

ORIGINAL ARTICLE

Helical 2, 6-dipicolinate complex of Ni (II) incorporating sodium ions and its decomposition in 4-methyl pyridine

Geetika Gupta, Subrato Bhattacharya*

Department of Chemistry, Banaras Hindu University, Varanasi-221005, (INDIA)

E-mail: s_bhatt@bhu.acin

Received: 14th September, 2013 ; Accepted: 20th October, 2013

Abstract : Sodium nickelate (II) *bis*(pyridine-2, 6-dicarboxylic acid) was synthesized by the reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, pyridine-2, 6-dicarboxylic acid (H_2dipic) and Na_2CO_3 in equimolar ratio. The molecule packs in a non-centrosymmetric manner in a head-to-tail motif with sodium ions in bridging positions, thereby, extending the structure in the form of a 1D polymeric helical chain. The decomposition of which in refluxing 4-methyl pyridine leads to a Ni(II) complex of 2,6-dipicolinic acid containing 4-methyl pyridine as auxil-

iary ligand. The complexes 1 and 2 have been characterized by FTIR, UV-Vis spectral, TGA and single crystal X-ray diffraction analyses. The molar conductance of 1 in aqueous solution indicates that the complexes behave as (1:1) weak-electrolyte. Both the molecules crystallize in the monoclinic system (space group $P2_1/c$).

Keywords : Helical chain; Nickel complex; Dipicolinic acid; Polymeric structure; Methyl pyridine.

INTRODUCTION

Multidimensional metal–organic compounds (MOCs) offer great potential in the context of extensive applications in wide ranging areas like supramolecular chemistry, catalysis, material science, biological science, crystal engineering^[1], etc. A substantial part of such MOCs might be constructed from different aromatic mono and poly-carboxylic acids, which are promising candidates^[2] for the generation of flexible and multidimensional H-bonded networks^[3] *via* extensive O–H—O interactions. Paramagnetic metal complexes with extended framework structures are important due

to their potential applications in the development of microporous and/or magnetic materials^[4]. Pyridine-2, 6-dicarboxylic acid (H_2dipic) is one of the most appropriate ligand systems for synthesizing potential pharmacologically active compounds because of the low toxicity, amphocyte nature and varied biological activities^[5]. It is a N, O-chelator and due to its versatile ligational ability^[6] with various metal ions. It can act as a tridentate chelating agent in the form of neutral^[7] (H_2dipic), monoanionic (Hdipic^-) and dianionic^[8] (dipic^{2-}) or can bind in a bridging mode^[9].

An octahedral geometry^[10] is offered by the metal complexes coordinated to two planar dipic^{2-} moieties

ORIGINAL ARTICLE

in two independent perpendicular planes where as the metal complexes containing one dipic^{2-} and an auxiliary ligand like a H_2O or N-based heterocyclic species, generates four or five coordination geometry^[11]. Recently a mononuclear neutral nickel (II) complex of pyridine-2, 6-dicarboxylate was isolated and its DNA binding studies have been investigated^[12]. In another report, a ternary complex of Ni(II) containing 4-methylpyridine and pyridine-2, 6-dicarboxylate ligands was isolated and its antimicrobial properties have been studied^[13].

We herein report on the synthesis and structural characterization of the Ni (II) pyridine dicarboxylate coordination polymer containing bridging Na^+ ions and its decomposition in refluxing 4-methyl pyridine resulting in a neutral Ni(II) ternary complex.

EXPERIMENTAL

Materials and methods

Solvents used were purified using standard methods^[14]. IR spectra were recorded using a Varian-3100 FTIR instrument. Elemental analyses were performed using an Exeter model E-440 CHN analyzer, and electronic absorption spectra were recorded using a Shimadzu UV-1700 PharmaSpec Spectrophotometer.

