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Nickel(II) complexes with N,N,O-donor Schiff bases. Self-assembly to two-dimensional network via hydrogen bonding

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The syntheses, characterization and crystal structures of two mononuclear nickel(II) complexes are described. Reactions of $Ni(O_2CCH_3)_2{\cdot}4H_2O$ with the Schiff bases derived from 2-pyridinecarbaldehyde and *ortho*-aminophenol (Hpaap) and 2-pyridinecarbaldehyde and *ortho*-aminobenzoic acid (Hpaab) in methanolic media afford the complexes in good yields. The elemental analysis, magnetic moments, and spectral features of the complexes are consistent with the formulae $[Ni(paap)_2]{\cdot}CH_3COOH{\cdot}H_2O$ and $[Ni(paab)_2]{\cdot}2H_2O$. Crystal data for $[Ni(paap)_2]{\cdot}CH_3COOH{\cdot}H_2O$: monoclinic, $P2_1/c$, $a = 9.675(2)$ Å, $b = 17.109(5)$ Å, $c = 14.403(4)$ Å, $\beta = 92.903(11)^\circ$, $V = 2381.1(11)$ Å^3, and $Z = 4$ and for $[Ni(paab)_2]{\cdot}2H_2O$: triclinic, $P\bar{1}$, $a = 9.834(3)$ Å, $b = 11.319(3)$ Å, $c = 13.130(4)$ Å, $\alpha = 84.68(3)$, $\beta = 67.54(3)$, $\gamma = 85.49(2)^\circ$, $V = 1343.4(6)$ Å^3, and $Z = 2$. In each complex, two tridentate monoanionic meridionally spanning ligands form a distorted octahedral N_4O_2 coordination sphere around the metal ion. In $[Ni(paap)_2]{\cdot}CH_3COOH{\cdot}H_2O$, two metal coordinated phenolate-O atoms are hydrogen bonded to CH_3COOH and H_2O, respectively. Intramolecular C—H···O interactions involving the water molecule and the C—H from azomethine and aromatic fragments lead to a two-dimensional network of $[Ni(paap)_2]{\cdot}CH_3COOH{\cdot}H_2O$ in the crystal lattice. An uncoordinated carboxylate O-atom in $[Ni(paab)_2]{\cdot}2H_2O$ is hydrogen bonded to both water molecules. One of the water molecules is again hydrogen bonded to the corresponding symmetry related water molecule forming a dimer. The azomethine groups and the metal coordinated carboxylate-O atoms in $[Ni(paab)_2]$ are involved in intermolecular C—H···O interactions forming a chain-like arrangement of the molecules. The water dimers act as bridges between these chains and a two-dimensional network of $[Ni(paab)_2]{\cdot}2H_2O$ is formed.

KEY WORDS: Nickel(II) complexes; Schiff bases; crystal structures; hydrogen bonding; self-assembly.

Introduction

Extended assemblies of complexed metal ions having one-, two-, and three-dimensional networks are of considerable current interest due to their photophysical, magnetic and conducting properties.[1] These metallo-organic based materials are also attractive with respect to mimicking the structural and functional features of zeolites.[2] Self-assembly of transition metal ion complexes into a desired structural network has been realized by utilizing the metal

