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Influential factors on assembly of first-row transition metal coordination polymers

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ABSTRACT

Herein, twenty-seven coordination polymers were synthesised using Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} in organic solvents. Structural analyses show that metal ions are the most important factor that influences coordination polymer assembly. Metal ions determine the type of metal centre and structural topology. The organic ligand benzene dicarboxylic acid is the second most influential factor. Synthetic conditions are not key factors in this research system.

1. Introduction

Coordination polymers have attracted intense research interest in recent years not only for their importance in chemistry [1–3] but also for their potential application in many areas [4–10]. Their most promising application is to be used as porous materials [11–15].

Coordination polymers comprise two parts: metal ions (inorganic) and ligands (in most cases, organic). Numerous metal ions are involved in coordination polymer assembly, and the first row transition metal ions are the best candidates because they are abundant and cheap with low toxicity. Such metal ions are also suitable for design and synthesis of low density porous materials given their relatively low atomic weight. Many highly porous coordination polymers (PCPs; also referenced as open metal-organic frameworks, MOFs) are assembled using Cu^{2+} or Zn^{2+} (a main group d^{10} ion) [16]. Moreover, most magnetic MOFs can be assembled by incorporating paramagnetic divalent first-row transition metals (Mn, Fe, Co, Ni and Cu) within distances sufficient for interaction [17]. The metal centre's structure and properties are extremely important in designing coordination polymers with various features [18]. It is critical to know when the metal ions tend to form discrete SBUs and when the infinite rod-shaped SBU (Secondary Building Unit) will be formed [19].

Most research has concentrated on design and synthesis of bridging ligands, which are the organic portion of coordination polymers [20–24]. Benzene polycarboxylic acids have been widely used for such studies. They can adopt various coordination modes, which have certain consequences for the product's structures and properties, and they often form highly stable MOFs [25–27]. Synthetic conditions, including *p*H value [28,29], temperature [30–33], solvents [34], and counter ions [35], also play an important role in synthesis. Polar organic solvents with a high boiling point, such as DMF (*N*,*N*-dimethylformamide), DEF (*N*,*N*-diethylformamide), and DMSO (dimethyl sulfoxide), are excellent solvents for reactants and can act as space-filling solvent molecules for porous MOFs [36,37]. We found that solvents and mixed solvent ratios can be used as media for adjusting the metal centres and structures in coordination polymers [38–41].

What is the decisive influential factor for assembly of first-row transition metal coordination polymers, and why are Cu^{2+} and Zn^{2+} over other metal ions so common in porous materials? To answer the above questions and to synthesise coordination polymers, we used the first-row transition metal ions Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} as well as Zn^{2+} as the inorganic components; benzene dicarboxylic acids were the bridging ligands; and polar high-boiling-point organic compounds were the solvents (Table 1). Here, we report structural analyses for the twenty-seven products generated as well as the conclusions for our research.

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Table 1
Ligands and solvents used in this work.

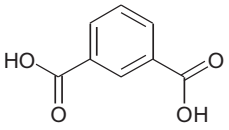
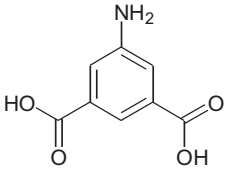
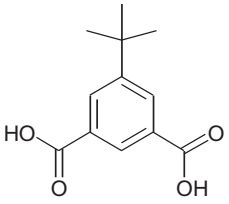
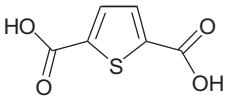
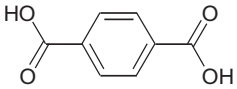
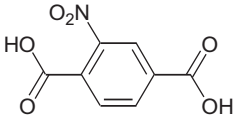
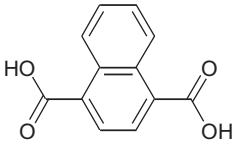
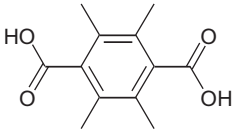
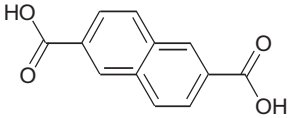
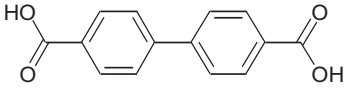
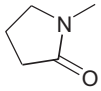
Ligand or solvent	Name	Short name	Length (Å) and angle (°) between two carboxyls
Short ligands			
	isophthalic acid	H_2**ip**	5.94, ~120
	5-aminoisophthalic acid	H_2**aip**	6.03, ~119
	5-*tert*-butylisophthalic acid	H_2**tbip**	5.93, ~119
	thiophenedicarboxylic acid	H_2**tdc**	6.44, ~153
Medium ligands			
	terephthalic acid	H_2**tp**	6.93
	2-nitroterephthalic acid	H_2**ntp**	6.92
	1,4-naphthalenedicarboxylic acid	H_2**1,4-ndc**	6.98, ~175
	tetramethylterephthalic acid	H_2**tmtp**	7.02
Long ligands			
	2,6-naphthalenedicarboxylic acid	H_2**2,6-ndc**	9.15
	biphenyldicarboxylic acid	H_2**bpdc**	11.22
Solvents			
	*N*,*N*-dimethylformamide	**DMF**	
	*N*,*N*-dimethylacetamide	**DMA**	
	N-methyl-2-pyrrolidone	**NMP**	

Table 1 (*continued*)

Ligand or solvent	Name	Short name	Length (Å) and angle (°) between two carboxyls
			
	dimethylsulfoxide	**DMSO**	
	pyridine	**PY**	

2. Experimental

2.1. Methods

The synthesis procedure for the compounds was as follows. A solution comprising the metal salt and ligand in an organic solvent (or mixed solvent) was placed at room temperature or heated 0.2 °C min^{-1} to a temperature in the range 70–140 °C and maintained at that temperature for approximately 4 days. Generally, the synthetic conditions for Mn or Zn compounds are similar, while Cu compounds are generated at lower temperatures. The products were collected by filtration and washed with pure solvents. The crystals produced were characterised using single X-ray crystallography, elemental analysis and Infrared spectrometry. IR spectra show strong bands in the range 1690–1500 cm^{-1} (ν_{as} stretching vibrations) and 1447–1340 cm^{-1} (ν_{s} stretching vibrations) for coordinated carboxylato groups, respectively. IR spectra also show weak bands at about 2930 for saturated C–H and 3100 for aromatic C–H vibrations, and broad peaks at about 3300 cm^{-1} for water molecules.

2.1.1. $[Mn(ip)(dma)]_n$ **1**

A mixture comprising a $Mn(NO_3)_2$ 50% aqueous solution (0.77 g, 4.3 mmol) and H_2ip (0.249 g, 1.5 mmol) in 8 mL DMA was heated at 90 °C for 4500 min. Colourless block crystals were generated (0.350 g, 76% based on H_2ip). The elemental analysis (*Anal.* Calc.) for $C_{12}H_{13}MnNO_5$ is as follows: C, 47.23 (47.07); H, 4.19 (4.28); N, 4.72 (4.57)%. IR (cm^{-1}): 3408, 2909 (w), 1592 (s), 1537, 1374 (s), 740 (w), and 720 (w).

