Molecular tectonics: from crystals to crystals of crystals

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Electronic supplementary materials

Experimental part

Materials and general techniques

The metal salts were purchased from commercial sources (Strem, Lancaster Chemicals) and used without further purification. The synthesis of 2,4,6 pyridinetricarboxylic acid (L) was achieved as described.[1] The synthesis of the bisamidinium cations **1**-2HCl has been recently published.[2]

IR spectra were recorded on KBr pellets on a FT Spectrometer PE apparatus.

Crystallisations conditions of [1-ML_2]

2,4,6-pyridinetricarboxylic acid (0.2 mmol, 42.2 mg) and NaOH (0.4 mmol, 16 mg) were dissolved in 4 mL of a 9:1 mixture of H_2O:DMSO while stirring at 50 ºC. **1**-2HCl (0.2 mmol, 112.1 mg) was dissolved at 50 ºC in a 9:1 mixture of H_2O:DMSO (2-3 mL) and gently layered on top of the solution containing the deprotonated ligand. The metal(II) chloride or nitrate salt (0.1 mmol) was dissolved in a 9:1 mixture of H_2O:DMSO (2 mL) at 50 ºC and then cooled to RT. The solution thus obtained was gently layered on top of the above-mentioned two layers solution, using a pipette. Upon leaving the three layers solution uncovered, single crystals suitable for X-ray diffraction techniques were obtained after several days.

$\mathbf{1}^{2+}$-$[CoL_2]^{2-}$ (Orange crystals):

Anal. Calcd. for $[Co(C_8H_3NO_6)_2][C_{12}H_{16}N_4]\bullet 4\ H_2O$: C, 43.93; H, 3.95; N, 10.98%. Found: C, 43.48; H, 3.77; N, 11.03%.

IR data (KBr/pellet, cm^{-1}): 3533, 3378, 3093, 2731, 1726, 1634, 1579, 1504, 1383, 1244, 1040, 859, 769, 691, 623, 509 and 430.

$\mathbf{1}^{2+}$-$[NiL_2]^{2-}$ (Green crystals):

Anal. Calcd. for $[Ni(C_8H_3NO_6)_2][C_{12}H_{16}N_4]\bullet 4\ H_2O$: C, 43.95; H, 3.95; N, 10.98%.

1 L. Syper, K. Kloc, J.Mlochowski, *Tetrahedron* 1980, **36**, 123.
2 S. Ferlay, P. Dechambenoit, N. Kyritsakas and M. W. Hosseini *Dalton Trans.,* 2013, Advance Article
DOI: 10.1039/C3DT51252E.

Found: C, 42.51; H, 3.29; N, 10.88%.

IR data (KBr/pellet, cm^{-1}): 3513, 3406, 3220, 3079, 2952, 2742, 1719, 1644, 1573, 1503, 1367, 1246, 1040, 767, 737, 690, 572, 508 and 440.

$\mathbf{1}^{2+}$-$[CuL_2]^{2-}$ (Light blue crystals):

Anal. Calcd. for $[Cu(C_8H_3NO_6)_2][C_{12}H_{16}N_4]\bullet 4\ H_2O$: C, 43.67; H, 3.92; N, 10.91%. Found: C, 42.72; H, 3.86; N, 11.09%.

IR data (KBr/pellet, cm^{-1}): 3536, 3415, 3233, 3083, 2911, 2729, 1714, 1635, 1575, 1504, 1369, 1238, 1198, 1097, 1030, 930, 857, 768, 740, 638, 627, 517 and 432.

$\mathbf{1}^{2+}$-$[ZnL_2]^{2-}$ (Colourless crystals):

Anal. Calcd. for $[Zn(C_8H_3NO_6)_2][C_{12}H_{16}N_4]\bullet 4\ H_2O$: C, 43.57; H, 3.91; N, 10.89%. Found: C, 42.67; H, 3.32; N, 10.98%.

IR data (KBr/pellet, cm^{-1}): 3474, 3383, 3193, 3010, 2881, 2797, 1648, 1558, 1445, 1352, 1314, 1269, 1215, 1076, 1035, 975, 927, 852, 785, 720, 690, 568, 507 and 421.