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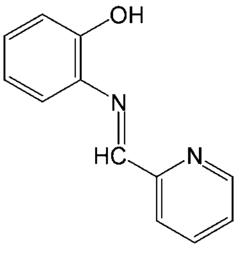
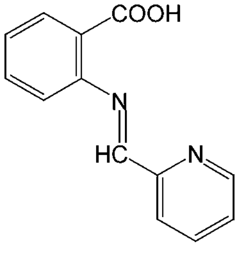
ion's preference for a particular coordination geometry, design and use of suitable ligands and weak noncovalent intermolecular interactions such as van der Waals interactions, hydrogen bonding and π–π interactions.[1–3] The proton of polarized azomethine (—CH=N—) group in metal coordinated Schiff bases may help in self-assembly of the complex molecules by participating in intermolecular hydrogen bonding.[4] The acceptor atom in this type of hydrogen bonding can be a part of the complex molecule or of the solvent molecule trapped in the crystal lattice. Thus the resulting network pattern can be influenced by the orientation of the acceptor atom with respect to the azomethine moiety. Herein, we report the syntheses, characterization and crystal structures of two hexacoordinated nickel(II) complexes with Schiff bases obtained by condensation reactions of 2-pyridinecarbaldehyde with *ortho*-aminophenol (Hpaap) and with *ortho*-aminobenzoic acid (Hpaab). In the deprotonated state, these Schiff bases can coordinate a metal ion via the pyridine-*N*, the imine-*N* and the phenolate-*O* (paap$^-$) or the carboxylate-*O* (paab$^-$). The paap$^-$ will form two five-membered chelate rings, whereas the paab$^-$ will form one six- and one five-membered chelate ring. The complexes have been isolated as [Ni(paap)$_2$]·CH$_3$COOH·H$_2$O and [Ni(paab)$_2$]·2H$_2$O. In the crystal lattice, both species form two-dimensional network via hydrogen bonding interactions involving the polarized azomethine moieties and the water molecules.



Hpaap



Hpaab

Experimental

Materials and physical measurements

The chemicals and solvents used in this work were of analytical grade available commercially and were used without further purification.

Microanalytical (C, H, N) data were obtained with a Perkin-Elmer Model 240C elemental analyzer. Room temperature solid state magnetic susceptibilities were measured by using a Sherwood Scientific magnetic susceptibility balance. Diamagnetic corrections calculated from Pascal's constants[5] were used to obtain the molar paramagnetic susceptibilities. Solution electrical conductivities were measured with a Digisun DI-909 conductivity meter. Infrared spectra were collected by using KBr pellets on a Jasco-5300 FT-IR spectrophotometer. Electronic spectra were recorded on a Shimadzu 3101-PC UV/vis/NIR spectrophotometer.

Synthesis of [Ni(paap)$_2$]·CH$_3$COOH·H$_2$O

To a methanol solution (20 mL) of 2-aminophenol (230 mg, 2.1 mmol), 0.2 mL (225 mg, 2.1 mmol) of 2-pyridinecarbaldehyde was added and the mixture was refluxed for 1.5 h. Powdered Ni(O$_2$CCH$_3$)$_2$·4H$_2$O (260 mg, 1.05 mmol) was added to the clear light yellow solution. The resulting red mixture was refluxed for another 1.5 h and then cooled to room temperature. The red–brown crystalline solid separated was collected by filtration, washed with ice-cold methanol and finally dried in air. Yield obtained was 470 mg (84%). A single crystal suitable for X-ray structure determination was selected from this material. Anal. Calcd for C$_{26}$H$_{24}$N$_4$O$_5$Ni: C, 58.77; H, 4.55; N, 10.54%. Found: C, 58.43; H, 4.39; N, 10.29%. Selected infrared bands (cm^{-1}): 3046 br, 1703 s, 1586 s, 1559 m, 1537 m, 1479 s, 1456 s, 1362 m, 1317 m, 1300 w, 1281 s, 1250 m, 1184 m, 1144 s, 1044 m, 864 m, 806 m, 756 s, 637 w, 586 w, 515 s, 447 w, 417 w. Electronic spectral data in CH$_3$OH solution

($\lambda_{\max}$, nm (ε, M^{-1} cm^{-1})): 855 (23), 480 (18,800), 323 (21,000), 241 (21,100). Solid state magnetic moment at 300 K (μ_{eff}, μ_{B}): 3.17.