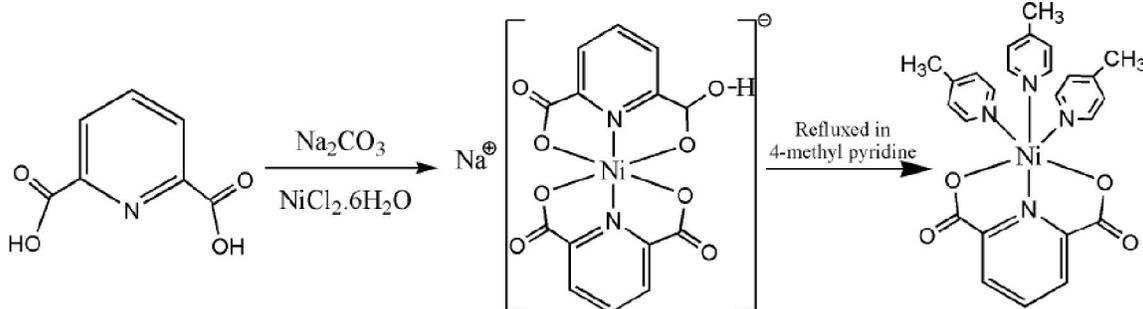
The molar conductance of freshly prepared 1×10^{-3} mol dm^{-3} aqueous solution of 1 was measured using ELICO CM 180 conductivity meter. Thermal analyses (TGA) were performed on a Perkin-Elmer – STA 1000 instrument in flowing N_2 with a heating rate of $10^\circ\text{C min}^{-1}$.

(a) Synthesis of 1

To a solution of pyridine-2, 6-dicarboxylic acid (0.167 g, 1 mmol) in water (20 ml) was added Na_2CO_3 (0.106 g, 1 mmol). The mixture was stirred until the CO_2 evolution ceased and then added a methanolic solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.119 g, 0.5 mmol). The resulting solution was stirred for 30 minutes and then dried in rotary evaporator. The residue was extracted with hot water and kept for crystallization. After 14 hours bright green single crystals suitable for X-ray data collection were obtained in 90% yield. Molar conductance: $69.0 \text{ S cm}^2 \text{ mol}^{-1}$ in water. Anal. Calcd. for $\text{C}_{14}\text{H}_9\text{N}_2\text{Na}_1\text{Ni}_1\text{O}_{10}$ (1): C, 37.62; H, 2.03; N, 6.27; Na, 5.14; Ni, 13.13; O, 35.80. Found: C, 37.60; H, 2.02; N, 6.28; Na, 5.14; Ni, 13.12; O, 36.23.

(b) Synthesis of 2

1 (0.089 g, 2 mmol) was refluxed in 4-methyl pyridine for 18 hrs and then kept the clear solution overnight for crystallization. After a day it afforded light blue crystals of 2 with 68% yield.



Scheme 1 : Synthetic route of the complexes

X-ray crystallography

Single crystal X-ray data of the complex was collected on a Xcalibur Oxford CCD Diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation at room temperature (20°C). Data integration was carried out using CrysAlis Pro software^[15]. The structures were solved by direct method (SHELXS-97)^[16] and refined by full-matrix least-squares method against F^2 (SHELXL-97) using a WinGX platform^[17] All non-

hydrogen-atoms were refined anisotropically while the hydrogen atoms of the pyridine were placed at calculated positions using SHELX default parameters. However, the hydrogen atoms of water molecules and the one of the carboxylic acid group were detected from the low intensity diffraction peaks. Crystallographic data, details of structure solution and refinement have been summarized in TABLE 1. Crystallographic data in CIF format (CCDC No. 909017 and 938646 for 1 and 2

respectively) can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK or by e-mail: deposit@ccdc.cam.ac.uk

TABLE 1 : Crystallographic and structure refinement data

Empirical formula	C ₁₄ H ₉ N ₂ Na ₁ Ni ₁ O ₁₀	C ₂₅ H ₂₄ N ₄ Ni ₁ O ₆
Formula weight	446.9	535.17
Temperature (K)	293K	293K
Crystal system	Monoclinic	Monoclinic
Space group	P ₁ 2 ₁ /c ₁	P ₁ 2 ₁ /c ₁
a/Å	13.6707 (5)	16.1521(7)
b/Å	10.0418 (3)	23.6660(8)
c/Å	13.7652(6)	14.5247(7)
β/deg	115.133(5)	112.083(5)
V/Å ³	1710.76(13)	5144.8(4)
Z	4	8
μ (mm ⁻¹)	1.22	0.800
F (000)	900	2224.0
GOF on F ²	1.035	0.896
Final R indices		
[I>2σI]	R1=0.0429 wR2=0.107	R1=0.065 wR2=0.131
R indices (all data)	R1=0.063 wR2=0.1213	R1=0.161 wR2=0.153
Largest diff.peak and hole (eÅ ⁻³)	0.621 and -0.746	1.535 and -0.424

