

Isostructurality of complexes of the type tetraaquabis(isonicotinato)metal(II)

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Structural investigations on a series of six analogous metal(II) isonicotinate tetrahydrates, $M(\text{iso})_2(\text{H}_2\text{O})_4$ with $M = \text{Mn, Fe, Co, Ni, Cu}$ and Zn , all crystallizing in $P\bar{1}$ space symmetry, have been carried out. In the crystal structure of each of the six metal complexes of type tetraaquabis(isonicotinato)metal(II), extensive intermolecular hydrogen bonds involving all possible donor and acceptor sites lead to the formation of a 3D supramolecular network that has been analysed by the graph-set approach. Their comparable lattice parameters and similar PXRD patterns indicate close structural similarity within the series. However, the crystallographic isostructurality of the species evaluated by the method of Kálmán and Fábíán suggests that the Cu species presents some differences from the rest. In an overall sense, this behaviour is reflective of the Irving-Williams order of stability of octahedral complexes formed by bivalent metal ions.

Keywords: Meta(II) isonicotinates, $R_4^4(12)$ graph-set, isostructurality, Kálmán and Fábíán, powder X-ray diffraction, Irving-Williams order.

Introduction

Chemical compounds having analogous composition and structure are commonly termed as isostructural. In a crystallographic sense, a pair of isostructural compounds is required to belong to the same structure type, i.e. their space groups are identical which ensures nearly identical crystal packing. Kálmán and Fábíán have developed an approach based on volumetric measure to estimate the degree of isostructurality between two crystalline compounds from a crystallographic point of view¹. Two crystal structures may be compared by a parameter called unit cell similarity index given by

$$\text{II} = [(a + b + c)/(a' + b' + c')] - 1$$
$$(a + b + c > a' + b' + c')$$

Here a, b, c and a', b', c' are the orthogonalized lattice parameters of the structures being compared. If the structural similarity is very high, the II value is expected to be practically equal to zero. Two other parameters viz. mean elongation value (ϵ) and the asphericity index (A), are also used to establish the structural closeness of the species being compared. The ϵ value describes the difference in cell size, the asphericity index (A) accounts for the shape distor-

tions of the two unit cells. The concept of isostructurality has also been studied in relation to the opposing concept of polymorphism for organic crystalline molecules². Formation of isostructural crystalline species was also reported to have resulted via an exchange of halogen atoms³.

Such studies on metal-organic compounds are not common, however. Using this approach, we had earlier evaluated the isostructurality of two species of composition $[\text{M}(\text{H}_2\text{O})_3(\text{SO}_4)(4\text{-CNpy})_2] \cdot \text{H}_2\text{O}$ for $M = \text{Co}$ and Ni which present an inverse bilayer structure due only to supramolecular effects⁴.

Isonicotinic (or 4-pyridine carboxylic) acid (isoH) is a potentially tridentate ligand and, by acting in this fashion, it is known to form polymeric species such as $\text{bis}(\text{iso})\text{M}^{\text{II}}$. Coordination of the pyridyl-N as well as the carboxyl ends of 4-pyridinecarboxylate anion occurs under non-aqueous/hydrothermal conditions⁵, while in complexes formed in aqueous medium the pyridyl-N atom is only coordinated⁶. The latter situation leaves the uncoordinated carboxyl end as a suitable acceptor in the formation of intermolecular hydrogen bonds. The 1D coordination polymer $[\text{Cl}(\text{isoH})\text{Cu}(\text{I})]_n$, pre-

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pared under hydrothermal conditions at 140°C, has N-bound isonicotinic acid as the ligand, while -COOH groups from two adjacent chains take part in the formation of a pair O-H...O bonds to add a second dimension to the coordination polymer⁷. Okabe *et al.* reported⁸ the crystal structure of a compound formulated as $\text{Cu}(\text{iso})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$. The Cu^{II} coordination geometry in this compound was described as being square planar with N_2O_2 coordination, with two additional water molecules being present in the crystal lattice as solvent of crystallization.

The crystal structures of several other metal(II) isonicotinates with a chemical composition analogous to $\text{Cu}(\text{iso})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$, but formulated either as $\text{M}(\text{iso})_2(\text{H}_2\text{O})_4$, or $\text{M}(\text{iso})_2 \cdot 4\text{H}_2\text{O}$ have been determined by us^{9,10} as well as other authors^{11–14}. The thermogravimetric (TG) behaviour of several metal(II) isonicotinate tetrahydrates formed by Mn, Fe, Co, Ni, Cu and Zn was also reported¹⁵ by us earlier. These compounds crystallize in triclinic $P\bar{1}$ space symmetry and comparable unit cell parameters. Herein, we present the detailed analysis of the crystal structure with an emphasis on the supramolecular aspects and also the powder X-ray diffraction behaviour of this series of six compounds, which may also be formulated as $\text{M}(\text{iso})_2 \cdot 4\text{H}_2\text{O}$, with M = Mn (**1**), Fe (**2**), Co (**3**), Ni (**4**), Cu (**5**) and Zn (**6**). Further, the close similarity of their crystal packing behaviour is analysed by evaluating the isostructurality of the crystalline species by following the method of Kálmán and Fábrián¹.

Experimental

Materials and methods:

All materials used in this work were obtained from commercial sources and used without further purification. 4-Cyanopyridine and isonicotinic acid were obtained from Sigma-Aldrich, while the metal salts-nickel(II) acetate, chlorides, nitrates or sulfates were purchased from various Indian manufacturers/suppliers.