Generation of crystals of crystals of the type $\mathbf{1}^{2+}$-$[M2L_2]^{2-}$@$\mathbf{1}^{2+}$-$[M1L_2]^{2-}$

A preformed crystal of $\mathbf{1}^{2+}$-$[M1L_2]^{2-}$ (approximately 0.1 x 0.06 x 0.02mm) was glued at the extremity of a nylon wire before it was immersed into a 9:1 mixture of H_2O:DMSO (8 mL) containing 2,4,6-pyridinetricarboxylic acid (0.2 mmol, 42.2 mg), NaOH (0.4 mmol, 16 mg), $\mathbf{1}^{2+}$- $2Cl^-$ (0.2 mmol, 112.1 mg) and the $M2X_2$ salt (0.1 mmol) (X = Cl^- or NO_3^-). After one week, in addition to few $\mathbf{1}^{2+}$-$[M2L_2]^{2-}$ crystals formed in solution, the glued crystals was found to be transformed into a contrasted coloured bicolour species. The crystal was detached and studied by X-ray diffraction methods. Following the same procedure, three crystals of crystals based on the following combinations $\mathbf{1}^{2+}$-$[M2L_2]^{2-}$@$\mathbf{1}^{2+}$-$[M1L_2]^{2-}$ (M1 = Ni; M2 = Zn), (M1 = Co; M2 = Zn) and (M1 = Co; M2 = Ni) have been generated.

Characterization of Crystals of crystals:

X-ray diffraction on crystals of crystal of the $\mathbf{1}^{2+}$-$[M2L_2]^{2-}$@$\mathbf{1}^{2+}$-$[M1L_2]^{2-}$ ((M1 = Ni; M2 = Zn), (M1 = Co; M2 = Zn) and (M1 = Co; M2 = Ni)) type has been carried out allowing to determine the cell parameters. The data led to an average unit cell metrics (table T3) lying between both pure crystals $\mathbf{1}^{2+}$-$[M1L_2]^{2-}$ and $\mathbf{1}^{2+}$-$[M2L_2]^{2-}$. The same first generation crystal of crystal was cut in order to obtain two pure crystalline phases corresponding to

$\mathbf{1}^{2+}$-$[M1L_2]^{2-}$ and $\mathbf{1}^{2+}$-$[M2L_2]^{2-}$. X-ray diffraction on each phase revealed the same parameters as those obtained independently for the pure crystals.

X-Ray Crystallography

Data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-K□ (□□= 0.71073) radiation. For all structures, diffraction data were corrected for absorption. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model). [3] CCDC 949324-949327 contains the supplementary crystallographic data for this contribution. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (Internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

[3] G. M. Sheldrick, *Programs for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1996**.

Table T1: Crystallographic parameters recorded at 173 K for $\mathbf{1}^{2+}$-$[ML_2]^{2-}$ (M = Co, Ni, Cu, Zn)

Formula	$\mathbf{1}^{2+}$-$[CoL_2]^{2-}$ $[Co(C_8H_3NO_6)_2][C_{12}H_{16}N_4] \cdot 4\,H_2O$	$\mathbf{1}^{2+}$-$[NiL_2]^{2-}$ $[Ni(C_8H_3NO_6)_2][C_{12}H_{16}N_4] \cdot 4\,H_2O$	$\mathbf{1}^{2+}$-$[CuL_2]^{2-}$ $[Cu(C_8H_3NO_6)_2][C_{12}H_{16}N_4] \cdot 4\,H_2O$	$\mathbf{1}^{2+}$-$[ZnL_2]^{2-}$ $[Zn(C_8H_3NO_6)_2][C_{12}H_{16}N_4] \cdot 4\,H_2O$
Molecular weight	765.51	765.29	770.12	771.95
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c
a(Å)	19.2011(5)	19.1971(5)	19.2201(5)	19.2791(5)
b(Å)	9.6470(3)	9.6310(2)	9.6352(3)	9.6312(3)
c(Å)	17.1082(6)	17.0962(4)	17.0833(5)	17.0771(5)
α(deg)	90	90	90	90
β(deg)	107.494(4)	106.581(11)	106.751(14)	107.809(14)
γ(deg)	90	90	90	90
V(Å^3)	3022.43(18)	3029.4(2)	3029.4(3)	3019.0(3)
Z	4	4	4	4
Colour	orange	green	blue	colourless
Crystal dim (mm^3)	0.14 x 0.14 x 0.14	0.14 x 0.12 x 0.12	0.14 x 0.14 x 0.12	0.14 x 0.12 x 0.10
D_{calc} (gcm^{-3})	1.682	1.678	1.689	1.698
F(000)	1580	1584	1588	1592
μ (mm^{-1})	0.660	0.733	0.813	0.906
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Number of data meas.	7687	7659	7870	6873
Number of data with I> $2_{\sigma(I)}$	4417 [R(int) = 0.0539]	4421 [R(int) = 0.0339]	4420 [R(int) = 0.0379]	4400 [R(int) = 0.0219]
R	R1 = 0.0517, wR2 = 0.1149	R1 = 0.0482, wR2 = 0.1218	R1 = 0.0489, wR2 = 0.1203	R1 = 0.0429, wR2 = 0.1084
R_W	R1 = 0.1220, wR2 = 0.1390	R1 = 0.0842, wR2 = 0.1405	R1 = 0.0887, wR2 = 0.1368	R1 = 0.0609, wR2 = 0.1178
GOF	1.002	1.032	1.069	1.012
Largest diff. peak and hole (e.Å-3)	0.630 and -0.673	0.796 and -0.727	0.694 and -0.632	0.712 and -0.731