RESULTS AND DISCUSSION

Synthesis

The reaction of disodium salt of dipicolinic acid (H₂dipic) with methanolic solution of nickel chloride hexahydrate at room temperature, afforded 1 in very good yield. The same product was also obtained when an equimolar ratio of H₂dipic and nickel chloride hexahydrate (in presence of a base like Na₂CO₃) were used for the reaction. 1 on refluxing in 4-methylpyridine afforded 2 in high yields. The latter being a stronger ligand easily replaces dipic ligands from the coordination sites of Ni(II) (Scheme 1). Though thermolysis of Ga(PtBu₂)₃ and In(PtBu₂)₃ in hot 4-ethylpyridine is known to decompose the compounds completely into quantum dots of InP and GaP^[18], no such decomposition (giving nickel oxide) was observed

in the present case.

The molar conductance (69.0 S cm² mol⁻¹) offered by aqueous solution of 1 indicates that the complex behaves as a 1:1 weak electrolyte. The low conductivity is due to the polymeric nature of the complex 1 which is possibly maintained in the solution state to a large extent that reduces the ionic mobility of the charged species. Complex 1 do not exchange with other cations easily as our attempts to do so using Ag⁺, Cu⁺, Sn²⁺ and Al³⁺ failed under normal conditions.

Spectral studies

The infrared spectrum of the complex 1 was consistent with its formulation. Broad bands in the region of 3500 cm⁻¹ to 3100 cm⁻¹ correspond to O–H stretching vibrations associated with both coordinated and free water molecules. The broadness of peaks can be attributed to the significant hydrogen bonding. The O–H bending vibration at 1394 cm⁻¹ can be attributed to the protonated carboxylate group. The sharp, medium intensity bands at 1285 cm⁻¹ and 1431 cm⁻¹ are due to the, ν(C–O), ν_s(C=O) vibrations respectively. A very strong band centred at 1611 cm⁻¹ corresponds to ν_{as}(C=O) vibration of the carboxylate groups. The magnitude of the separation [Δν = (ν_{asym} - ν_{sym}) = 180 cm⁻¹] is considerably large suggesting a unidentate binding mode of the carboxylate group to the Ni(II) ion^[19], as disclosed by the X-ray structure.

Similar bands are also observed in the IR spectrum of 2. Important bands involving O–H vibrations of carboxylate group; namely, the C–OH in-plane bending and out-of-plane O–H deformation modes are absent, hence showing complete deprotonation of the –COOH group. The CH aromatic ring stretching band appears at 3067 cm⁻¹, whilst the CH stretching of the methyl group of 4-methylpyridine appears at a lower frequency of 2925 cm⁻¹. Four strong bands between 1620 and 1420 cm⁻¹ may be assigned to the ring stretching vibrations of pyridine. The δ_{O–C–O} in-plane deformation appears as a sharp band at 691 cm⁻¹ and at 695 cm⁻¹ in 1 and 2 respectively.

The UV/visible spectra of 1 and 2 were recorded using 10⁻²M solutions in water and DMSO respectively. In octahedral environment Ni(II) hexaaqua complex exhibits three spin allowed *d–d* transition to the ³T_{2g}, ³T_{1g} (*F*) and ³T_{1g} (*P*) levels with maxima at 8500,

ORIGINAL ARTICLE

13800 and 25300 cm^{-1} respectively with comparatively low intensities, where shifting occur to higher wave numbers depending on the nature of the coordinating ligand^[20]. The electronic spectra of 1 in aqueous medium and that of 2 in DMSO (Figure 1) exhibit three absorption bands (TABLE 2) consistent with an octahedral Ni(II) ion.