*Preparation and crystallization of $\text{M}(\text{iso})_2(\text{H}_2\text{O})_4$ [M = Mn (**1**), Fe (**2**), Co (**3**), Ni (**4**), Cu (**5**), Zn (**6**):*

The metal(II) isonicotinate tetrahydrates were prepared in very good to excellent yield by following procedures described by us earlier^{10a}. Neutralized isonicotinic acid (4-pyridine carboxylic acid) was reacted with appropriate salts of the above metals and the reaction mixture was stirred for 2–4 h. The microcrystalline products formed were filtered,

washed with water followed by rectified spirit and diethyl ether and dried in air. Yield: ~70% (M = Fe, Co); ~100% (M = Mn, Ni, Cu, Zn). Analytical and other data on the complexes were reported earlier¹⁰.

X-Ray crystallographic procedures:

Molecular and crystal structures of **1–6** were determined by using the method of single crystal X-ray diffraction. While the crystals of compounds **1**, **2**, **3**, **5** and **6** were obtained from undisturbed preparative reaction mixtures kept at room temperature, to obtain compound **4** in crystalline form $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was reacted with 4-cyanopyridine under hydrothermal conditions at 210°C. The chosen crystals of suitable size were mounted on glass fibres for intensity data collection at room temperature using graphite monochromatized Mo-K α radiation (0.7107 Å) on a Bruker SMART CCD Diffractometer¹⁶. The crystals were found to be stable against thermal/oxidative decomposition and X-radiation induced decay at room temperature. The crystal structures were solved by direct methods (SHELXS) and refined by full-matrix least squares technique (SHELXL) with SHELX-97¹⁷ using the WinGX¹⁸ platform. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in all the six compounds were located in difference Fourier maps and refined with isotropic atomic displacement parameters. The structural diagrams were drawn using ORTEP-III¹⁹ for Windows, Diamond²⁰ and Mercury²¹. Crystal and structure refinement data for **1–6** are summarized in Table 1.

Powder X-ray diffraction data in the 3–60° 2 θ -range were recorded on a Philips X'Pert PRO instrument using Cu-K α radiation (1.5418 Å) at a scan rate of 0.5 s (0.5° 2 θ) per step at 40 KV/30 mA. The calculated diffraction patterns assuming Bragg-Brentano geometry were obtained from results of single crystal structure analyses using PowderCell²².

Results and discussion

The complexes **1**, **2**, **3**, **4**, **5**, and **6** of the type $\text{M}(\text{iso})_2(\text{H}_2\text{O})_4$ with M = Mn, Fe, Co, Ni, Cu, Zn respectively have been prepared at room temperature following a high yield general route^{10a}. In this procedure the sodium salt of isonicotinic acid is treated with a suitable M^{2+} salt in aqueous solution to obtain the desired products as precipitates. The Ni^{II} analogue, **4** was originally prepared as a mixture of rod-shaped crystals and powder by reacting nickel acetate tetrahydrate with 4 cyanopyridine under hydrothermal conditions at 210°C²³. Under the high-pressure condition, the

Table 1. Crystal and structure refinement data for compounds 1-6

Compound	Mn (1)	Fe (2)	Co (3)	Ni (4)	Cu (5)	Zn (6)
Chemical formula	$C_{12}H_{16}N_2O_8Mn$	$C_{12}H_{16}N_2O_8Fe$	$C_{12}H_{16}N_2O_8Co$	$C_{12}H_{16}N_2O_8Ni$	$C_{12}H_{16}N_2O_8Cu$	$C_{12}H_{16}N_2O_8Zn$
Formula weight	371.21	372.12	375.20	374.98	379.81	381.64
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a, b, c, \alpha, \beta, \gamma$ (Å and °)	6.3895(6), 6.8854(6), 9.3540(9), 95.229(2), 104.428(2), 112.631(1)	6.349(1), 6.938(1), 9.303(2), 95.601(3), 104.613(3), 113.375(2)	6.3521(1), 6.8984(1), 9.2455(2), 96.1110(1), 104.7030(1), 113.176(5)	6.311(2), 6.900(2), 9.253(3), 96.487(5), 105.160(5), 113.176(5)	6.340(1), 6.896(2), 9.181(2), 99.434(4), 105.234(4), 108.244(4)	6.3423(2), 6.9175(3), 9.2713(3), 96.247(2), 105.004(2), 112.839(2)
Volume (Å ³)	359.72(6)	354.9(1)	350.70(1)	346.8(2)	354.3(1)	351.94(2)
Z, D _{calc} (g/cm ³)	1, 1.714	1, 1.741	1, 1.777	1, 1.796	1, 1.780	1, 1.461
μ (mm ⁻¹)	0.964	1.110	1.271	1.447	1.588	1.754
F(000)	191	192	193	194	195	156
Crystal size (mm)	0.6×0.3×0.2	0.13×0.17×0.29	0.7×0.22×0.12	0.29×0.16×0.12	0.28×0.19×0.09	0.11×0.17×0.48
θ range for data collection	2.30 to 27.47	2.32 to 28.23	2.34 to 29.11	2.35 to 28.09	2.39 to 27.50	2.34 to 28.32
hkl ranges	$-8 \leq h \leq 7, -8 \leq k \leq 8,$ $-8 \leq l \leq 11$	$-8 \leq h \leq 8, -8 \leq k \leq 9,$ $-12 \leq l \leq 11$	$-8 \leq h \leq 8, -9 \leq k \leq 9,$ $-12 \leq l \leq 12$	$-7 \leq h \leq 7, -8 \leq k \leq 8,$ $-11 \leq l \leq 12$	$-7 \leq h \leq 8, -8 \leq k \leq 7,$ $-11 \leq l \leq 11$	$-8 \leq h \leq 8, -9 \leq k \leq 9,$ $-11 \leq l \leq 11$
Reflections collected/unique	2059/1516	3473/1585	4079/1751	3207/1512	2130/1525	1453/838
Refinement method	Full-matrix LS on F^2	Full-matrix LS on F^2	Full-matrix LS on F^2	Full-matrix LS on F^2	Full-matrix LS on F^2	Full-matrix LS on F^2
Data/restraints/parameters	1516/0/139	1585/0/139	1751/0/138	1512/0/139	1525/0/138	838/0/138
Goodness of fit* on F^2	1.092	1.129	1.177	1.112	1.123	1.072
R indices† (all data)	$R_1 = 0.0257,$ $wR_2 = 0.0709$	$R_1 = 0.0222,$ $wR_2 = 0.0618$	$R_1 = 0.0205,$ $wR_2 = 0.0555$	$R_1 = 0.0281,$ $wR_2 = 0.0748$	$R_1 = 0.0268,$ $wR_2 = 0.0727$	$R_1 = 0.0290,$ $wR_2 = 0.0691$
(Shift/esd) _{max}	0.000	0.000	0.000	0.000	0.000	0.000
Largest diff. peak and hole	0.407 and -0.274 e.Å^{-3}	0.311 and -0.201 e.Å^{-3}	0.351 and -0.233 e.Å^{-3}	0.494 and -0.425 e.Å^{-3}	0.242 and -0.398 e.Å^{-3}	0.396 and -0.369 e.Å^{-3}
† $wR_2 = \{\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2\}^{1/2}, R_1 = \sum F_o - F_c / \sum F_o , \text{Goof} = S = \{\sum [w(F_o^2 - F_c^2)]^2 / (n - p)\}^{1/2}.$						