2.1.2. $[Mn(tdc)(dma)]_n$ **2**

A mixture comprising a $Mn(NO_3)_2$ 50% aqueous solution (0.30 g, 1.7 mmol) and H_2tdc (0.086 g, 0.50 mmol) in a mixed solvent of 8 mL DMA and 2 mL ethanol was heated at 100 °C for 5000 min. Pale yellow crystals were obtained (0.128 g, 82%). Elemental analysis, *Anal.* (Calc.) for $C_{10}H_{11}MnNO_5S$: C, 38.39 (38.47); H, 3.58 (3.55); N, 4.51 (4.49)%. IR (cm^{-1}): 3371, 1624, 1551 (vs), 1508 (s), 1452 (w), 1372 (vs), 1126 (w), 1044, 779 (s), 681 (w), 540 (w), 496 (w).

2.1.3. $[Mn(tdc)(nmp)]_n$ **3**

Same procedure for **2** was applied with NMP in place of DMA. Pale yellow crystals were obtained (0.134 g, 83%). Elemental analysis, *Anal.* (Calc.) for $C_{11}H_{11}MnNO_5S$: C, 40.66 (40.75); H, 3.44 (3.42); N, 4.33 (4.32)%. IR (cm^{-1}): 3429, 1618 (s), 1583 (s), 1527 (s), 1383 (s), 1367 (vs), 1312, 1050 (w), 772 (s), 676 (w), 476(w).

2.1.4. $[Mn(tdc)(dmso)]_n$ **4**

Same procedure for **2** was applied with DMSO in place of ethanol. Pale yellow crystals were obtained (0.099 g, 65%). Elemental analysis, *Anal.* (Calc.) for $C_8H_8MnO_5S_2$: C, 31.63 (31.69); H, 2.65 (2.66)%. IR (cm^{-1}): 3446, 1575 (s), 1528 (s), 1373 (vs), 1315, 996, 940, 793, 772 (w), 677 (w), 475.

2.1.5. $[Mn(tp)(dmf)]_n$ **5**

A mixture comprising a $Mn(NO_3)_2$ 50% aqueous solution (0.30 g, 1.7 mmol) and H_2tp (0.166 g, 1.0 mmol) in a mixed solvent of 6 mL DMF and 4 mL ethanol was heated at 90 °C for 4000 min. Pale yellow crystals were obtained (0.187 g, 64% based on H_2tp). Elemental analysis, *Anal.* (Calc.) for $C_{22}H_{22}Mn_2N_2O_{10}$: C, 45.20 (45.18); H, 2.65 (2.64); N, 4.78 (4.79)%. IR (cm^{-1}): 3069 (w), 2929 (s), 2886, 1662 (vs), 1627 (vs), 1578 (vs), 1385 (vs), 1153, 1104 (s), 1020, 891 (w), 866 (w), 819 (s), 752 (vs), 673.

2.1.6. $[Mn(tmtp)(dmf)]_n$ **6**

A mixture comprising a $Mn(NO_3)_2$ 50% aqueous solution (0.036 g, 0.20 mmol) and H_2tmtp (0.044 g, 0.20 mmol) in a mixed solvent of 2 mL DMF and 1 mL ethanol was heated at 90 °C for 4000 min. Colorless crystals were obtained (0.033 g, 48% based on H_2tmtp). There was not enough product for elemental analysis and IR measurement.

2.1.7. $\{[Co(ntp)(H_2O)]\cdot 1.25H_2O\}_n$ **7**

A mixture comprising $Co(NO_3)_2\cdot 6H_2O$ (0.146 g, 0.50 mmol) and H_2ntp (0.105 g, 0.50 mmol) in a mixed solvent of 10 mL DMF and 3 mL H_2O was heated at 100 °C for 5000 min. Red crystals were obtained (0.132 g, 87%). Elemental analysis, *Anal.* (Calc.) for $C_8H_{7.5}CoNO_{8.25}$: C, 32.66 (31.14); H, 2.23 (2.45); N, 4.79 (4.54)%. IR (cm^{-1}): 3447, 2928 (w), 1618 (s), 1537(w), 1387 (s), 1011, 773, 607 (w), 541 (s).

2.1.8. $[Zn(1,4\text{-}ndc)(dmf)]_n$ **8**

A mixture comprising $ZnCl_2$ (0.136 g, 1.0 mmol) and H_2(1,4-ndc) (0.216 g, 1.0 mmol) in a mixed solvent of 10 mL DMF and 3 mL H_2O was heated in a 20 mL Teflon lined vessel at 120 °C for 4320 min. Purple block crystals were obtained (0.330 g, 94%). Elemental analysis, *Anal.* (Calc.) for $C_8H_{7.5}CoNO_{8.25}$: C, 51.45 (51.04); H, 3.58 (3.69); N 3.93 (3.97)%.

2.1.9. $[Cu_2(tdc)_2(NH_3)_4]_n$ **9**

A mixture comprising $Cu(NO_3)_2\cdot 2H_2O$ (0.121 g, 0.50 mmol) and H_2tdc (0.086 g, 0.50 mmol) in a mixed solvent of 8 mL DMA (or NMP) and 2 mL aqueous ammonia was left to stand at room temperature for 1 month. Blue crystals were obtained (0.073 g, 55%). Elemental analysis, *Anal.* (Calc.) for $C_8H_6CuN_2O_4S$: C, 33.16 (33.03); H, 2.09 (2.10); N, 9.67 (9.71)%. IR (cm^{-1}): 3355, 2989 (w), 1634, 1586 (s), 1552, 1523, 1384 (s), 1361 (vs), 823 (w), 767, 476 (w).

2.1.10. $[Cu_2(tbip)_2(dma)_2]_n$ **10**

A mixture comprising $Cu(NO_3)_2\cdot 2H_2O$ (0.072 g, 0.30 mmol) and H_2tbip (0.067 g, 0.30 mmol) in 10 mL DMA was heated at 70 °C for

5760 min. Blue crystals were obtained (0.115 g, 58%). Elemental analysis, *Anal.* (Calc.) for $C_{16}H_{21}NO_5Cu$: C, 51.92 (51.81); H, 5.69 (5.71); N, 3.81 (3.78)%. IR (cm^{-1}): 3427 (vs), 2956, 1612 (vs), 1382 (vs), 1267(w), 787, 730.

2.1.11. $\{[Cu_2(ip)_2(nmp)_2\{Cu_2(ip)_2(H_2O)_2\}_2]\cdot 5NMP\cdot 2H_2O\}_n$ ***11***

A mixture comprising $Cu(NO_3)_2\cdot 2H_2O$ (0.048 g, 0.20 mmol) and H_2ip (0.033 g, 0.20 mmol) in a mixed solvent of 4 mL NMP and 6 mL ethanol was left to stand at room temperature for 4 months. Blue crystals were obtained (0.018 g, 26%). Elemental analysis, *Anal.* (Calc.) for $C_{83}H_{99}Cu_6N_7O_{37}$: C, 47.96 (45.98); H, 4.32 (4.60); N, 4.89 (4.52)%. IR (cm^{-1}): 3427 (s), 2925 (w), 1633(vs), 1575 (w), 1443 (w), 1388 (vs), 1065, 746 (w), 723(w), 485(s).

