(1S)...O(17)	1.00	1.94	2.855(4)	150.7
N(1T)—H(1T)...O(5)	1.00	2.44	3.226(4)	135.2
N(1T)—H(1TA)...O(6)	1.00	1.86	2.842(4)	168.1

Symmetry transformations used to generate equivalent atoms: #1 $-x+2, -y, -z$, #2 $-x+1, -y, -z+1$, #3 $-x+1, -y, -z$, #4 $-x+2, -y, -z+1$, #5 $x, y+1, z$.

CONCLUSIONS

The reaction between Ni(OAc)₂ and H₂pydc in acetonitrile in the presence of triethylamine creates a new trinuclear nickel(II) ONO pincer complex [Ni(pydc)₂]₂[Ni(H₂O)₅]·2H₂O·2(C₆H₁₅N) (**1**). The packing pattern and hydrogen bonding clearly showed a supramolecular framework constructed through the pincer complex. The architecture of the complex is constructed by bridging the [Ni(pydc)₂] units through [Ni(H₂O)₅] and water molecules *via* coordination and hydrogen bonding.

This study is very helpful to understand the coordination behavior of ONO pincer ligands towards Ni(II). The authors are thankful to DST SERB for the financial support (Project No. SR/S1/IC-72/2010).

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