nitrile group of 4-cyanopyridine (py-4-CN) undergoes hydrolysis to form 4-pyridine carboxylic acid, i.e. isonicotinic acid (py-4-COOH) which reacts *in situ* with the nickel salt to produce **4**. Although these complexes may be prepared^{9a} from the isolated metal(II) salts and sodium isonicotinate taken in the 1:2 ratio, the method was subsequently simplified^{9b} by making use of a NaOH-neutralized aqueous solution of isonicotinic acid instead of sodium isonicotinate in solid form.

The crystalline compounds are characteristically coloured, air-stable and moisture-insensitive solids that are sparingly soluble in water and common organic solvents. The bright yellow colour of the air stable iron(II) compound, **2**, resulting from an absorption occurring at 388 nm due to an MLCT transition^{10a}, is quite notable. In addition, this iron(II) complex characterized by its $^1A_{1g}$ ground state instead of the more usual $^5T_{2g}$ ground state is diamagnetic in nature^{10a}. The μ_{eff} values observed (at 298 K) for the paramagnetic species, **1** (5.67 BM), **3** (4.74 BM), **4** (3.15 BM) and **5** (1.79 BM) are in the expected ranges for high-spin $d^5\text{-Mn}^{2+}$ (5.65–6.10 BM), high-spin $d^7\text{-Co}^{2+}$ (4.30–5.20 BM), $d^8\text{-Ni}^{2+}$ (2.80–3.50 BM) and $d^9\text{-Cu}^{2+}$ (1.70–2.20 BM) respectively^{10a}. Thermal decomposition of the compounds takes place in two well-defined steps in the 50–600°C range¹⁵. While the first step involves dehydration commencing at relatively high initiation temperatures, the second step is due to the decomposition of the isonicotinato ligands to produce metal oxides as the final products.

Crystal structures of **2**^{10b} and **5**^{10a} were reported earlier from this laboratory. Herein we present a detailed analysis of supramolecular aspects of the crystal structures of **1–6** and the same time, a comparison of the structural parameters of the six analogues formed by the bivalent metal ions. The crystallographic and structure refinement data on all members of this series are presented in Table 1. All six compounds crystallize with triclinic unit cells of analogous distance and angular parameters. In all cases the metal ions lie at a centre of symmetry (0,0,0) in the crystal lattice. Thus, in each case the asymmetric unit consists of one-half the octahedral complex. The thermal ellipsoid plot shown in Fig. 1 is for the manganese compound (**1**), but similar diagrams may be drawn for the other compounds as well. We compare the geometric parameters for all six structures in Table 2. Identifi-

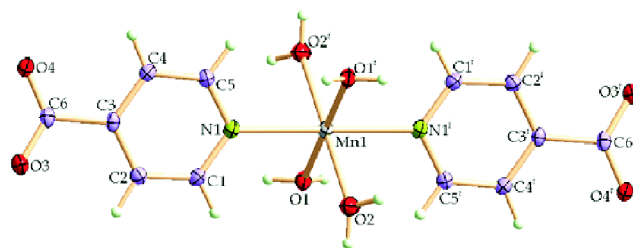


Fig. 1. Thermal ellipsoid plot of $\text{Mn(iso)}_2(\text{H}_2\text{O})_4$ (**1**) with anisotropic atoms drawn as 50% probability ellipsoids. The 'i' superscripted atoms belong to the centrosymmetrically related half of the molecule.

