ESI

Crystal packing description

[Co(H$_{-2}$L1)]·3H$_2$O (1). In the crystal packing cobalt complexes are held together by some strong H-bonds and π-π interactions. The O(1w) and O(2w) oxygen atoms present in the asymmetric unit belong to a group of three water molecules linked together by H-bonds (see Table S1 and Figure S1a) which connects cobalt complexes to form ribbons which develop themselves along the ac plane diagonal (Figure S1b). Parallel ribbons are linked *via* π-π interactions between maltol rings of symmetry related complexes (-x,-y,-z+1; centroid distances 3.70(1) Å) to form sheets perpendicular to b axis (Figure S1b).

[Co(H$_{-2}$L2)]·2CH$_3$OH (2). Each methanol molecule present in the cobalt complex of **2** is linked *via* strong H-bonds to both oxygen atoms of the phenolate rings (see Table S1). In the crystal packing, since twofold screw axes are present, two zigzag ribbon types which develop themselves along the a axis can be identified, differing only for the orientation (face up –purple- and face down –blue-) of the building blocks (Figure S2).

[[Co(H$_{-2}$L1)]Na(H$_2$O)](ClO$_4$)(H$_2$O) (3). The two water molecules present in the asymmetric unit of **3** are connected through a strong hydrogen bond which involves a hydrogen atom bound to O(1w) and the oxygen atom O(2w) (see Table S2). The crystal packing is build up by some strong hydrogen bonds and π-π interactions. The former connect the metal complex dimers (Figure S3a) through interactions between water molecules (O(2w)$\cdots$O(2)^b, see Table S2), producing zigzag ribbons along the a axis (Figure S3b). These ribbons are surrounded by parallel rows of perchlorate anions. The π-π interactions involve two symmetry related maltol rings (-x+1, -y +1, -z+1) belonging to two facing dimers (Figure S3a), the distance between the two centroids being 3.524(6) Å; such interactions connect ribbons in order to form planes perpendicular to the c axis (Figure S3c).

$[Cu_2(H_{-2}L1)(H_2O)]_2(ClO_4)_4 \cdot 6H_2O$ (4)

In the crystal lattice, units of **4** are held together by a wide network of strong hydrogen bonds connecting all the water molecules and all the perchlorate anions (Table S3) to form planes which are perpendicular to the b axis (Figure S4a). These parallel planes are visible along the a axis (Figure S4b).

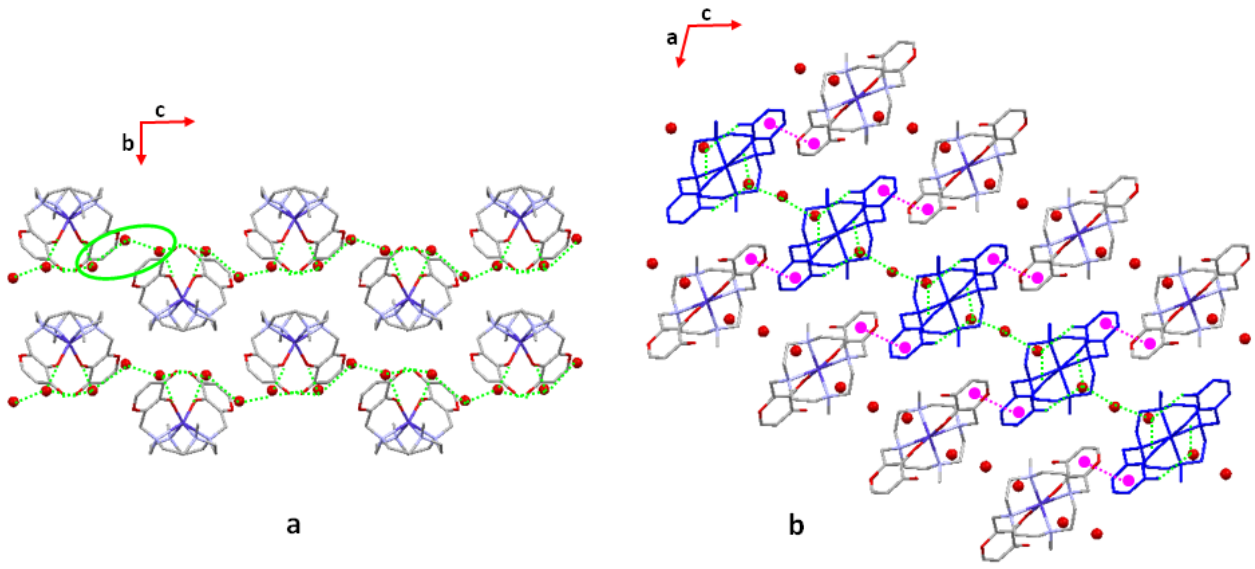

Figure S1 Crystal packing of **1**; **a**: view along the a axis. H-bonds are depicted in light blue. The circle indicates a group of three water molecules. **b:** view along the b axis. A ribbon is depicted in blue, H-bonds in light blue and π-π interactions in purple.