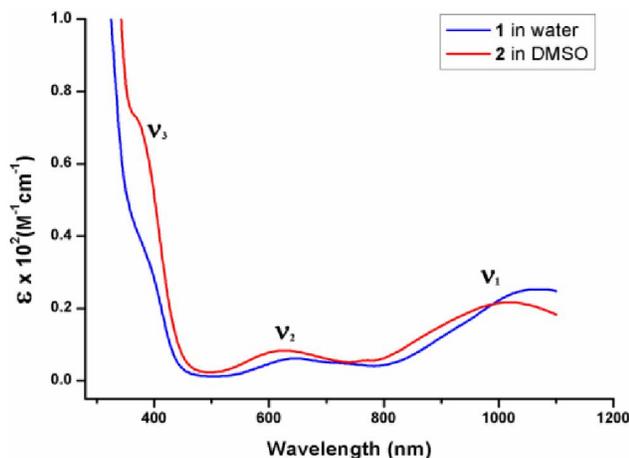


Figure 1 : Electronic absorption spectra of 1 and 2

TABLE 2 : Electronic spectral data for 1 and 2

Transitions	1		2	
	Band positions (nm)	Molar absorptivity (ϵ) ($\text{M}^{-1}\text{cm}^{-1}$)	Band positions (nm)	Molar absorptivity (ϵ) ($\text{M}^{-1}\text{cm}^{-1}$)
${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1)	1058-1082	25	1007-1032	21.6
${}^3A_{2g} \rightarrow {}^3T_{1g}$ (ν_2)	636-657	6.1	615-638	8.3
${}^3A_{2g} \rightarrow {}^3T_{1g}$ (ν_3)	387	34.5	362	74

Thermal analysis

Compounds 1 and 2 were subjected to thermogravimetric analysis under flowing N_2 to probe their dehydration and decomposition behaviour. Both the compounds exhibit multi-step thermolytic patterns (Figure 2).

The Ni coordination polymer 1 underwent dehydration with elimination of uncoordinated and coordinated water molecules in the initial steps of decomposition. Though it is not possible to predict the step wise decomposition of the compound from the thermal data, yet the end product (26.29%) is seemingly NaNiO_2 (Calcd 25.43%).

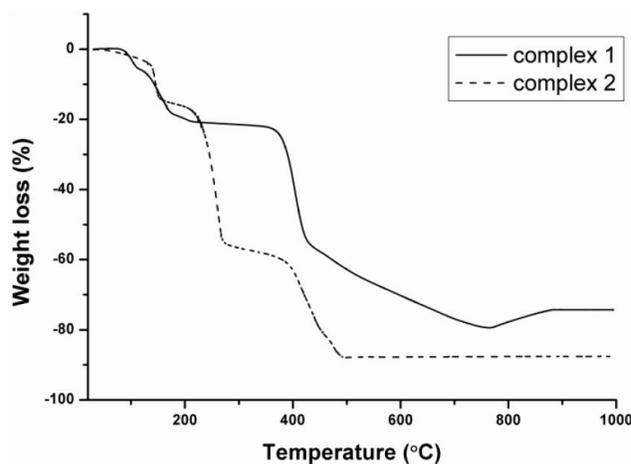


Figure 2 : TGA plot of 1 and 2

The complex 2 began to dehydrate immediately upon heating, with loss of all uncoordinated water molecules, so the first and second stages of decomposition witness the liberation of water molecules along with 4-methyl pyridine moiety with 55.49% weight loss (Calcd 55.53%). The third decomposition spans from 278°C to 482°C corresponding to 31% weight loss consistent with the expulsion of dipicolinate moiety (Calcd 30.4%); leaving behind mass remnant of 13.5% indicative of deposition of NiO as the end product (Calcd 13.9%).