Table 2. Comparison of selected bond parameters in compounds **1**, **2**, **3**, **4**, **5** and **6**

Bond parameters	Mn (1)	Fe (2)	Co (3)	Ni (4)	Cu (5)	Zn (6)
Distances (Å)						
M(1)-O(1)	2.206(1)	2.122(1)	2.083(1)	2.061(2)	1.986(1)	2.100(2)
M(1)-O(2)	2.171(1)	2.137(1)	2.132(1)	2.100(2)	2.452(2)	2.167(2)
M(1)-N(1)	2.274(1)	2.206(1)	2.150(1)	2.092(2)	2.006(2)	2.130(2)
O(3)-C(6)	1.262(2)	1.253(2)	1.256(2)	1.255(3)	1.253(2)	1.249(3)
O(4)-C(6)	1.255(2)	1.257(2)	1.254(2)	1.250(3)	1.248(2)	1.259(3)
Angles (°)						
O(1) ⁱ -M(1)-O(2)	86.45(4)	86.03(5)	86.80(4)	86.97(7)	85.99(7)	86.69(8)
O(1) ⁱ -M(1)-N(1)	86.65(4)	87.25(4)	88.37(4)	88.11(6)	90.09(6)	88.31(8)
O(2) ⁱ -M(1)-N(1)	87.64(4)	87.69(4)	88.22(4)	89.21(6)	91.16(6)	88.54(8)
O(2)-M(1)-O(1)	93.55(4)	93.97(5)	93.20(4)	93.03(7)	94.01(7)	93.31(8)
O(2)-M(1)-N(1)	92.36(4)	92.31(5)	91.78(4)	90.79(6)	88.84(6)	91.46(8)
O(1)-M(1)-N(1)	93.35(4)	92.75(4)	91.63(4)	91.89(6)	89.91(6)	91.69(8)
O(4)-C(6)-O(3)	125.8(1)	125.6(1)	125.6(1)	125.9(2)	125.9(2)	125.8(3)

Symmetry code: $i, -x, -y, -z$.

cal atom naming schemes have been adopted for the structures.

The M-O and M-N bond lengths in these compounds (**1-6**) of type $M(\text{iso})_2(\text{H}_2\text{O})_4$ are clearly dependent on the metal ions present in them. The observed M-N(1) bond distances in compounds **1-6** follow the order given below, which is also the order of the M^{2+} ionic radii²⁴.

M^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
M-N1, Å	2.274	2.206	2.150	2.092	2.006	2.130
r_M^{2+} , Å	0.97	0.92	0.89	0.83	0.87	0.88

A plot of the observed M-N(1) (and also the M-O(2)) distances with respect to the metal ions present in the complexes is shown in Fig. 2. It is interesting to note that the

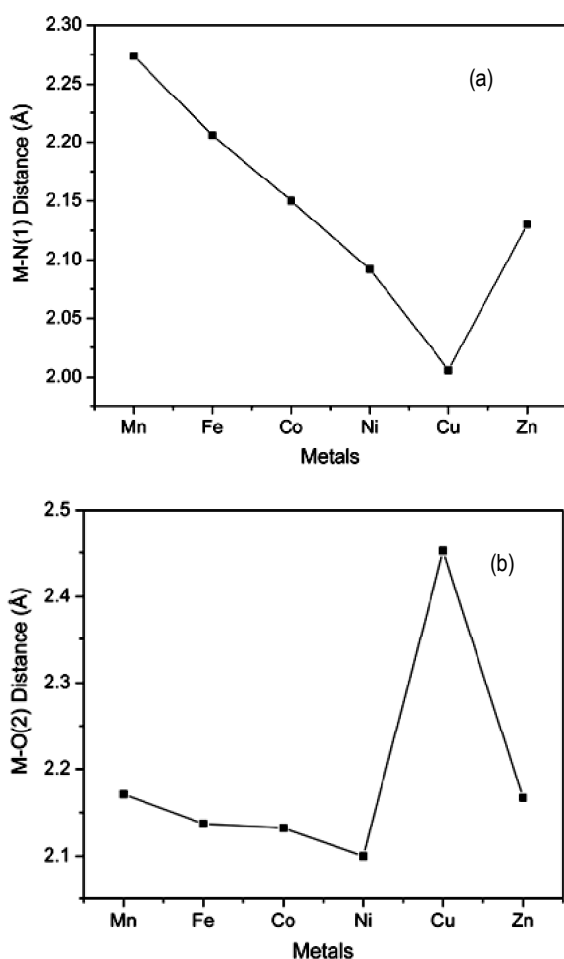


Fig. 2. The (a) M-N(1) and (b) M-O(2) bond distances of $M(\text{iso})_2(\text{H}_2\text{O})_4$ in **1-6**.

observed M-N(1) distances are according to the well-known Irving-Williams series ($\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$). It is also seen that in going from Mn to Zn the M-O(2) bond distances follow the same order with the only exception of Cu. This is attributed to the distorted octahedral geometry of six-coordinate copper(II) complex resulting from Jahn-Teller effect which is common in six-coordinate complexes of Cu^{2+} . In the crystal structure of $\text{Cu}(\text{iso})_2(\text{H}_2\text{O})_4$ (**5**) two of the M-L bonds [M-O(2)] are over 2.4 Å in length, while the other four [M-O(1) and M-N(1)] are near 2.0 Å.

The most remarkable structural feature in the crystal structure of **1** and its analogues is the formation of an exhaustive hydrogen-bonded network involving all possible hydrogen bond acceptors and donors (Fig. 3). The discrete complexes $[M(\text{iso})_2(\text{H}_2\text{O})_4]$ are thus strongly linked to one another to give rise to a supramolecular polymer. As shown in Fig. 4, hydrogen bonds between dangling carboxyl groups from the isonicotinato ligand and the water molecules join the molecules into layers that are interconnected through further hydrogen bonds forming a robust 3D architecture. The O-H...O bond lengths and angles listed in Table 3 indicate that their shortness coupled with near-linearity results in strong hydrogen-bonding interactions leading to stability against the loss of coordinated water molecules under ambient conditions as well as low solubility in water and other media.