2.1.12. $[Zn_2(tp)_2(nmp)_2]_n$ ***12***

A mixture comprising $Zn(NO_3)_2\cdot 6H_2O$ (0.297 g, 1.0 mmol) and H_2tp (0.166 g, 1.0 mmol) in 10 mL NMP was heated at 90 °C for 6000 min. Colorless block crystals were obtained (0.192 g, 59%). Elemental analysis, *Anal.* (Calc.) for $C_{13}H_{13}NO_5Zn$: C, 47.40 (47.51); H, 4.70 (3.99); N, 5.18 (4.26)%.

2.1.13. $[Zn_2(2,6\text{-}ndc)_2(dmf)_2]_n$ ***13***

A mixture comprising $Zn(NO_3)_2\cdot 6H_2O$ (0.297 g, 1.0 mmol) and H_2(2,6-ndc) (0.216 g, 1.0 mmol) in 15 mL DMF was heated in a 20 mL Teflon lined vessel at 120 °C for 4000 min. Pale yellow block crystals were obtained (0.276 g, 78%). Elemental analysis, *Anal.* (Calc.) for $C_{15}H_{13}NO_5Zn$: C, 51.45 (51.09); H, 3.56 (3.72); N, 3.93 (3.97)%.

2.1.14. $[Zn_2(tdc)_2(dma)_2]_n$ ***14***

A mixture comprising $Zn(NO_3)_2\cdot 6H_2O$ (0.149 g, 0.50 mmol) and H_2tdc (0.086 g, 0.50 mmol) in 10 mL DMA was heated at 90 °C for 7000 min. Colorless crystals were obtained (0.110 g, 56%). IR (cm^{-1}): 3421, 1635 (s), 1577, 1528 (w), 1383 (vs), 1261, 771 (w), 686(w), 494.

2.1.15. $[Zn_2(tdc)_2(py)_2]_n$ ***15***

A mixture comprising $Zn(NO_3)_2\cdot 6H_2O$ (0.149 g, 0.50 mmol) and H_2tdc (0.086 g, 0.50 mmol) in a mixed solvent of 8 mL DMA (or NMP) and 2 mL pyridine was heated at 90 °C for 7000 min. Colorless crystals were obtained (0.118 g, 75%). IR (cm^{-1}): 3440, 1607 (s), 1573, 1528, 1384 (vs), 1218 (w), 770, 501(w).

2.1.16. $[Mn_3(2,6\text{-}ndc)_3(dmf)_4]_n$ ***16***

A mixture comprising a $Mn(NO_3)_2$ 50% aqueous solution (0.50 mmol) and H_2(2,6-ndc) (0.108 g, 0.50 mmol) in 15 mL DMF was heated at 90 °C for 4000 min. Colorless block crystals were obtained (0.222 g, 43%). Elemental analysis, *Anal.* (Calc.) for $C_{48}H_{46}Mn_3N_4O_{16}$: C, 52.17 (52.42); H, 4.17 (4.21); N 5.16 (5.09)%.

2.1.17. $[Mn_3(2,6\text{-}ndc)_3(dma)_4]_n$ ***17***

A mixture comprising a $Mn(NO_3)_2$ 50% aqueous solution (0.50 mmol) and H_2(2,6-ndc) (0.108 g, 0.50 mmol) in 15 mL DMA was heated at 100 °C for 4320 min. Orange block crystals were obtained (low yield). There was not enough product for elemental analysis and IR measurement.

2.1.18. $[Mn_3(2,6\text{-}ndc)_3(nmp)_4]_n$ ***18***

A mixture comprising a $Mn(NO_3)_2$ 50% aqueous solution (0.50 mmol) and H_2(2,6-ndc) (0.108 g, 0.50 mmol) in a mixed solvent of 8 mL NMP and 8 mL ethanol was heated at 100 °C for 4000 min. Yellow block crystals were obtained (low yield). There was not enough product for elemental analysis and IR measurement.

2.1.19. $[Mn_3(bpdc)_3(dma)_4]_n$ ***19***

A mixture comprising $MnCl_2\cdot 4H_2O$ (0.050 g, 0.25 mmol) and H_2-bpdc (0.061 g, 0.25 mmol) in 10 mL DMA was heated at 100 °C for 4320 min. Yellow crystals were obtained (0.050 g, 49%). Elemental analysis, *Anal.* (Calc.) for $C_{58}H_{60}N_4O_{16}Mn_3$: C, 56.93 (56.46); H, 4.83(4.90); N, 4.68 (4.54)%. IR (cm^{-1}): 3388 (s), 2926 (w), 1576 (vs), 1524 (vs), 1386 (vs), 1180 (w), 796 (vs), 672(w).

2.1.20. $[Co_3(2,6\text{-}ndc)_3(dma)_4]_n$ ***20***

A mixture comprising $Co(NO_3)_2\cdot 6H_2O$ (0.146 g, 0.50 mmol) and H_2(2,6-ndc) (0.054 g, 0.50 mmol) in a mixed solvent of 10 mL DMA and 2 mL ethanol was heated at 100 °C for 2880 min. Red crystals were obtained (low yield). There was not enough product for elemental analysis and IR measurement.

2.1.21. $[Mn_3(tp)_3(nmp)_4]_n$ ***21***

A mixture comprising a $Mn(NO_3)_2$ 50% aqueous solution (0.090 g, 0.50 mmol) and H_2(2,6-ndc) (0.108 g, 0.50 mmol) in 10 mL NMP was heated at 90 °C for 4000 min. Colorless block crystals were obtained (0.267 g, 76%). Elemental analysis, *Anal.* (Calc.) for $C_{44}H_{48}Mn_3N_4O_{16}$: C, 50.17 (50.15); H, 4.53 (4.59); N, 5.29 (5.32)%. IR (cm^{-1}): 3056 (w), 2944, 1648 (vs), 1604 (vs), 1557 (vs), 1506 (s), 1382 (vs), 1304 (s), 1260 (s), 1172 (w), 1114 (w), 1018, 984 (w), 885 (w), 843, 815, 748 (vs), 666 (w).

2.1.22. $\{[Co_3(bpdc)_3(dma)_2]\cdot 4DMA\}_n$ ***22***

A mixture comprising $Co(NO_3)_2\cdot 6H_2O$ (0.073 g, 0.25 mmol) and H_2(2,6-ndc) (0.054 g, 0.25 mmol) in 10 mL DMA was heated at 100 °C for 4320 min. Red crystals were obtained (0.151 g, 64%). Elemental analysis, *Anal.* (Calc.) for $C_{66}H_{78}Co_3N_6O_{18}$: C, 57.24 (55.82); H, 5.38 (5.54); N, 6.11 (5.92)%. IR (cm^{-1}): 3603(w), 3427 (w), 1684(vs), 1594(vs), 1540(s), 1396 (vs), 1295, 1178 (w), 843, 773 (s), 676 (w).