Molecular structure

The complex 1 was crystallised in monoclinic system with space group $P2_1/c$. There is a water molecule crystallised in the lattice. A perspective view of the complex has been depicted (Figure 3). The central nickel(II) ion is coordinated by two dipicolinate moieties each acting as tridentate O, N, O- chelating ligands. The O–Ni–N bite angles in the complex are in the range of 76.64°–78.71°, which are significantly shorter from the expected octahedral 90° value thereby making the coordination environment around the central nickel (II) as a distorted octahedron. The four Ni–O and two Ni–N bond distances (TABLE 3) lie in the ranges which are typical for a six-coordinated nickel (II) d^8 system^[21].

The C–O bond lengths of carboxylate groups are significant to understand the nature of bonding. C1–O7 and C14–O6 bond lengths are 1.24 and 1.22 Å respectively that are typical of a CO double bond, whereas C7–O8 bond length^[22] is 1.27 Å which is indicative of partial double bond character due to the coordination of O8 with the sodium ion. C8–O5 bond length of 1.29 Å is consistent with the protonated na-

ture of O5. A hydrogen bond with the uncoordinated water molecule Ow2 holds the latter in close proximity of the coordination polymer backbone which provides a 3-D ancillary interwoven pathway (Figure 4), which is quite different from the earlier reported the structural findings on Co(II) and Ni(II) complexes forming water channels^[23].

TABLE 3 : Selected bond distances (Å), bond angles (°) for 1

Ni N1	1.960(2)	Ni O4	2.100(2)
Ni N2	1.970(2)	O4 Na	2.597(3)
Ni O1	2.168(2)	O8 Na	2.459(4)
Ni O2	2.096(2)	Na Ow	2.527(8)
Ni O3	2.194(2)	C8 O5	1.285(4)
N1 Ni N2	176.39(10)	N2 Ni O3	76.64(9)
N2 Ni O2	104.78(9)	O2 Ni O3	93.24(8)
N1 Ni O4	100.50(9)	O4 Ni O3	155.22(9)
N2 Ni O4	78.58(10)	O1 Ni O3	91.45(8)
N1 Ni O1	77.20(9)	O2 Ni O4	92.81(9)
N2 Ni O1	99.33(9)	O2 Ni O1	155.88(9)
N1 Ni O2	78.72(9)	O8 Na O4	114.22(12)
O4 Ni O1	92.77(9)	O8 Na Ow	92.32(18)
N1 Ni O3	104.25(9)	Ow Na O4	130.2(4)

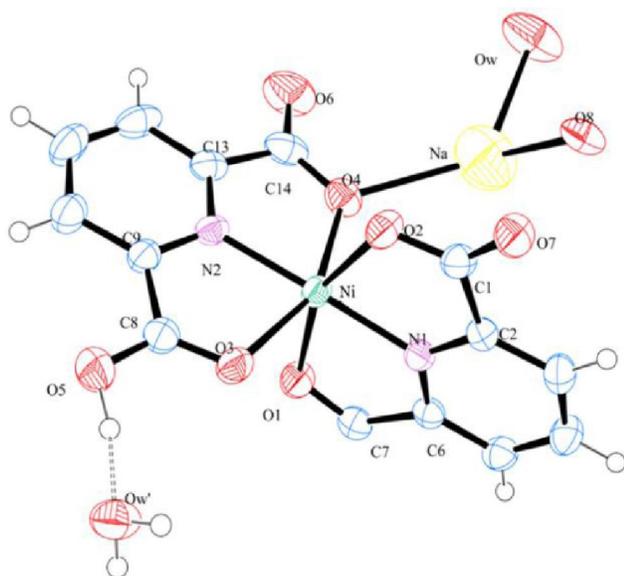


Figure 3 : Ortepe view of asymmetric unit of the complex 1

The disordered water molecule O_w , in 1 attached to sodium ion was modelled by splitting into two parts and their s.o.f. were found to be almost equal [$O_w(0.49) / O_w(0.51)$] on refinement. The structure is extended by means of the sodium ions affording a 1-D helical structure as seen in Figure 5.