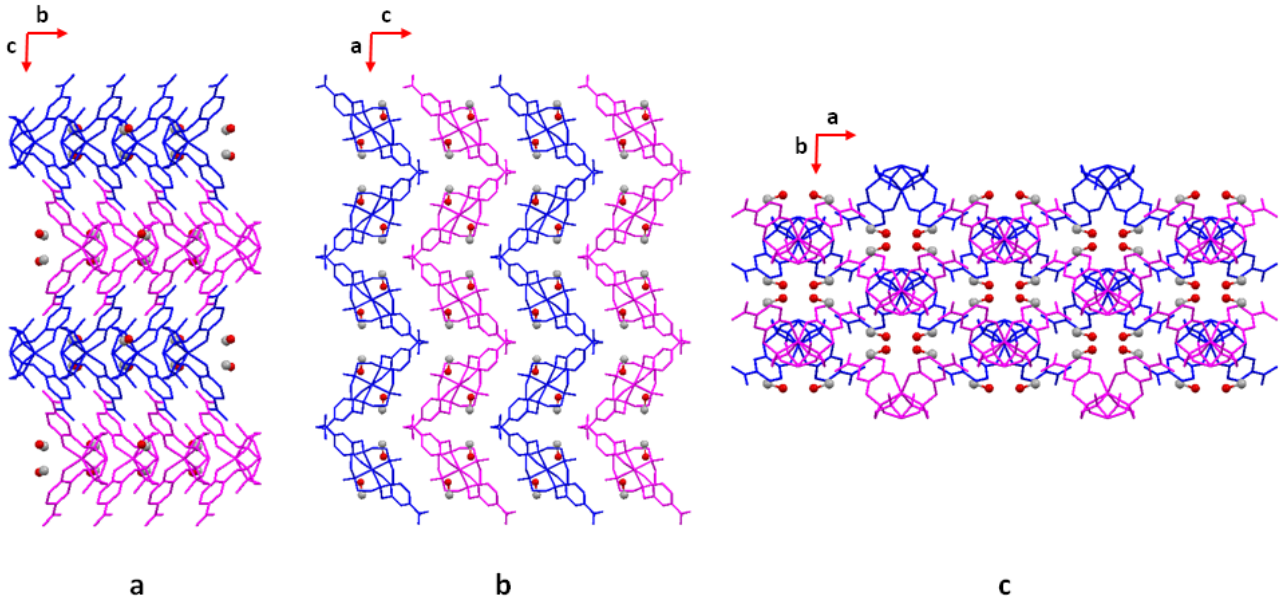

Figure S2. Crystal packing of **2**; **a**, **b** and **c**: views along a, b and c axes. Purple: face-up building blocks; blue: face-down building blocks.

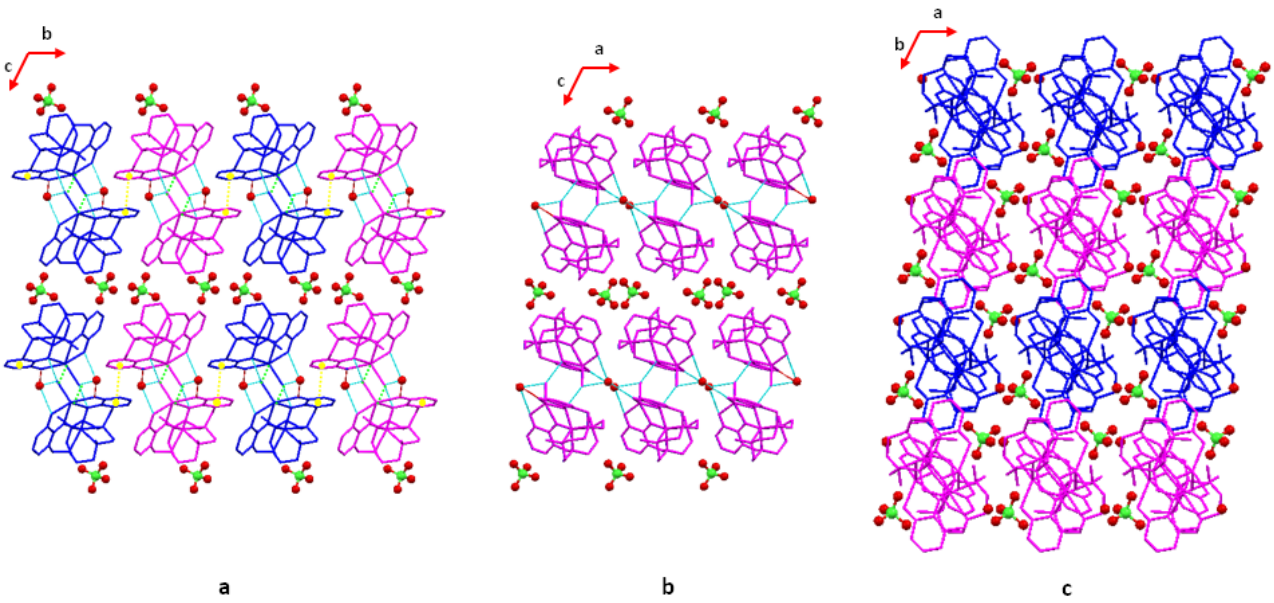

Figure S3. Crystal packing of **3**; **a**: view along a axis. Parallel blue and purple ribbons along the a axis linked by π-π interactions are visible. **b:** view along the b axis. Purple zigzag ribbons along the a axis surrounded by two parallel rows of perchlorate anions are visible. **c**: view along the c axis. Planes perpendicular to the c axis, formed by blue and purple ribbons linked by π-π interactions, are visible. H-bonds are depicted in light blue, π-π interactions in yellow, Na^+-water interactions in green.