2.1.23. $\{[Zn_3(bpdc)_3(dmf)_2]\cdot 4DMF\cdot 0.5H_2O\}_n$ ***23***

A mixture comprising $Zn(NO_3)_2\cdot 6H_2O$ (0.297 g, 1.0 mmol) and H_2bpdc (0.242 g, 1.0 mmol) in 20 mL DMF was filtrated and heated at 80 °C for 8000 min. Colorless crystals were obtained (0.177 g, 39%). There was not enough product for elemental analysis and IR measurement.

2.1.24. $\{[Zn_3(bpdc)_3(nmp)_2]\cdot 4NMP\}_n$ ***24***

Same procedure for **23** was applied with NMP instead of DMF. Colorless crystals were obtained (low yield). There was not enough product for elemental analysis and IR measurement.

2.1.25. $\{[Ni(2,6\text{-}ndc)(H_2O)_4]\cdot 2NMP\cdot 2H_2O\}_n$ ***25***

A mixture comprising $Co(NO_3)_2\cdot 6H_2O$ (0.073 g, 0.25 mmol) and H_2(2,6-ndc) (0.054 g, 0.25 mmol) in 5 mL NMP was microwave heated at 120 °C for 10 min then cooled down to room temperature. Green block crystals were obtained (0.068 g, 47%). Elemental analysis, *Anal.* (Calc.) for $C_{22}H_{36}N_2O_{12}Ni$: C, 44.36 (45.62); H, 6.41 (6.26); N, 4.96 (4.84)%. IR (cm^{-1}): 3423, 2928 (w), 1642 (s), 1564, 1390 (s), 1189 (w), 793, 774, 476.

2.1.26. $[Mn(Haip)_2(H_2O)_2]_n$ ***26***

A mixture comprising $Mn(NO_3)_2$ 50% aqueous solution (0.090 g, 0.50 mmol) and H_2aip (0.091 g, 0.50 mmol) in a mixed solvent of 4 mL DMA and 4 mL H_2O was heated at 110 °C for 4000 min. Colorless block crystals were obtained (low yield). There was not enough product for elemental analysis and IR measurement.

2.1.27. $[Zn(aip)(dma)]_n$ ***27***

A mixture comprising $Zn(NO_3)_2\cdot 6H_2O$ (0.297 g, 1.0 mmol) and H_2aip (0.091 g, 0.50 mmol) in a mixed solvent of 7 mL DMA and 2 mL ethanol was heated at 95 °C for 3000 min. Brown block crys-

Table 2
Crysltal data for **1**–**27**.

	1	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{12}H_{13}MnNO_5$	$C_{10}H_{11}MnNO_5S$	$C_{11}H_{11}MnNO_5S$	$C_8H_8MnO_5S_2$	$C_{22}H_{22}Mn_2N_2O_{10}$	$C_{15}H_{19}MnNO_5$	$C_8H_{7.50}CoNO_{8.25}$
Formula weight	306.17	312.20	324.21	303.20	584.30	348.25	308.58
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal	orthorhombic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	$P2_1/c$	$I4_1/a$	*I*mma
F(000)	1256	1272	1320	1224	1192	2896	622
T/K	297(2)	299(2)	296(2)	296(2)	296(2)	223(2)	173(2)
a (Å)	12.6006(8)	11.8527(6)	11.7729(2)	11.2759(4)	13.5792(6)	20.324(1)	17.9930(6)
b (Å)	16.3414(10)	18.2900(7)	18.2439(4)	18.4795(4)	10.1898(4)		7.2497(3)
c (Å)	12.6527(8)	11.4991(6)	11.7165(2)	11.2782(4)	17.6223(7)	15.2571(7)	11.5979(4)
α (°)							
β (°)	107.792(1)	99.020(5)	99.6134(19)	96.217(4)	90.738(1)		
γ (°)							
V (Å^3)	2480.7(3)	2462.0(2)	2481.17(8)	2336.25(13)	2438.18(17)	6302.3(4)	1512.87(10)
Z	8	8	8	8	4	16	4
$D_{calc.}$ (g cm^{-3})	1.640	1.685	1.736	1.724	1.592	1.468	1.355
μ (mm^{-1})	1.080	1.253	1.247	1.487	1.094	0.860	1.162
Reflection collected/unique	9112/2928	11022/4108	11389/4164	7540/2740	20635/5806	26550/3807	3587/992
Data/restraints/parameters	2928/0/197	4108/6/165	4164/0/175	2740/0/151	5806/0/361	3807/0/203	992/0/78
R_{int}	0.0271	0.0759	0.0229	0.0240	0.0307	0.0313	0.0178
S	1.197	0.847	1.085	1.135	1.046	1.209	1.059
R_1 [$I > 2\sigma(I)$]	0.0556	0.0456	0.0315	0.0574	0.0406	0.0542	0.0411
wR_2 (all data)	0.1194	0.1780	0.1169	0.1829	0.1009	0.1177	0.1343
Δρ (e A^{-3})	0.542/−0.445	0.904/−0.778	0.642/−0.650	0.717/−0.911	0.522/−0.389	0.587/−0.402	1.067/−0.689

	8	**9**	**10**	**11**	**12**	**13**	**14**
Empirical formula	$C_{30}H_{26}N_2O_{10}Zn_2$	$C_6H_8CuN_2O_4S$	$C_{16}H_{21}CuNO_5$	$C_{83}H_{99}Cu_6N_7O_{37}$	$C_{13}H_{13}NO_5Zn$	$C_{15}H_{13}NO_5Zn$	$C_{10}H_{11}NO_5SZn$
Formula weight	705.27	267.74	370.88	2167.93	328.61	352.63	322.63
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	Monoclinic	monoclinic
Space group	*Pc*	*C*2/*c*	$P2_1/c$	*C*2/*c*	$P2_1/c$	$P2_1/c$	$P2_1/n$
F(000)	720	1080	772	4464	672	720	656
T/K	295(2)	173(2)	173(2)	173(2)	253(2)	295(2)	153(2)
a (Å)	7.1781(2)	7.6170(6)	12.1599(4)	30.528(5)	7.4479(5)	6.7716(4)	8.4866(2)
b (Å)	14.0979(3)	12.6984(8)	10.6507(3)	19.241(3)	13.9477(9)	18.590(1)	14.8476(4)
c (Å)	16.0641(4)	19.1943(14)	14.7652(5)	20.103(4)	12.7644(8)	11.6437(6)	10.1406(3)
α (°)							
β (°)	121.726(2)	100.373(8)	104.768(3)	128.611(3)	103.500(1)	97.383(1)	100.734(2)
γ (°)							
V (Å^3)	1382.71(6)	1826.2(2)	1849.09(10)	9227(3)	1289.34(14)	1453.60(14)	1255.41(6)
Z	2	8	4	4	4	4	4
$D_{calc.}$ (g cm^{-3})	1.694	1.948	1.332	1.561	1.693	1.611	1.707
μ (mm^{-1})	1.800	2.609	1.203	1.450	1.923	1.712	2.133
Reflection collected/unique	11048/6641	8137/2217	10775/4320	27799/10781	14647/3087	11320/3343	8051/3095
Data/restraints/parameters	6641/2/402	2217/0/129	4320/38/227	10781/44/679	3087/0/182	3343/0/225	3095/0/185
R_{int}	0.0474	0.0608	0.0318	0.0976	0.0474	0.0220	0.0298
S	0.944	1.175	0.966	1.061	1.252	1.054	0.938
R_1 [$I > 2\sigma(I)$]	0.0500	0.0642	0.0430	0.0646	0.0666	0.0368	0.0340
wR_2 (all data)	0.1568	0.1985	0.1234	0.1901	0.1411	0.1011	0.0846
Δρ (e A^{-3})	0.663/−1.197	1.676/−0.785	1.331/−0.405	2.238/−0.658	0.814/−0.893	0.457/−0.218	1.210/−0.628