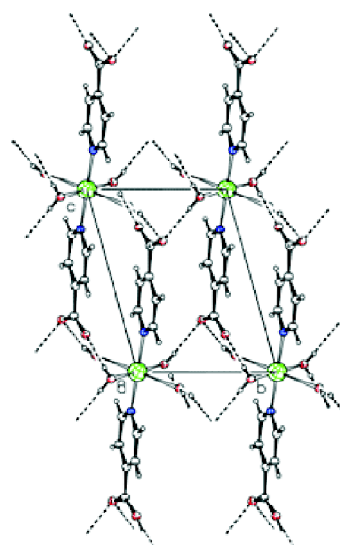


Fig. 3. Unit cell packing diagram viewed along *a* in crystal structures of $M(\text{iso})_2(\text{H}_2\text{O})_4$ (**1-6**).

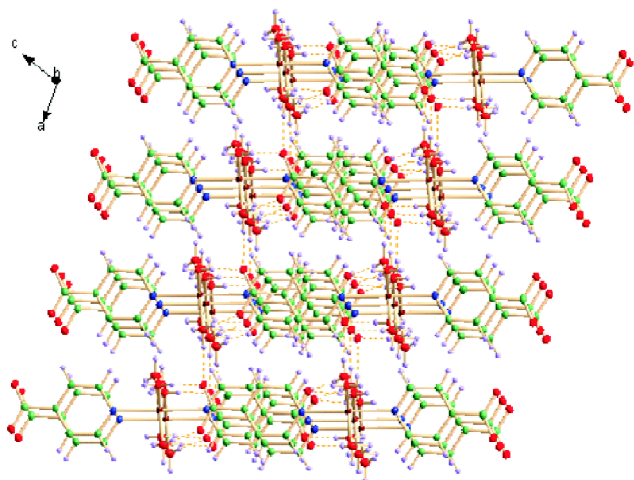


Fig. 4. The 3-D network produced by O-H...O hydrogen bonds present in crystals of $M(\text{iso})_2(\text{H}_2\text{O})_4$.

As shown in Fig. 5, graph set analysis of the crystal structure of $M(\text{iso})_2(\text{H}_2\text{O})_4$ suggests the presence of three rings formed by O-H...O hydrogen bonds. The 8-membered ring comprised of two aqua ligands, a carboxylate anion and the metal ion generates a $R_2^2(8)$ cyclic motif as per notations of Bernstein *et al.*²⁴. A 12-membered twisted ring involving two

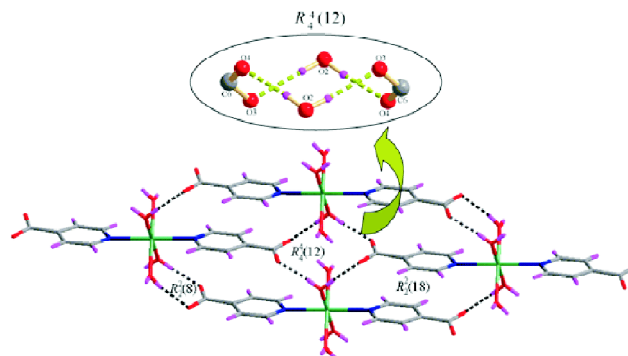


Fig. 5. Graph-set description of the hydrogen-bonded network occurring in the crystal structure of $M(\text{iso})_2(\text{H}_2\text{O})_4$ (**1-6**). The inset at the top shows the twisted ring of description $R_4^4(12)$.

aqua ligands and two carboxylate anions with a description of $R_4^4(12)$ is also observed as a unique pattern in the crystal structures of **1-6**. We are not aware about the occurrence of such rings in other reported crystal structures. This ring unites four $M(\text{iso})_2(\text{H}_2\text{O})_4$ molecules involving two coordinated water molecules and two $-\text{COO}^-$ groups from the isonicotinate ligands. An even larger 18-membered $R_2^2(18)$ ring involving two isonicotinate ligands, two aqua ligands and two metal centres is also found in the crystal structure of the compounds.

Table 3. Hydrogen bond parameters (distances in Å and angles in °) in compounds **1-6**

Hydrogen bonds	Mn (1)	Fe (2)	Co (3)	Ni (4)	Cu (5)	Zn (6)
O(1)-H(5)...O(4)#1						
d(D-H)	0.86(3)	0.81(3)	0.82(2)	0.73(3)	0.71(3)	0.74(6)
d(H...A)	1.90(3)	1.84(3)	1.82(2)	1.92(4)	2.03(3)	2.07(5)
d(D...A)	2.762(2)	2.650(1)	2.642(1)	2.651(2)	2.73(2)	2.793(3)
∠(DHA)	177(2)	178(2)	177(2)	178(3)	168(3)	165(5)
O(1)-H(6)...O(3)#2						
d(D-H)	0.85(3)	0.79(2)	0.81(2)	0.73(3)	0.70(3)	0.81(5)
d(H...A)	1.97(3)	2.01(2)	1.98(2)	2.06(3)	1.92(4)	2.07(5)
d(D...A)	2.816(2)	2.796(2)	2.787(1)	2.792(2)	2.623(2)	2.868(3)
∠(DHA)	171(2)	176(2)	174(2)	171(3)	176(4)	166(6)
O(2)-H(7)...O(3)#3						
d(D-H)	0.83(3)	0.84(3)	0.82(3)	0.89(4)	0.75(4)	0.73(5)
d(H...A)	1.95(3)	2.01(3)	2.04(3)	2.00(4)	2.08(4)	2.08(5)
d(D...A)	2.775(2)	2.833(2)	2.854(2)	2.872(2)	2.827(3)	2.787(3)
∠(DHA)	174(2)	170(3)	173(2)	169(3)	175(4)	164(5)
O(2)-H(8)...O(4)#4						
d(D-H)	0.85(3)	0.83(2)	0.81(2)	0.82(3)	0.80(4)	0.81(5)
d(H...A)	1.79(3)	1.94(2)	1.97(2)	1.99(3)	2.18(4)	1.83(5)
d(D...A)	2.643(2)	2.761(2)	2.784(2)	2.811(2)	2.961(3)	2.642(3)
∠(DHA)	174(3)	179(2)	179(2)	177(3)	163(3)	180(4)