Synthesis of [Ni(paab)$_2$]·2H$_2$O

[Ni(paab)$_2$]·2H$_2$O was prepared in methanolic medium from 2-aminobenzoic acid, 2-pyridinecarbaldehyde and Ni(O$_2$CCH$_3$)$_2$·4H$_2$O (2:2:1 mole ratio) as brown microcrystalline solid in 75% yield by following the same procedure as described above. Single crystal suitable for X-ray structure determination was obtained directly from the synthetic reaction mixture. Anal. calcd. for $C_{26}H_{22}N_4O_6Ni$: C, 57.26; H, 4.07; N, 10.27%. Found: C, 57.05; H, 3.96; N, 10.14%. Selected infrared bands (cm^{-1}): 3397 br, 1589 s, 1560 s, 1483 m, 1441 m, 1358 s, 1236 w, 1153 w, 1101 w, 1049 m, 1017 m, 918 s, 864 s, 824 s, 777 s, 745 m, 692 s, 640 m, 579 w, 546 w, 488 w, 417 m. Electronic spectral data in CH$_3$OH solution ($\lambda_{\max}$, nm (ε, M^{-1} cm^{-1})): 900 (15), 350sh (15,300), 328 (19, 800), 243sh (16,700). Solid state magnetic moment at 300 K (μ_{eff}, μ_{B}): 3.19.

X-ray crystallography

For each of the two complexes, the crystal was mounted at the end of a glass fibre and covered with a thin layer of epoxy. The data were collected on an Enraf-Nonius Mach-3 single crystal diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) by ω-scan method. Unit cell parameters of [Ni(paap)$_2$]·CH$_3$COOH·H$_2$O and [Ni(paab)$_2$]·2H$_2$O were determined by the least-squares fit of 25 reflections having 2θ values in the range 19–21° and 18–22°, respectively. Stability of the crystal was monitored by measuring the intensities of three check reflections after every 1.5 h during the data collection. No decay was observed in either case. [Ni(paap)$_2$]·CH$_3$COOH·H$_2$O and [Ni(paab)$_2$]·2H$_2$O crystallize in $P2_1/c$ and $P\bar{1}$ space group, respectively. In each case, the position of the unique nickel atom was determined from a Patterson map. The remaining non-hydrogen atoms were determined from successive Fourier difference syntheses. The model was then refined by full-matrix least-squares procedures on F^2. For both structures all the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the water molecule and the —COOH goup in [Ni(paap)$_2$]·CH$_3$COOH·H$_2$O were located in a difference map. For [Ni(paab)$_2$]·2H$_2$O hydrogen atoms of only one water molecule could be located in a difference map. For each structure all the hydrogen atoms were included in the model at idealized positions for structure factor calculation, but not refined. Calculations were done using the programs of WinGX[6] for data reduction, and SHELX-97 programs[7] for structure solution and refinement. The Ortex6a[8] and Platon[9] packages were used for molecular graphics. Significant crystal data are summarized in Table 1.

Results and discussion

Synthesis and some properties

Two new hexacoordinated nickel(II) complexes have been synthesized in good yields by reacting one mole equivalent of Ni(O$_2$CCH$_3$)$_2$·4H$_2$O with the Schiff bases Hpaap and Hpaab preformed in methanolic media by refluxing 2 mole equivalents each of 2-pyridinecarbaldehyde and the corresponding ortho substituted anilines. The elemental analysis data for the isolated crystalline solids are consistent with the formulae [Ni(paap)$_2$]·CH$_3$COOH·H$_2$O and [Ni(paab)$_2$]·2H$_2$O. The solid state room temperature (300 K) magnetic moments of [Ni(paap)$_2$]·CH$_3$COOH·H$_2$O and [Ni(paab)$_2$]·2H$_2$O are 3.17 and 3.19 μ_{B}, respectively. These values are consistent with an $S = 1$ spin state of the metal ion in each complex. Both species are electrically nonconducting in methanol solutions. Thus the ligands are monoanionic and the oxidation state of the metal ion is +2 in each complex.