	15	**16**	**17**	**18**	**19**	**20**	**21**
Empirical formula	$C_{11}H_7NO_4SZn$	$C_{48}H_{46}Mn_3N_4O_{16}$	$C_{52}H_{54}Mn_3N_4O_{16}$	$C_{56}H_{54}Mn_3N_4O_{16}$	$C_{58}H_{60}Mn_3N_4O_{16}$	$C_{52}H_{54}Co_3N_4O_{16}$	$C_{44}H_{48}Mn_3N_4O_{16}$
Formula weight	314.61	1099.71	1155.81	1203.85	1233.92	1167.78	1053.68
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	*C*2/*c*	*C*2/*c*	$P2_1/c$	$P2_1/c$	*C*2/*c*	$P2_12_12_1$
F(000)	632	2260	2388	1242	1278	2412	2172
T/K	173(2)	223(2)	298(2)	297(2)	173(2)	173(2)	173(2)
a (Å)	7.6939(2)	13.2373(6)	14.3217(3)	11.8731(4)	13.9430(4)	14.1239(3)	9.7175(4)
b (Å)	15.9643(4)	17.9155(8)	18.4222(4)	18.4743(7)	18.2501(6)	18.3243(4)	18.0168(8)
c (Å)	9.8577(3)	21.4035(10)	20.9869(4)	20.5194(5)	12.1687(4)	20.6657(3)	26.7918(11)
α (°)							
β (°)	97.670(3)	100.105(1)	99.570(2)	142.563(1)	113.169(4)	99.1218(18)	
γ (°)							
V (Å^3)	1199.97(6)	4997.2(4)	5460.07(19)	2736.03(17)	2846.72(16)	5280.86(18)	4690.7(3)
Z	4	4	4	2	2	4	4
$D_{calc.}$ (g cm^{-3})	1.741	1.462	1.406	1.461	1.440	1.469	1.492
μ (mm^{-1})	2.224	0.820	0.754	0.756	0.728	1.004	0.869
Reflection collected/unique	6642/2831	28344/5977	15834/6751	31189/6560	19451/7796	22412/6334	54343/11289
Data/restraints/parameters	2831/0/163	5977/29/334	6751/1/383	6560/10/380	7796/0/373	6334/16/383	11289/1/606
R_{int}	0.0296	0.0254	0.0260	0.0330	0.0210	0.0422	0.0326
S	0.932	1.079	1.009	1.086	1.047	1.035	1.078
R_1 [$I > 2\sigma(I)$]	0.0265	0.0519	0.0376	0.0531	0.0297	0.0401	0.0487
wR_2 (all data)	0.0574	0.1355	0.1114	0.1255	0.0799	0.0975	0.1247
Δρ (e A^{-3})	0.648/−0.363	0.882/ −0.442	0.616/ −0.310	0.586/ −0.387	0.631/ −0.289	0.451/ −0.500	1.103/ −0.639

(*continued on next page*)

Table 2 (*continued*)

	22	23	24	25	26	27
Empirical formula	$C_{66}H_{78}Co_3N_6O_{18}$	$C_{120}H_{132}N_{12}O_{37}Zn_6$	$C_{72}H_{78}N_6O_{18}Zn_3$	$C_{22}H_{36}N_2NiO_{12}$	$C_{16}H_{16}MnN_2O_{10}$	$C_{12}H_{14}N_2O_5Zn$
Formula weight	1420.13	2726.60	1511.51	579.24	451.25	331.62
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2/c$	$P2_1/c$
$F(000)$	1482	2824	1572	306	462	680
T/K	173(2)	273(2)	223(2)	123(2)	173(2)	173(2)
a (Å)	12.2756(2)	20.0297(10)	12.1580(5)	7.1977(3)	6.9972(2)	10.1163(3)
b (Å)	14.1032(2)	14.8284(7)	14.0426(5)	7.2645(4)	10.0161(3)	7.7922(2)
c (Å)	25.8603(4)	22.9351(11)	25.9262(8)	12.8111(7)	13.8929(5)	16.0161(5)
α (°)				81.631(4)		
β (°)	129.437(1)	111.256(1)	127.589(1)	83.686(4)	124.842(2)	90.522(2)
γ (°)				78.332(4)		
V (Å^3)	3457.74(9)	6348.5(5)	3507.5(2)	646.79(6)	799.13(5)	1262.47(6)
Z	2	2	2	1	2	4
$D_{calc.}$ (g cm^{-3})	1.364	1.426	1.431	1.487	1.875	1.745
μ (mm^{-1})	0.783	1.199	1.092	0.816	0.896	1.967
Reflection collected/unique	21817/8052	54359/15099	40257/8483	4612/2784	4044/1850	19861/3160
Data/restraints/parameters	8052/0/452	15099/0/816	8483/0/450	2784/30/214	1850/2/152	3160/2/192
R_{int}	0.0243	0.0516	0.0489	0.0132	0.0248	0.0731
S	0.985	1.111	1.098	1.105	1.001	0.971
R_1 [$I > 2\sigma(I)$]	0.0318	0.0739	0.0586	0.0284	0.0293	0.0325
wR_2 (all data)	0.0793	0.2116	0.1355	0.0783	0.0794	0.0872
$\Delta\rho$ (e A^{-3})	0.463/−0.387	1.792/−0.636	0.797/−0.704	0.354/−0.395	0.322/−0.399	0.659/−0.611