The aromatic rings of the isonicotinato ligands are involved in intermolecular π - π interactions in the crystal structures of $M(\text{iso})_2(\text{H}_2\text{O})_4$ (Fig. 6). The centroid-centroid contact between two pyridine ring fragments in compound **1** is found to be 3.894 Å. The observed π - π interaction involving the pyridyl rings in **1-6** is of offset or slipped stacking type because the aromatic rings are displaced from each other in a parallel manner to give rise to a π - σ type of attraction between the stacked rings. The displacement value of $\alpha = 27^\circ$, i.e. the angle (α) between the ring-centroid vector and the

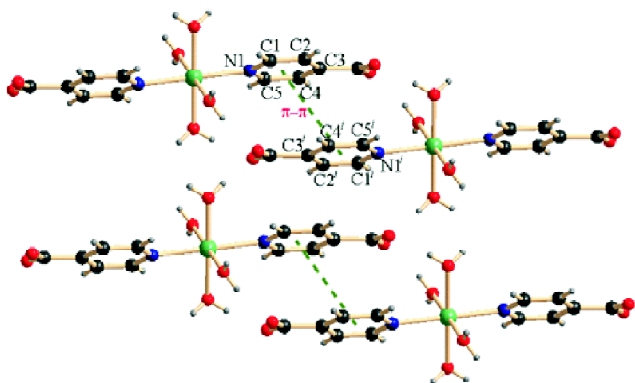


Fig. 6. π - π interactions observed between the pyridyl rings of isonicotinato ligands in compounds **1-6**. Symmetry code: i , $1-x, -y, 1-z$.

ring normal to one of the pyridine ring planes in **1** is comparable with values observed for other nitrogen containing aromatic ligands²⁶. Similar values can be obtained for the other complexes in the series. The centroid-centroid distances for **1-6** are listed in Table 4. The displacement of the pyridyl rings of **5** is greater and hence a higher centroid-centroid separation of 4.248 Å is observed in this compound. Once again, the departure of the Cu species from the expected range of values may be attributed to the structural differences between compound **5** and the other member of the series.

Table 4. Pyridine ring centroid...centroid distances in **1-6**

Compounds	Centroid...Centroid separations (Å)
Mn(iso) ₂ (H ₂ O) ₄ 1	3.894
Fe(iso) ₂ (H ₂ O) ₄ 2	3.880
Co(iso) ₂ (H ₂ O) ₄ 3	3.882
Ni(iso) ₂ (H ₂ O) ₄ 4	3.878
Cu(iso) ₂ (H ₂ O) ₄ 5	4.248
Zn(iso) ₂ (H ₂ O) ₄ 6	3.910

It is evident from the various structural data that except the Cu complex (**5**), the other complexes are more similar. In compound **5**²⁹, the coordination sphere is considerably distorted due to Jahn-Teller effect which leads to the familiar (4,2) coordination geometry around the copper(II) centre. The two *trans* isonicotinato ligands are present at distances [Cu(1)-N(1) = 2.006(2) Å] comparable to those of the others. On the other hand, while the Cu(1)-O(1) distance of 1.986(1) Å is normal, the Cu(1)-O(2) distance of 2.452(2) Å is much longer. The four-fold rotation axis of the approximately D_{4h} coordination geometry around Cu is along the O(2)-Cu(1)-O(2)^{*i*} direction, which is perpendicular to the plane formed by O(1), N(1), O(1)^{*i*}, N(1)^{*i*} and Cu(1).

The Powder X-ray diffraction patterns of compounds **1-6** are shown in Fig. 7. For each species the powder diffraction patterns calculated from the atomic coordinates obtained from

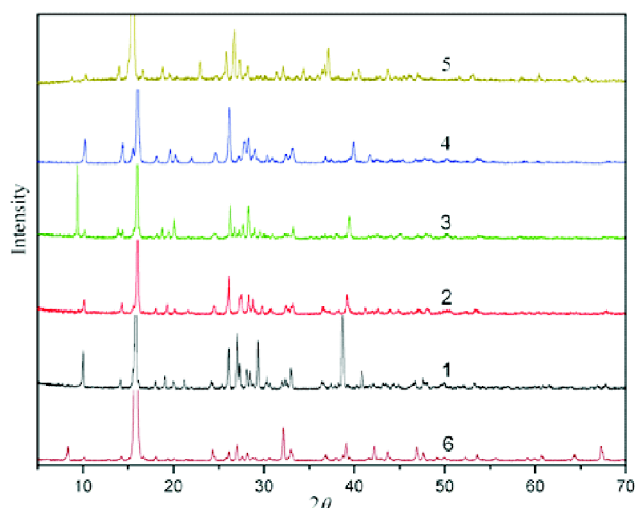


Fig. 7. Comparison of powder XRD patterns observed for compounds **1-6**.

single-crystal X-ray diffraction data are closely similar to the observed patterns (Fig. 8). The close similarities between observed and calculated XRD patterns suggest the purity of crystalline bulk samples of the compounds and correctness of the structures described by us. The *d*-spacings and relative intensities found by us for compounds **1-6** are given in Table 5. The indexing of the powder patterns is based on the comparison of the experimental and calculated powder XRD patterns. It is interesting to note that identical reflections with similar relative intensities are observed for all the compounds.