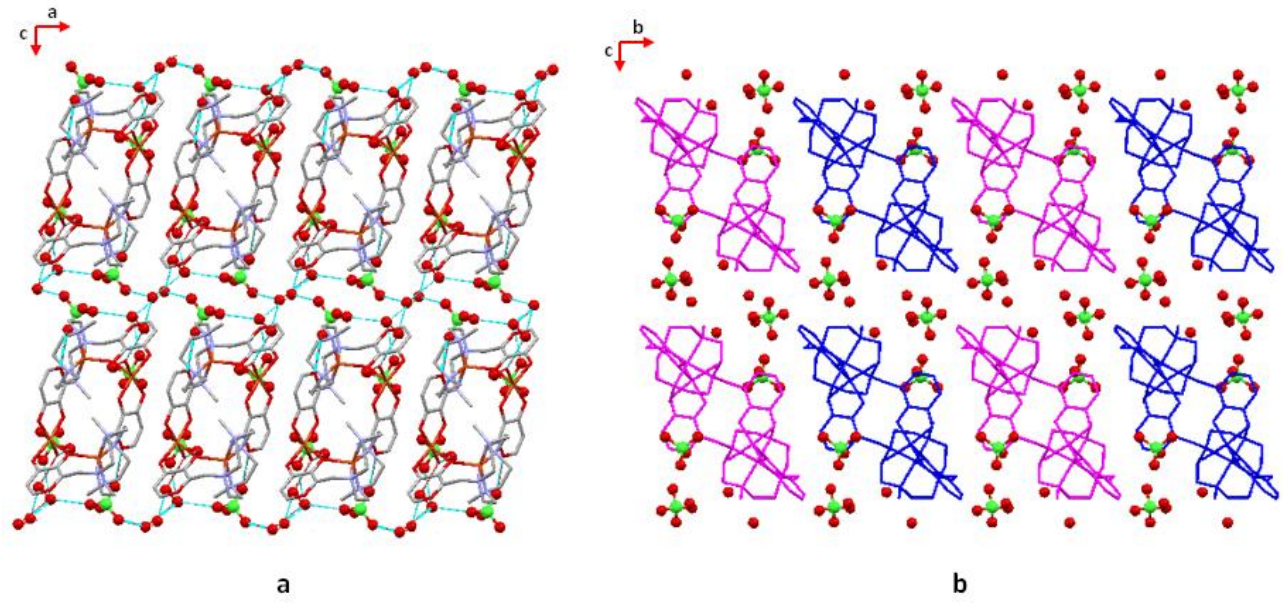

Figure S4. Crystal packing of **4**; **a**: view along the b axis. H-bonds are depicted in light blue. **b:** view along the a axis. Parallel planes are alternatively depicted in purple and blue.

Table S1. Selected intermolecular hydrogen bonds (D···A, Å) for compounds **1** and **2**

	1	**2**
O(1)···O(1w)	2.730(7)	
O(2)···O(1w)[a]	2.804(9)	
O(1w)···O(2w)	3.00(1)	
O(2w)···O(1w)[b]	2.63(1)	
O(1)···O(4)		3.123(8)
O(1)···O(4)[c]		2.909(7)

[a] = -x+½ ,y,-z+½; [b] = -x+1,-y,-z+1; [c] = -x, y, -z +½

Table S2. Selected intermolecular hydrogen bonds (D···A, Å) for compound **3**

	3
O(1w)···O(2w)	2.787(5)
O(1w)···O(1)[a]	2.738(4)
O(2w)···O(2)[b]	2.806(5)

[a] = -x+1,-y+2,-z+1; [b] = -x+2,-y+2,-z+1

Table S3. Selected intermolecular hydrogen bonds (D···A, Å) for compound **4**

	4
O(1w)···O(7)	3.005(5)
O(1w)···O(2w)	2.643(4)
O(2w)···O(3w)[a]	2.814(4)
O(2w)…O(4w)[b]	2.758(4)
O(3w) ···O(9)[c]	2.850(4)
O(3w) ···O(14)[d]	3.025(6)
O(3w)···O(4w)	2.831(4)
O(4w) ···O(12)	2.923(6)

[a] = x,+y-1,+z; [b] = -x-1,-y+1,-z+1; [c] = x,+y+1,+z; [d] = x+1,+y,+z