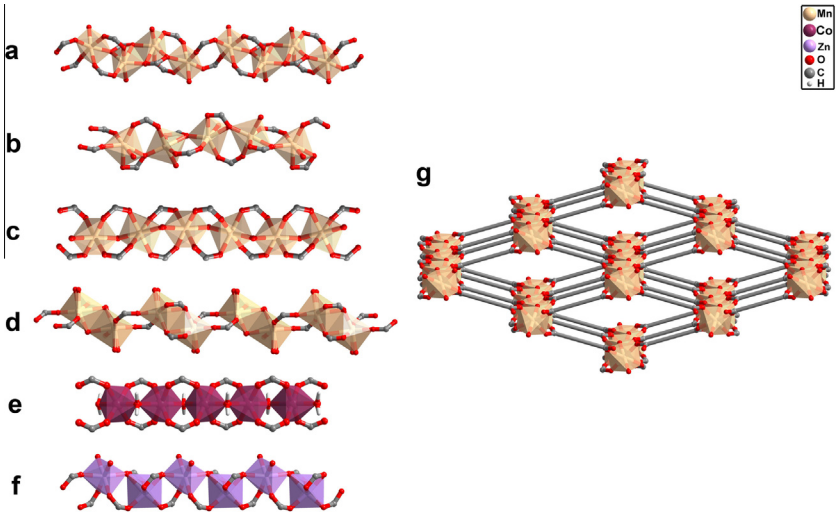


Fig. 1. Rod-shaped SBUs in **1** (a), **2**–**4** (b), **5** (c), **6** (d), **7** (e), and **8** (f); **pcu** topology for the rod packing structure simplified from compound **4**.

tals were obtained (0.067 g, 40% based on H_2aip). Elemental analysis, *Anal.* (Calc.) for $C_{12}H_{14}N_2O_5Zn$: C, 42.64 (43.16); H, 5.53 (4.26); N 8.93 (8.45)%.

2.2. X-ray structure determination

The data were collected on a Bruker SMART Apex CCD diffractometer or an Oxford Gemini S Ultra CrysAlis CCD diffractometer with monochromatic graphite Mo Kα radiation. Structure solutions and full-matrix least-square refinements based on F^2 were performed using the SHELXS-97 and SHELXL-97 program packages, respectively. All the non-hydrogen atoms were refined anisotropically. The H atoms on ligands were positioned geometrically and were allowed to ride on the C atoms in the subsequent refinement (aromatic C–H = 0.93 Å, U(H) = 1.2 Ueq(C), methyl C–H = 0.95 Å, U(H) = 1.5 Ueq(C)). The water H-atoms were located and refined with O–H = 0.85 Å, U(H) = 1.5 Ueq(O) restraints. The water H-atoms were set to proper positions so that more hydrogen bonds can be formed. Crystal data for all the compounds are listed in Table 2.

3. Results and discussion

The compounds can be classified into six groups according to their structural features.

3.1. Rod-packing ***pcu*** *assembled with rod-shaped SBUs*

The structural topology for the following eight compounds is rod-packing **pcu** (Fig. 1.) [7]: $[Mn(ip)(dma)]_n$ **1**, $[Mn(tdc)(dma)]_n$ **2**, $[Mn(tdc)(nmp)]_n$ **3**, $[Mn(tdc)(dmso)]_n$ **4**, $[Mn(tp)(dmf)]_n$ **5**, $[Mn(tmtp)(dmf)]_n$ **6**, $\{[Co(ntp)(H_2O)]\cdot 1.25H_2O\}_n$ **7** and $[Zn(1,4\text{-}ndc)(dmf)]_n$ **8**. These compounds were assembled using short ligands (e.g., H_2**ip** and its derivatives ~5.9 Å as well as H_2tdc ~6.4 Å), and medium-length ligands (H_2**tp** and its derivatives ~7 Å). Metal ions, such as Mn^{2+}, Co^{2+} and Zn^{2+}, form M_n metal centres or rod-shaped SBUs composed of corner-sharing octahedra, while the Mn^{2+} ion with the largest size can also form edge-sharing octahedral rod-shaped SBUs (Fig. 1a, d). Six of the eight compounds in this group were formed using Mn^{2+} ions, which demonstrates

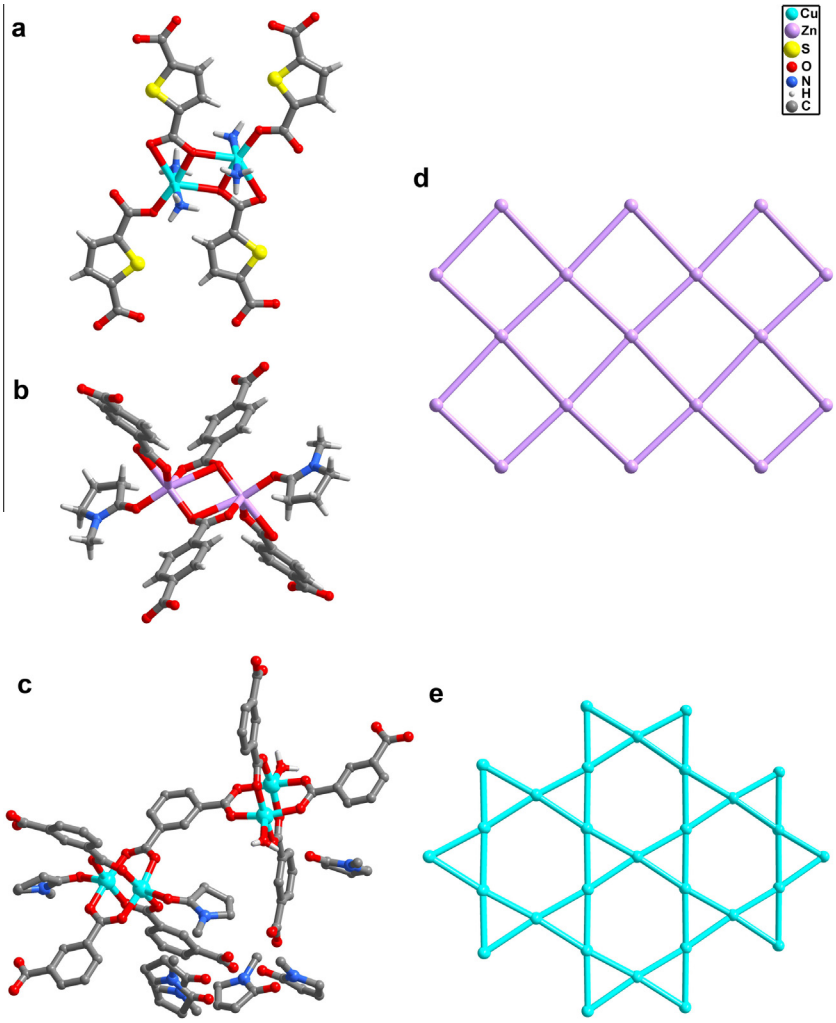


Fig. 2. Dinuclear metal centres appear in **9** (a), **12** (b), and **11** (c, C–H hydrogen atom omitted); **sql** net for **9**, **10**, and **12**–**15** (d); **kgm** net for **11** (e).