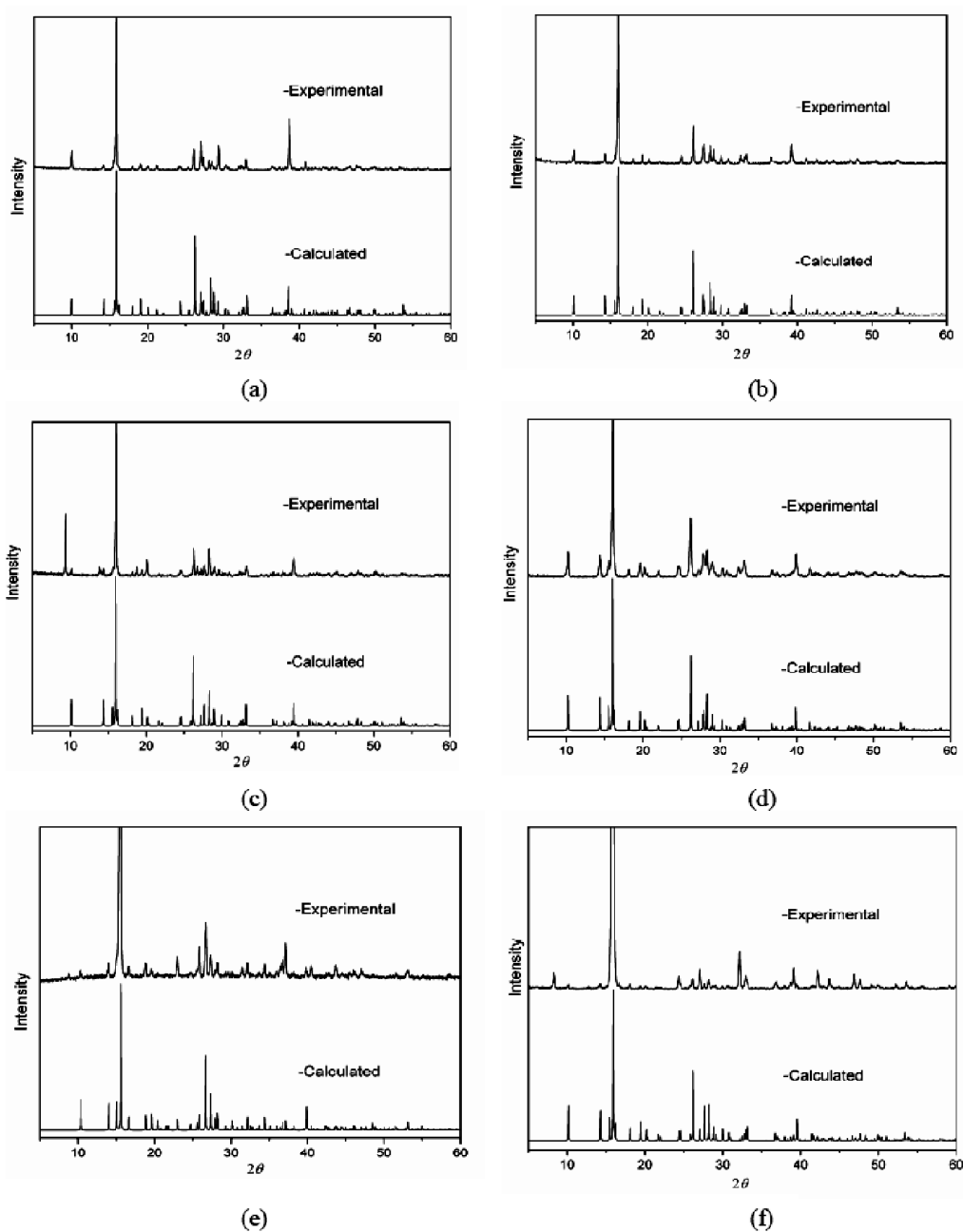


Fig. 8. Experimental and calculated X-ray powder diffraction patterns for compounds (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5** and (f) **6**.

There is however one odd member (**5**) in the group because the structure of the copper compound is significantly influenced by Jahn-Teller distortion which renders two of the six Cu-L bonds to become different from the other four. Further, in spite of the identical space symmetry of the six compounds, compound **5** has the longest as well as the shortest hydro-

gen bonds among the six compounds (Table 3). Differences in the molecular and supramolecular structures shown by **5** from the rest of the members in this family are thus believed to be responsible for the differences in 2θ values and relative intensities of some of the diffraction maxima obtained in the PXRD patterns observed for **5**.

Table 5. Indexed PXRD reflections with *d*-values and relative intensities for compounds 1-6