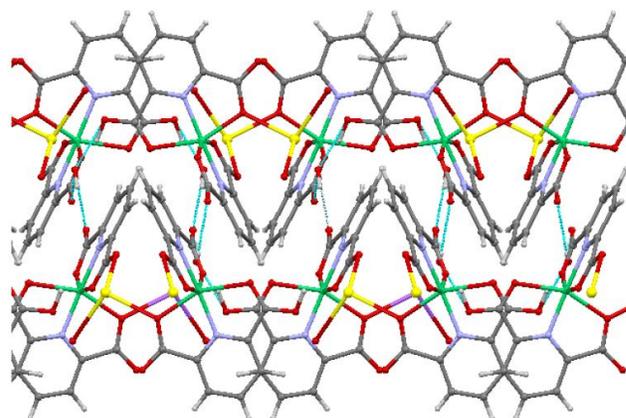


Figure 4 : 3D interwoven pathway through extended H- bonds

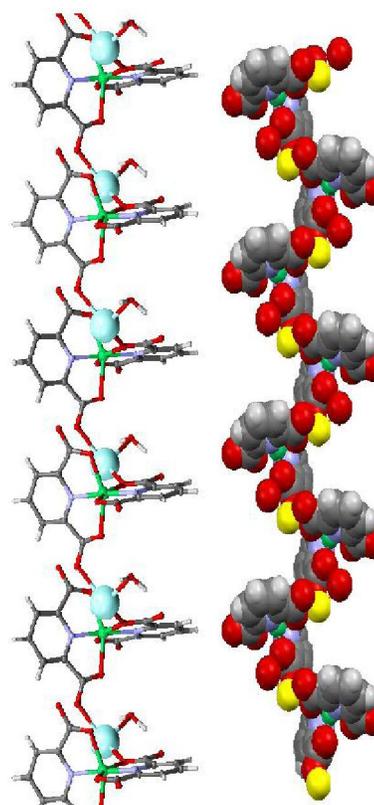


Figure 5 : The helical chain architecture viewed parallel to the crystallographic *a* axis

It may be noted that two such helical chains run anti-parallelly and both left and right handed helices are present facing each other. Sodium ion functions as a node to connect the two Ni(II) dipicolinate moieties to form a polymeric structure which is different to the interactions of alkali metal cations with dipicolinate Ni(II) compound where polymeric chain like structures are formed by oxo and aqua bridges^[24]. In an earlier study of ionic dipicolinato complexes, $[\text{Co}(\text{dipic})(\text{Py})_3]^+$ cations were comparable in size with $[\text{Co}(\text{dipic})_2]^-$ an-

ORIGINAL ARTICLE

ions and were associated in a layer-like structure^[25] contrary to the present case where cation encapsulation takes place.

The complex 2 was crystallised in monoclinic system with space group $P2_1/c$. notably, there are large number of uncoordinated water molecules in the lattice (sixteen in each unit cell). A perspective view of the complex has been depicted (Figure 6).

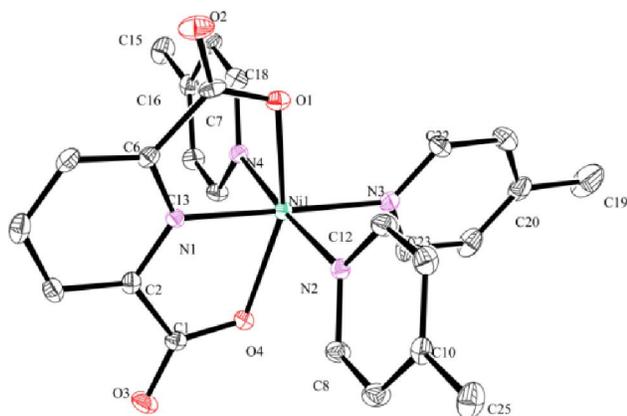


Figure 6 : Ortep view of asymmetric unit of the complex 2

In the complex, the Ni(II) ion is in a distorted octahedral environment, bonded to O1, O4 and N1 atoms of divalent anionic dipic ligand and the nitrogen atoms of the three 4-methylpyridine groups. The two planes constituted by N2 N3 N4 and N1O1O4 are almost perpendicular to each other with an interplaner angle of 89.48° . The higher basicity of the nitrogen atom of the dipic is due to the presence of two carboxylate groups in ortho positions; thereby making it to be the strongest donor site^[26]. As a consequence the Ni1-N1 distance (1.98 \AA) is significantly shorter than Ni1-N2, Ni1-N3 and Ni1-N4 distances (TABLE 4). The dipic chelate bite angles are 78.08° and 77.93° , comparable to those found in other dipicolinate nickel complexes^[12].