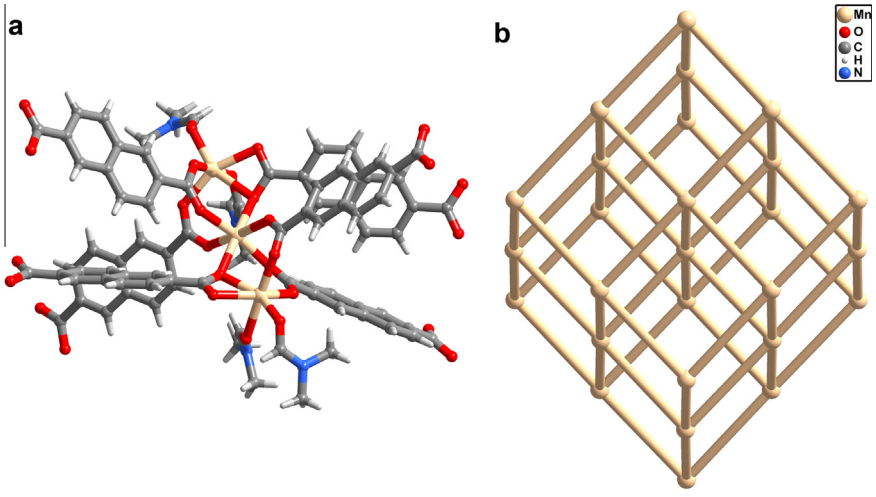


Fig. 3. Trinuclear SBU for **16** (a) and structural topology **pcu** for **16**–**20** (b).

that Mn^{2+} has a strong tendency to form rod-shaped SBUs. Notably, **2**, **3** and **4** were synthesised in different solvents and are isostructures, which demonstrates that the solvents did not influence the structures. Compounds **5** and **6** were synthesised using H_2tp and tetramethyl-substituted H_2tmtp, and their structures have same topology.

3.2. *sql* and *kgm* nets assembled with dinuclear metal centres

The following seven compounds contain dinuclear metal centres with four coordination points: $[Cu_2(tdc)_2(NH_3)_4]_n$ **9**, $[Cu_2(tbip)_2(dma)_2]_n$ **10**, $\{[Cu_2(ip)_2(nmp)_2\{Cu_2(ip)_2(H_2O)_2\}_2]\cdot 5NMP\cdot 2H_2O\}_n$ **11**, $[Zn_2(tp)_2(nmp)_2]_n$ **12**, $[Zn_2(2,6\text{-ndc})_2(dmf)_2]_n$ **13**, $[Zn_2(tdc)_2(dma)_2]_n$ **14** and $[Zn_2(tdc)_2(py)_2]_n$ **15** (Fig. 2). When the same ligands with short-medium lengths as for group 1 were used (except for **13**, which was assembled with the long ligand H_2(2,6-ndc), Cu^{2+} and Zn^{2+} tended to form dinuclear metal centres instead of rod-shaped SBUs, and the topology of the structures were **sql**, which is related to a node with four coordination points. Most of the paddle-wheel M_2 metal centres adopted a **sql** topology, while the structure for **11** was assembled using a bent ligand, H_2**ip**, which adopted a **kgm** net [42].

3.3. *pcu* net assembled with trinuclear metal centres

The following five compounds contain trinuclear metal centres with six coordination points, and their structure topology is **pcu** (Fig. 3): $[Mn_3(2,6\text{-ndc})_3(dmf)_4]_n$ **16**, $[Mn_3(2,6\text{-ndc})_3(dma)_4]_n$ **17**, $[Mn_3(2,6\text{-ndc})_3(nmp)_4]_n$ **18**, $[Mn_3(bpdc)_3(dma)_4]_n$ **19**, and $[Co_3(2,6\text{-ndc})_3(dma)_4]_n$ **20**. These compounds were assembled using relatively long ligands (H_2(2,6-ndc) 9.15 Å and H_2bpdc 11.22 Å). Although the ligands are long, the structures contain no voids for guest molecules. In the linear M_3 metal centre, each metal ion at the end was connected to two organic solvent molecules as auxiliary ligands that occupy a potential vacancy in the crystal structure. Although the compounds **16**, **17** and **18** were synthesised in DMF, DMA and NMP, respectively, their metal centre types and structure topologies were the same.

3.4. *hxl* net assembled with trinuclear metal centres

The following four compounds also contain trinuclear metal centres with six coordination points similar to the compounds discussed above, but their structures adopted a **hxl** net (Fig. 4.): $[Mn_3(tp)_3(nmp)_4]_n$**21**, $\{[Co_3(bpdc)_3(dma)_2]\cdot 4DMA\}_n$**22**, $\{[Zn_3(bpdc)_3(dmf)_2]\cdot 4DMF\cdot 0.5H_2O\}_n$**23**, and $\{[Zn_3(bpdc)_3(nmp)_2]\cdot 4NMP\}_n$**24**. The compound **21** was assembled with the medium-long ligand H_2**tp**, but **22**, **23** and **24** were assembled with the long ligand H_2**bpdc**. Furthermore, except for Mn^{2+} ion at the end of the Mn_3 metal centre, which combines two organic solvent molecules, each Co^{2+} or Zn^{2+} ion coordinated with only one solvent molecule. Clearly, Co^{2+} and Zn^{2+} are smaller than Mn^{2+} and can have a lower coordination number. This coordination mode produced a large void in crystalline structures. Guest solvent molecules occupied the voids and stabilised the crystal structures. Compounds **23** and **24** were synthesised in DMF and NMP, respectively, and are isostructures.

3.5. 1D structure assembled with a mononuclear metal centre

In this group, there is only one compound, $\{[Ni(2,6\text{-ndc})(H_2O)_4]\cdot 2NMP\cdot 2H_2O\}_n$**25**, which was assembled with a Ni^{2+} ion and bridging ligand H_2(2,6-ndc) to form a 1D structure (Fig. 5a). Compared with the other first-row transition metal elements, nickel analogues are often difficult to generate or have not been reported. Furthermore, the Ni^{2+} ion is often coordinated with more than one water molecule, which prevents the Ni^{2+} ion from connecting to more bridging ligands and formation of high dimensional structures. The coordination behaviour of the Ni^{2+} ion may be due to the small ion radius.