Mn (1)			Fe (2)			Co (3)			Ni (4)			Cu (5)			Zn (6)		
<i>hkl</i>	<i>d_{obs}</i> (Å)	<i>I_{obs}/Rel</i>	<i>hkl</i>	<i>d_{obs}</i> (Å)	<i>I_{obs}/Rel</i>	<i>hkl</i>	<i>d_{obs}</i> (Å)	<i>I_{obs}/Rel</i>	<i>hkl</i>	<i>d_{obs}</i> (Å)	<i>I_{obs}/Rel</i>	<i>hkl</i>	<i>d_{obs}</i> (Å)	<i>I_{obs}/Rel</i>	<i>hkl</i>	<i>d_{obs}</i> (Å)	<i>I_{obs}/Rel</i>
001	8.829	13	001	8.708	8	001	8.674	5	001	8.640	16	001	8.459	2	001	8.725	1
010	6.263	4	010	6.193	6	010	6.159	6	010	6.142	14	100	6.325	3	010	6.193	1
101	5.587	100	101	5.518	100	101	5.525	100	101	5.518	100	011	5.687	100	101	5.566	100
111	4.916	3	111	4.810	4	111	4.878	3	111	4.884	5	110	5.333	2	111	4.900	1
011	4.655	5	011	4.584	5	011	4.560	4	011	4.519	10	111	4.714	3	011	4.588	1
111	4.443	3	111	4.403	3	111	4.416	10	111	4.390	6	101	4.542	2	111	4.416	1
111	3.680	3	111	3.635	6	111	3.620	3	111	3.612	8	111	3.865	4	111	3.655	2
120	3.413	14	120	3.410	21	120	3.390	16	120	3.405	36	112	3.444	6	120	3.408	2
112	3.294	19	112	3.272	4	112	3.268	4	112	3.270	5	210	3.332	7	112	3.294	2
112	3.261	9	112	3.237	11	112	3.221	7	112	3.235	4	201	3.258	4	112	3.228	1
021	3.172	7	021	3.152	11	021	3.154	16	021	3.150	17	102	3.161	3	021	3.165	1
202	2.792	3	202	2.760	6	202	2.767	3	202	2.760	7	003	2.842	2	202	2.779	4
113	2.715	8	113	2.702	5	113	2.694	6	113	2.707	11	113	2.784	3	113	2.715	2
222	2.462	3	222	2.463	5	222	2.442	3	222	2.443	5	221	2.606	3	222	2.445	1
212	2.327	34	212	2.292	9	212	2.293	4	212	2.287	3	122	2.421	5	212	2.301	3
213	2.140	8	213	2.122	4	103	2.283	11	103	2.256	15	213	2.261	2	213	2.139	2
204	2.079	2	204	2.066	3	213	2.125	2	213	2.128	4	013	2.229	2	204	2.071	2
313	1.944	3	313	1.933	3	313	1.931	2	313	1.928	3	024	2.072	2	313	1.935	2
124	1.910	4	124	1.899	2	124	1.897	4	124	1.905	4	214	1.971	2	124	1.909	1

Table 6. Isostructurality parameters for $M(\text{iso})_2(\text{H}_2\text{O})_4$ (**1-6**) evaluated by Kálmán-Fábián method¹

Structure pairs	Unit cell similarity index (π)	Mean elongation value (ϵ)	Asphericity index (A)	Lattice distortion index (ϵA)
1/2	0.0030	0.0045	1.3298	0.0060
1/3	0.0073	0.0085	1.0166	0.0087
1/4	0.0095	0.0122	1.1221	0.0137
1/5	0.0084	0.0051	5.7229	0.0289
1/6	0.0060	0.0077	1.4178	0.0109
2/3	0.0043	0.0039	0.9385	0.0037
2/4	0.0065	0.0077	1.1031	0.0085
2/5	0.0054	0.0005	52.039	0.0272
2/6	0.0030	0.0032	1.8648	0.0060
3/4	0.0021	0.0037	1.4526	0.0054
3/5	0.0011	0.0035	7.3526	0.0254
3/6	0.0014	0.0008	3.5381	0.0027
4/5	0.0010	0.0071	3.2269	0.0232
4/6	0.0035	0.0045	0.6418	0.0029
5/6	0.0024	0.0027	8.8577	0.0236

The similar chemical composition, close similarity of lattice parameters, identical space group symmetry and powder XRD patterns of compounds **1-6** suggest the isostructurality among the compounds. In view of this, we have studied the crystal structures by the method of Kálmán and Fábián¹, whereby two structures can be compared by their unit cell similarity index (π), mean elongation value (ϵ), asphericity index (A) and the lattice distortion index (ϵA). Since we have six structures to be studied, a total of 15 different sets of calculations have been performed. The calculated parameters obtained for each pair of structures are summarized in Table 6. The nearly zero value of π for each pair of compounds suggests close similarity among the structures. However, on careful examination one can notice relatively higher A values for the pairs of structures containing **5** (the Cu species) as a member viz. 5.72, 52.04, 7.35, 3.23 and 8.86 for the compound pairs **1/5**, **2/5**, **3/5**, **4/5** and **6/5** respectively. These higher values indicate structural dissimilarities between the two structures under comparison. As discussed above, $\text{Cu}(\text{iso})_2(\text{H}_2\text{O})_4$ (**5**) has a more distorted structure compared to the other members in the group. This deviation is therefore supported by the isostructurality parameters determined by us.

Conclusions

Discrete molecular entities of $M(\text{iso})_2(\text{H}_2\text{O})_4$ ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) are structurally similar with the Cu species presenting some differences resulting from Jahn-Teller distortion. The complexes are intimately linked to one another via O-H...O hydrogen bonds involving all acceptor ($-\text{COO}^-$) and donor (water molecules) groups to form robust 3D supramolecular architectures of the species in the crystalline state. The observed π - π stacking interaction between pyridyl rings is another important structure director for the compounds. The analogous powder XRD patterns of the species indicate the close structural relationship among the six compounds. The isostructurality of the compounds in the series, as evaluated crystallographically via volume-based isostructurality measures, are found to tally with the well-known Irving-Williams series of coordination chemistry.

Acknowledgements

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Supporting Information

CCDC 1902011, 1902012, 1902013, 164613, 628462, and 1008892 contain the crystallographic data for the six

crystal structures described in this paper in CIF format. Copies of this information may be obtained free of charge from <http://www.ccdc.cam.ac.uk> or from the corresponding author.

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