Table 1. Crystallographic Data

Compound	$[Ni(paap)_2]\cdot CH_3COOH\cdot H_2O$	$[Ni(paab)_2]\cdot 2H_2O$
CCDC deposition no.	216554	216555
Empirical formula	$NiC_{26}H_{24}N_4O_5$	$NiC_{26}H_{22}N_4O_6$
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	9.675(2)	9.834(3)
b (Å)	17.109(5)	11.319(3)
c (Å)	14.403(4)	13.130(4)
α (°)	90	84.68(3)
β (°)	92.903(11)	67.54(3)
γ (°)	90	85.49(2)
V (Å^3)	2381.1(11)	1343.4(6)
Z	4	2
$\rho_{\text{calcd.}}$ (g cm^{-3})	1.482	1.348
μ (mm^{-1})	0.861	0.768
Reflections collected	4287	4487
Unique reflections	4033	4487
R_{int}	0.214	0.00
Reflections ($I > 2\sigma(I)$)	2594	2797
Parameters	326	334
$R1$, $wR2$ ($I > 2\sigma$(I))	0.0747, 0.1899	0.0790, 0.1908
$R1$, $wR2$ (all data)	0.1206, 0.2249	0.1292, 0.2275
Goodness-of-fit on F^2	1.060	1.009
Largest peak, hole (e Å^{-3})	0.747, −0.748	0.694, −0.392

Infrared and electronic spectral characteristics

The infrared spectrum of $[Ni(paap)_2]\cdot CH_3COOH\cdot H_2O$ displays a broad band centered at 3046 cm^{-1} and a strong band at 1703 cm^{-1}. These two bands are ascribable to the carboxyl group[10] of the acetic acid molecule that is hydrogen bonded to the metal coordinated phenolate-O of one of the two ligands (*vide infra*). The strong and sharp band observed at 1586 cm^{-1} is most likely due to the azomethine C=N stretching.[11] The medium to strong bands in the range 1559–1456 cm^{-1} are possibly due to the vibrations associated with the aromatic C=C fragments of the ligands.[11] The broad band observed at 3397 cm^{-1} in the infrared spectrum of $[Ni(paab)_2]\cdot 2H_2O$ is most likely due to the lattice water molecules.[12] The origin of the strong band with a shoulder at 1589 cm^{-1} and another strong band at 1358 cm^{-1} might involve the metal coordinated carboxylate functionalities present in the ligands. The former is assigned to the ν_{as} stretch and the latter is assigned to the ν_{s} stretch.[13] The shoulder at the higher energy band is possibly due to the —HC=N— group of the ligand. Like $[Ni(paap)_2]\cdot CH_3COOH\cdot H_2O$, $[Ni(paab)_2]\cdot 2H_2O$ also displays medium to strong bands in the range 1560–1441 cm^{-1} attributable to the aromatic parts of the ligands.

In methanol solutions, $[Ni(paap)_2]\cdot CH_3COOH\cdot H_2O$ and $[Ni(paab)_2]\cdot 2H_2O$ display a weak absorption at 855 and 900 nm, respectively. This absorption is assigned to the ν_1 transition for an octahedral nickel(II) complex.[14] The difference in this band position suggests that paap$^-$ is a stronger ligand than paab$^-$. The other two coordinating atoms being same in both ligands the better σ-bonding ability of the phenolate-*O* compared to that of the carboxylate-*O* is likely to be one of the major reasons for this observation. In addition to this weak absorption, both complexes display three intense absorptions in the range 480–240 nm. These higher energy absorptions are most likely due to ligand-to-metal charge transfer and intraligand transitions.

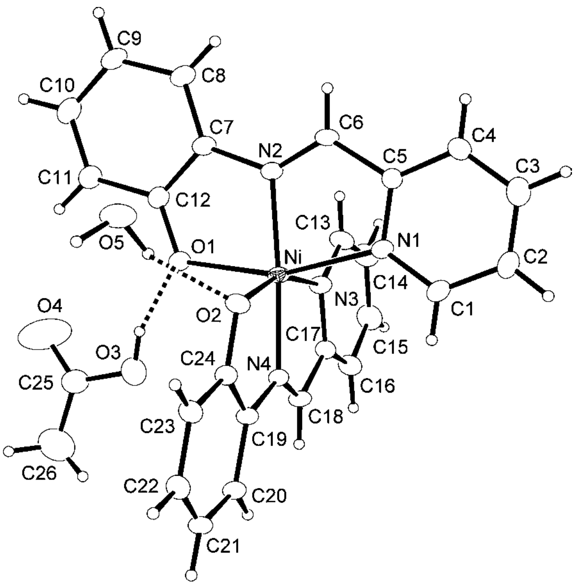


Fig. 1. Structure of $[Ni(paap)_2]{\cdot}CH_3COOH{\cdot}H_2O$ with the atom-labeling scheme. All non-hydrogen atoms are represented by their 15% probability thermal ellipsoids. Hydrogen bonding interactions are shown by dashed lines.