TABLE 4 : Selected bond distances (\AA), bond angles ($^\circ$) for 2

Ni N1	1.987(3)	Ni O4	2.118(3)
Ni N2	2.142(3)	Ni O1	2.118(3)
Ni1 N3	2.062(4)	Ni1 N4	2.140(3)
N1 Ni1 N3	178.95(13)	O4 Ni1 N4	91.42(12)
N1 Ni1 O1	77.96(13)	N1 Ni1 N2	92.06(13)
N3 Ni1 O1	101.85(14)	N3 Ni1 N2	88.96(13)
N1 Ni1 O4	78.07(12)	O1 Ni1 N2	88.40(12)
N3 Ni1 O4	102.15(13)	O4 Ni1 N2	90.91(11)
N1 Ni1 N4	91.82(13)	N4 Ni1 N2	175.82(12)
N3 Ni1 N4	87.16(13)	O1 Ni1 N4	90.87(12)

As mentioned already there are a number of water molecules in the lattice. Four oxygen atoms of water molecules, together with two carboxylate oxygens of 2; each from a different unit., furnish a six membered planer ring thereby interlinking the monomeric units of 2 (Figure 7). These O-O distances vary from 2.76 \AA to 2.89 \AA .

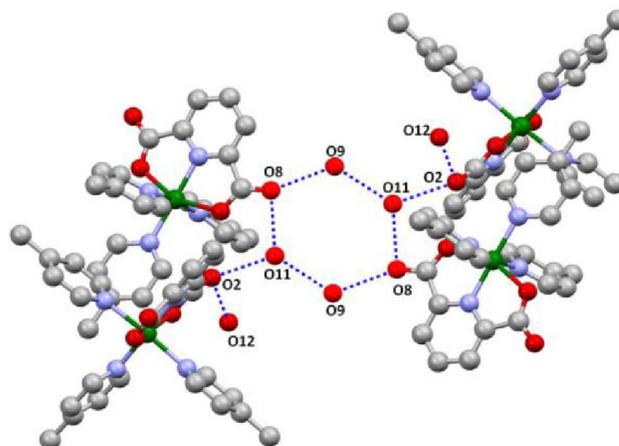


Figure 7 : Interconnection of monomeric units of 2

CONCLUSION

Mixed N-, O- donor ligands, offer a wide range of possibilities for MOF construction and may lead to supramolecular interactions of hydrogen bonding and π - π stacking types. Combining the advantages of Heterocyclic N-donor ligands being good donor ligands due to the presence of one nitrogen atom with rigid backbones of aromatic rings and flexible binding behaviour from monodentate and chelating to multibridging mode of carboxylate groups, we have constructed metal-organic frameworks of carboxylate moiety mixed with pyridine-functionality linkers. We may expect that with a rational design, more unusual coordination architectures with new mixed-ligand systems will be feasible for far-flung applications. The outcome of such designed syntheses will be likely to have great importance in crystal engineering and supramolecular chemistry.

ACKNOWLEDGEMENTS

Financial support from the University Grants Commission, India in the form of a major project is grate-

fully acknowledged.