Table T2: Comparison of the useful distances for $\mathbf{1}^{2+}$-$[ML_2]^{2-}$ (M = Co, Ni, Cu, Zn) compounds

	$\mathbf{1}^{2+}$-$[CoL_2]^{2-}$	$\mathbf{1}^{2+}$-$[NiL_2]^{2-}$	$\mathbf{1}^{2+}$-$[CuL_2]^{2-}$	$\mathbf{1}^{2+}$-$[ZnL_2]^{2-}$
M-O (Å)	2.1336(16) 2.1572(17)	2.1192(16) 2.1165(15)	2.1712(16) 2.1850(16)	2.1157(14) 2.2523(14)
M-N (Å)	2.009(2)	1.9612(18)	1.9346(18)	2.0100(15)
NMN (°)	165.28(11)	169.08(10)	169.02(11)	159.63(9)
OMN (°)	76.37(7)-112.89(7)	77.97(7)-109.10(7)	78.24(7)-109.45(7)	74.73(6)-115.09(6)
OMO (°)	91.37(7)-153.57(7)	91.43(6)-156.47(6)	90.72(6)-156.30(5)	90.34(5)-153.41(5)
N-(H)-O	2.740 2.892	2.723 2.856	2.726 2.852	2.744 2.888
O-(H)-O Protonated carboxylic	2.558	2.556	2.550	2.544
Ow-(H)-O	2.711 2.925	2.732 2.895	2.721 2.899	2.699 2.932

Table T3: Cell parameters recorded at 173 K for $\mathbf{1}^{2+}$-$[ML_2]^{2-}$ (M = Co, Ni, Cu, Zn) and $\mathbf{1}^{2+}$-$[ZnL_2]^{2-}$@$\mathbf{1}^{2+}$-$[NiL_2]^{2-}$, $\mathbf{1}^{2+}$-$[ZnL_2]^{2-}$@$\mathbf{1}^{2+}$-$[CoL_2]^{2-}$ and $\mathbf{1}^{2+}$-$[NiL_2]^{2-}$@$\mathbf{1}^{2+}$-$[CoL_2]^{2-}$

Compound	$\mathbf{1}^{2+}$-$[CoL_2]^{2-}$	$\mathbf{1}^{2+}$-$[NiL_2]^{2-}$	$\mathbf{1}^{2+}$-$[CuL_2]^{2-}$	$\mathbf{1}^{2+}$-$[ZnL_2]^{2-}$	$\mathbf{1}^{2+}$-$[ZnL_2]^{2-}$ @$\mathbf{1}^{2+}$-$[NiL_2]^{2-}$	$\mathbf{1}^{2+}$-$[ZnL_2]^{2-}$@$\mathbf{1}^{2+}$-$[CoL_2]^{2-}$	$\mathbf{1}^{2+}$-$[NiL_2]^{2-}$@$\mathbf{1}^{2+}$-$[CoL_2]^{2-}$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	C2/c	C2/c	C2/c
a(Å)	19.2011(5)	19.1971(5)	19.2201(5)	19.2791(5)	19.2343(5)	19.2331(5)	19.1991(5)
b(Å)	9.6470(3)	9.6310(2)	9.6352(3)	9.6312(3)	9.6315(3)	9.6411(3)	9.6441(3)
c(Å)	17.1082(6)	17.0962(4)	17.0833(5)	17.0771(5)	17.0912(4)	17.1085(5)	17.1031(5)
α(deg)	90	90	90	90	90	90	90
β(deg)	107.494(4)	106.581(11)	106.751(14)	107.809(14)	106.954(5)	107.263(5)	107.206(5)
γ(deg)	90	90	90	90	90	90	90
V(Å^3)	3022.43(18)	3029.4(2)	3029.4(3)	3019.0(3)	3028.59(15)	3029.44(15)	3024.99(15)