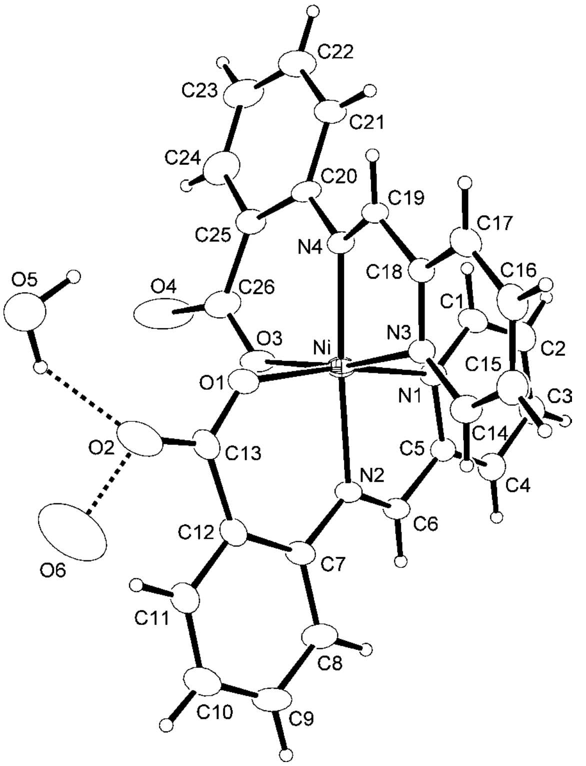


Fig. 2. Structure of $[Ni(paab)_2]{\cdot}2H_2O$ with the atom-labeling scheme. All non-hydrogen atoms are represented by their 15% probability thermal ellipsoids. Hydrogen bonding interactions are shown by dashed lines.

Description of structures

The structures of $[Ni(paap)_2]{\cdot}CH_3COOH{\cdot}H_2O$ and $[Ni(paab)_2]{\cdot}2H_2O$ are depicted in Figs. 1 and 2, respectively. In each complex, the tridentate ligands bind the metal ion meridionally and form a N_4O_2 coordination sphere. The bond parameters associated with the metal ion (Tables 2 and 3) indicate a distorted octahedral coordination geometry. The average chelate bite angle (78.23°) in the five-membered ring formed by the pyridine-*N* and the imine-*N* in $[Ni(paap)_2]$ is slightly smaller than that (80.57°) in $[Ni(paab)_2]$. The same for the other five-membered ring constituted by the imine-*N* and the phenolate-*O* in $[Ni(paap)_2]$ is 81.32°. On the other hand, for $[Ni(paab)_2]$ the average chelate bite angle (89.36°) in the six-membered ring formed by the imine-*N* and the carboxylate-*O* is very close to the ideal value of 90°. As a consequence, the average *trans* N—Ni—O angle (169.62°) in $[Ni(paab)_2]$ is significantly larger than that (159.41°) in $[Ni(paap)_2]$. However, the *trans* *N*(imine)—Ni—*N*(imine) angles are very similar in both complexes. The values are 176.13(19) and 176.6(2)° for $[Ni(paap)_2]$ and $[Ni(paab)_2]$, respectively. The Ni—N(pyridine), Ni—N(imine), Ni—O(phenolate), and Ni—O(carboxylate) bond distances observed in these complexes are within the range reported for nickel(II) complexes having the same coordinating atoms.[14a,15] In $[Ni(paap)_2]{\cdot}CH_3COOH{\cdot}H_2O$, the acetic acid molecule is hydrogen bonded to one of the phenolate-*O* atoms (Fig. 1). The O1···O3 distance and the O1···H—O3 angle are 2.605(8) Åand 148.54°, respectively. The water molecule is hydrogen bonded with the other phenolate-O atom. The O2···O5 distance and the O2···H—O5 angle are 2.721(8) Åand 112.23°, respectively. On the other hand, both water molecules are hydrogen bonded to the same uncoordinated carboxylate-*O*