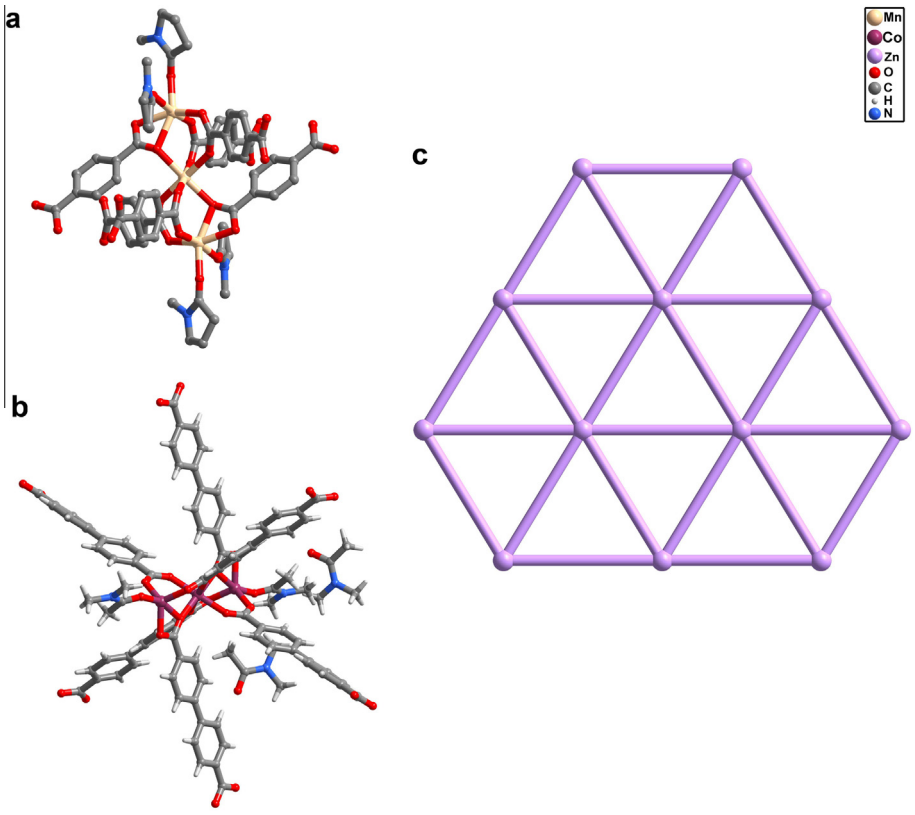


Fig. 4. Trinuclear metal centres appear in **21** (a, C–H hydrogen atom omitted), **22** (b), and the **hxl** net for **21**–**24** (c).

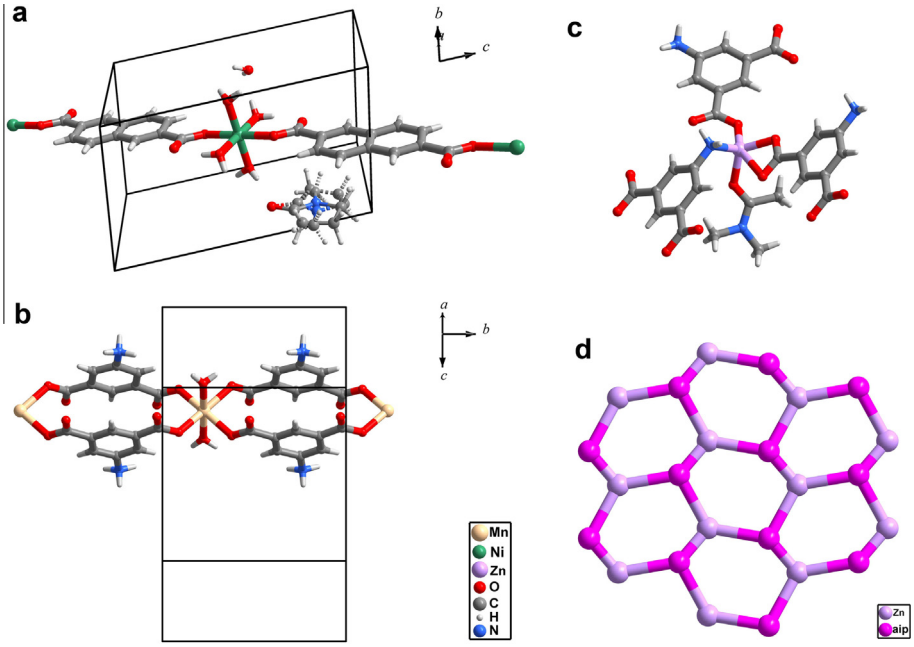


Fig. 5. 1D structure for **25** (a) and **26** (b); coordination mode of the metal centre (c) and the **hcb** net for **27** (d).

Table 3
Summary of the structural features for coordination polymers **1**–**25** and metal ions/ligands.

Ligand	Metal centre (SBU)	Topology	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Short–medium	Rod-shaped	**pcu**	6	1			1
	M_2	**sql**				3	3
Medium–long	M_3	**pcu**	4	1			
	M_3	**hxl**	1	1			2
Long	M	1D			1		

3.6. Two structures assembled using a protonated or tritopic ligand

$[Mn(Haip)_2(H_2O)_2]_n$**26** and $[Zn(aip)(dma)]_n$**27** are different from the compounds discussed above. In **26**, the amino group is protonated; thus, the Mn^{2+}:H**aip** ratio should be 1:2, and Mn^{2+} ions were bridged by pairs of H**aip** ligands to form a 1D structure (Fig. 5b). In **27**, **aip** is a building block with three connections and amino groups coordinated with a Zn^{2+} ion; each Zn^{2+} ion also coordinated with three **aip** bridging ligands and one DMA (Fig. 5c). The result is an **hcb** net (Fig. 5d).

The relationships between the coordination polymers' structural features (metal centre and topology) and metal ions or ligands are summarised in Table 3.

The data clearly show that Mn^{2+} tends to form rod-shaped SBUs and densely packed structures, which are generated from the large size and high coordination number of the Mn^{2+} ion. Given the potential for more bridging and auxiliary ligands connected to the metal centre, Mn^{2+} is a poor candidate for porous structures.

In contrast, Cu^{2+} and Zn^{2+} tend to form discrete metal centres with a limited number of metal ions, especially the M_2 metal centre (paddle-wheel-shaped). The M_2 metal centre with four coordination points typically forms a **sql** topology when linked by linear bridging ligands. Solvent molecules are often included in the crystal structure voids.

It is difficult to react Ni^{2+} with benzene dicarboxylic acid to yield coordination polymers, and Ni^{2+} PCPs are rare [43]. The presence of many coordinated water molecules on the Ni^{2+} ion prevents it from connecting to more bridging ligands and produces low dimensional structures. This was also observed in coordination polymer assemblies that were hydrothermally synthesised [44]. The size and coordination and assembly behaviours for Co^{2+} lie between Mn^{2+} and Ni^{2+}.

The different synthetic conditions in this research, such as temperature, solvent and solvent mixture ratio, did not significantly influence the assembly.

4. Conclusion

The metal ion used is the most important factor that influences coordination polymer assembly. It determines the type of metal centre, interaction between metal ions, and topology for the entire structure. A carefully selected metal ion with the proper ion radius, coordination number and electron configuration is vital for design and synthesis of inorganic-organic hybrid crystalline materials.

The organic ligand is also important, but it is the second most important influential factor in this context. Changes in ligand shape and properties, including bend, length, and substituent, can change the distances between the metal centres or SBUs, the structure void, or level of guest solvent molecules in the structure; however, such changes do not influence the inorganic portion of the compounds or net topology. This is the foundation for many design principles, such as the "expansion" strategy for porous MOFs [45].

Synthetic conditions are not key factors in this research. Three small groups of compounds synthesised in different solvents, for example, **2**–**4**, **16**–**18**, **23** and **24**, show that solvents also act as

the auxiliary ligands but do not influence the assemblies. Temperature also did not influence the structural features in this work.

Acknowledgement

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Appendix A. Supplementary material

CCDC 897845–897871 contain the supplementary crystallographic data for **1**–**27**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.03.042.

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