REFERENCES

- [1] (a) M.J.Zaworotko; *Angew.Chem.Int.Ed.*, **37**, 1211-1213 (1998); (b) L.J.Boerner, J.M.Zaleski; *Curr.Opin.Chem.Biol.*, **9**, 135-144 (2005) and references cited therein.
- [2] (a) H.L.Gao, L.Yi, B.Zhao, X.Q.Zhao, P.Cheng, D.Z.Liao, S.P.Yan; *Inorg.Chem.*, **45**, 5980-5988 (2006); (b) L.L.Wen, D.B.Dang, C.Y.Duan, Y.Z.Li, Z.F.Tian, Q.J.Meng; *Inorg.Chem.*, **44**, 7161-7170 (2005).
- [3] (a) S.K.Ghosh, P.K.Bharadwaj; *Inorganica Chimica Acta*, **359**, 1685-1689 (2006); (b) S.Kitagawa, K.Uemura; *Chem.Soc.Rev.*, **34**, 109-119 (2005).
- [4] (a) C.Hong, J.Koo, S.Son, Y.Lee, Y.Kim, Y.Do; *Chem.Eur.J.*, **7**, 4243-4252 (2001); (b) M.H.Zeng, W.X.Zhang, X.Z.Sun, X.M.Chen; *Angew.Chem.Int.Ed.*, **44**, 3079-3082 (2005); (c) O.Kahn; *Molecular Magnetism.*, Wiley-VCH, New York (1993).
- [5] B.Setlow, P.Setlow; *Appl.Environ.Microbiol.*, **59**, 640-643 (1993).
- [6] H.Park, A.J.Lough, J.C.Kim, M.H.Jeong, Y.S.Kang; *Inorganica Chimica Acta*, **360**, 2819-2823 (2007).
- [7] L.C.Nathan, T.D.Mai; *J.Chem.Crystallogr.*, **30**, 509-518 (2000).
- [8] J.C.MacDonald, T.J.M.Luo, G.T.R.Palmore; *Crystal Growth & Design*, **4**, 1203-1209 (2004).
- [9] S.K.Ghosh, J.Ribas, P.K.Bharadwaj; *Crys.Eng. Commu.*, **6**, 250-256 (2004).
- [10] M.V.Kirillova, M.F.C.Guedes da Silva, A.M.Kirillov, J.J.R.Frausto da Silva, A.J.L.Pombeiro; *Inorganica Chimica Acta*, **360**, 506-512 (2007).
- [11] (a) S.M.Saylor, R.M.Supkowski, R.L.LaDuca; *Inorganica Chimica Acta*, **361**, 317-326 (2008); (b) A.Girrane, A.Pastor, A.Ienco, C.Mealli, A.Galindo; *J.Chem.Soc.Dalton Trans.*, 3771-3777 (2002).
- [12] Q.Wang, W.Li, A.Liu, B.Zhang, F.Gao, S.Li, X.Liao; *Journal of Molecular Structure*, **985**, 129-133 (2011).
- [13] A.S.Zafar, M.Khalid, S.Kumar, M.Shahid, S.Noor; *European Journal of Medicinal Chemistry*, **45**, 264-269 (2010).
- [14] B.S.Furniss, A.J.Hannaford, P.W.G.Smithand, A.R.Tatchell; *Vogel's Textbook of Practical Organic Chemistry*, 5th Edition, Dorling Kindersley, India, (2006).
- [15] CrysAlis Pro, Agilent Technologies Ltd.
- [16] G.M.Sheldrick; *Acta Crystallogr.*, **A46**, 467-473 (1990).
- [17] L.J.Farrugia; *J.Appl.Crystallography*, **32**, 837-838 (1999).
- [18] M.Green, P.O'Brien; *J.Mater.Chem.*, **14**, 629-636 (2004).
- [19] S.D.Robinson, M.F.Uttley; *J.Chem.Soc.Dalton Trans.*, **18**, 1912-1920 (1973).
- [20] A.B.P.Lever; *Electronic Spectra of Inorganic and Coordination Compounds*, John Wiley, New York, (1968).
- [21] T.K.Prasad, M.V.Rajasekharan; *Polyhedron*, **26**, 1364-1372 (2007).
- [22] S.Singh, J.Chaturvedi, S.Bhattacharya; *Dalton Trans.*, **41**, 424-431 (2012).
- [23] L.C.Nathan, T.D.Mai; *Journal of Chemical Crystallography*, **30**, 509-518 (2000).
- [24] B.Das, J.B.Baruah; *Inorganica Chimica Acta*, **363**, 1479-1487 (2010).
- [25] B.Das, K.Ghosh, J.B.Baruah; *Journal of Coordination Chemistry*, **64**, 583-589 (2011).
- [26] İ.Uçar, İ.Bulut, A.Bulut, O.Büyükgüngör; *Journal of Coordination Chemistry*, **61**, 2449-2456 (2008).