Table 2. Selected Bond Parameters for $[Ni(paap)_2]\cdot CH_3COOH\cdot H_2O$

Bond distances (Å)			
Ni—N(1)	2.114(5)	Ni—N(4)	2.005(5)
Ni—N(2)	2.007(5)	Ni—O(1)	2.053(4)
Ni—N(3)	2.122(5)	Ni—O(2)	2.086(4)
Bond angles (°)			
N(1)—Ni—N(2)	78.17(19)	N(2)—Ni—O(2)	98.65(19)
N(1)—Ni—N(3)	90.0(2)	N(3)—Ni—N(4)	78.3(2)
N(1)—Ni—N(4)	105.68(19)	N(3)—Ni—O(1)	91.51(19)
N(1)—Ni—O(1)	159.01(18)	N(3)—Ni—O(2)	159.82(18)
N(1)—Ni—O(2)	92.99(18)	N(4)—Ni—O(1)	95.12(18)
N(2)—Ni—N(3)	101.5(2)	N(4)—Ni—O(2)	81.64(19)
N(2)—Ni—N(4)	176.13(19)	O(1)—Ni—O(2)	92.77(18)
N(2)—Ni—O(1)	81.01(18)		

in $[Ni(paab)_2]\cdot 2H_2O$ (Fig. 2). The O2···O5 and O2···O6 distances are 2.728(13) and 3.25(2) Å, respectively. The O2···H—O5 angle is 143.28°. There is no interaction between the two water molecules.

Hydrogen bonding and self-assembly

The self-assembly of $[Ni(paap)_2]\cdot CH_3COOH\cdot H_2O$ and $[Ni(paab)_2]\cdot 2H_2O$ via intermolecular hydrogen bonding interactions leads to the two-dimensional network in each case (Figs. 3 and 4). For $[Ni(paap)_2]\cdot CH_3COOH\cdot H_2O$ acetic acid has no role in the formation of the network. As mentioned before it is only connected to one of the phenolate-*O* in $[Ni(paap)_2]$ through a hydrogen bond. In the crystal lattice, the water molecules are the basic units for linking the $[Ni(paap)_2]\cdot CH_3COOH$ units into a two-dimensional arrangement (Fig. 3). Each water molecule acts as the bridge between three of these units by participating in three hydrogen bonding interactions. These are one O—H···O and two C—H···O interactions. In the O—H···O interaction, the O-atom of the water molecule acts as the donor atom and the phenolate-*O* of one $[Ni(paap)_2]$ moiety acts as the acceptor atom (*vide supra*). In the C—H···O interactions, the water O-atom acts as the acceptor atom. The aromatic C-atom (C20) meta to the phenolate-O of the second $[Ni(paap)_2]$ unit and the C-atom (C6) of the azomethine fragment of the third $[Ni(paap)_2]$ unit act as the donor atoms in these two hydrogen bonds. The C20···O5 and C6···O5 distances are 3.364(10) and 3.424(8) Å,

Table 3. Selected Bond Parameters for $[Ni(paab)_2]\cdot 2H_2O$

Bond distances (Å)			
Ni—N(1)	2.085(5)	Ni—N(4)	2.045(5)
Ni—N(2)	2.064(4)	Ni—O(1)	2.011(5)
Ni—N(3)	2.079(5)	Ni—O(3)	2.011(5)
Bond angles (°)			
N(1)—Ni—N(2)	81.26(19)	N(2)—Ni—O(3)	92.20(18)
N(1)—Ni—N(3)	96.09(18)	N(3)—Ni—N(4)	79.89(19)
N(1)—Ni—N(4)	96.00(19)	N(3)—Ni—O(1)	87.6(2)
N(1)—Ni—O(1)	169.87(18)	N(3)—Ni—O(3)	168.38(18)
N(1)—Ni—O(3)	90.4(2)	N(4)—Ni—O(1)	93.94(18)
N(2)—Ni—N(3)	98.31(19)	N(4)—Ni—O(3)	89.86(19)
N(2)—Ni—N(4)	176.6(2)	O(1)—Ni—O(3)	87.7(2)
N(2)—Ni—O(1)	88.87(19)		

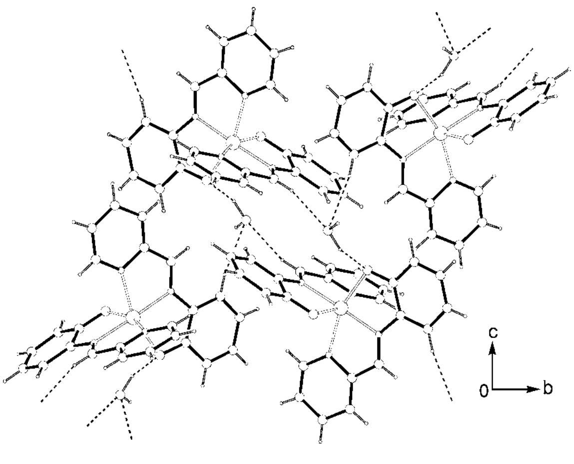


Fig. 3. A view of the two-dimensional network of [Ni(paap)$_2$]·CH_3COOH·H_2O along the *a*-axis. The acetic acid molecules are not shown for clarity.

respectively. The corresponding C—H···O angles are 161.19 and 163.81°, respectively.

In the self-assembly of [Ni(paab)$_2$]·2H_2O, the azomethine groups of the ligands play the crucial role. Two azomethine fragments and the two metal coordinated carboxylate-*O* atoms in each [Ni(paab)$_2$] molecule are involved in two pairs of reciprocal C—H···O interactions with its two neighbours on both sides (Fig. 4). The C6···O3 and C19···O1 distances are 3.172(7) and 3.256(7) Å, respectively. The corresponding C—H···O angles are 142.95 and 150.32°, respectively. Due to these interactions [Ni(paab)$_2$] molecules exist in a chain-like arrangement. Both water molecules are hydrogen bonded to one of the uncoordinated carboxylate-*O* atoms (*vide supra*). The O-atom (O6) of one of these two water molecules is at a distance of 3.10(3) Å from the O-atom of the corresponding symmetry related water molecule. This distance suggests that they exist as a hydrogen bonded water dimer. These water dimers provide the bridges between the chains of [Ni(paab)$_2$]·H_2O moieties (Fig. 4) and complete the two dimensional network of [Ni(paab)$_2$]·2H_2O.

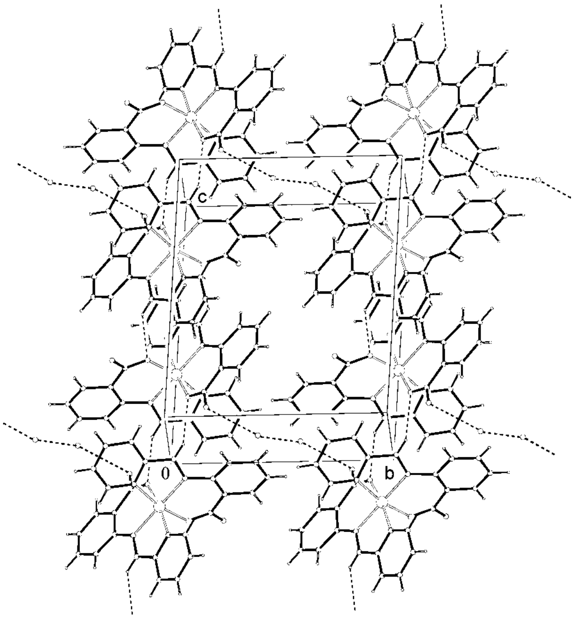


Fig. 4. Two-dimensional network of [Ni(paab)$_2$]·2H_2O. For clarity the water molecule having no role in the formation of the network is not shown.

Acknowledgments

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