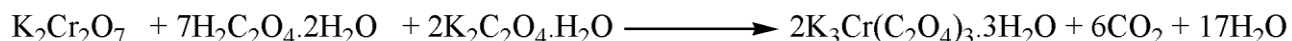
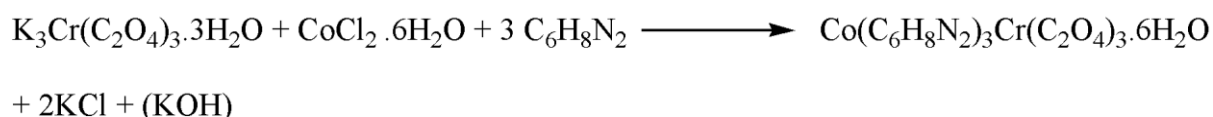


Synthesis of the Catena-{Co(amp)₃Cr(ox)₃.6H₂O} (I)

All reagents and solvents were purchased from commercial sources and used as received but the reagent K₃Cr(C₂O₄)₃.3H₂O was prepared by following the reaction equation below as reported in literature (Bailar & Jones, 1939) and using 11.5g of K₂C₂O₄.H₂O, 27.5 g H₂C₂O₄.2H₂O and 9.5 g of K₂Cr₂O₇.



Then, 1.57g (3.22 mmol) of the crystals obtained was dissolved in 10 mL of water at 60 °C and 15 minutes later, a mixture of 2-aminomethylpyridine (1 mL, 9.7 mmol) and CoCl₂.6H₂O (0.77g, 3.2 mmol) was added. The solution was then stirred for 30 minutes at 60 °C. The brown mass formed was filtered off and the filtrate was concentrated. After one week, brown prismatic crystals of suitable size obtained from this solution (yield 64%) were filtered off and washed with ethanol and acetone. The reaction equation of this second step of the synthesis of I is:



The hydroxides ions may come from the reduction of oxygen molecules dissolved into water. This easy reaction is due to the coulombic attraction between the Co(amp)₃³⁺ ions (hydrogen donor, (D)) and Cr(ox)₃³⁻ (ox = C₂O₄²⁻) ions (Hydrogen acceptor ,(A)). Indeed during the reaction the neutral amp ligand reacted with Co²⁺ ions in the usual oxidative process in air to produce the [Co(amp)₃]³⁺ cations as observed during the synthesis of the salt [Co(C₆H₈N₂)₃][(C₂B₉H₁₀(CH₂OH)₂)₂][Cl].[C₂B₁₀H₁₀(CH₂OH)₂].MeOH (Oki et al., 2003). This oxidation of Co²⁺ ions is usually catalyzed by ammonia and amine ligands (see for example, Yin et al., 2013; Bélombé et al.; 1993).

Elemental analysis of Catena- $\{\text{Co}(\text{amp})_3\text{Cr}(\text{ox})_3 \cdot 6\text{H}_2\text{O}\}$

The elemental analysis of C, H, O and N was carried out with a Thermo Finnigan EA 1112. The results well agree with the chemical formulation of the compound: Anal. Calc. for $\text{Co}(\text{amp})_3\text{Cr}(\text{ox})_3 \cdot 6\text{H}_2\text{O}$: H: 4.494%; O: 35.663%; N: 10.407%. Found: H: 3.96%; O: 33.35%; C: 35.32%; N: 10.29%.

FT-IR analysis Catena- $\{\text{Co}(\text{amp})_3\text{Cr}(\text{ox})_3 \cdot 6\text{H}_2\text{O}\}$

The Fourier Transform Infrared spectrum (FT-IR, See Fig.S1) recorded in the range of $4000\text{--}450\text{ cm}^{-1}$ on a SHIMADZU IR Affinity¹ FT-IR spectrometer confirms the presence of all the vibrational bands characteristic of the organic function in the compound: $\nu_{\text{O-H}}$ and $\nu_{\text{N-H}}$ ($3490\text{--}3280\text{ cm}^{-1}$); $\nu_{\text{C=O}}$ and $\nu_{\text{C-N}}$ ($1600\text{--}1450\text{ cm}^{-1}$), aromatic peaks at 1200 cm^{-1} and $\nu_{\text{C-O}}$ at 890 cm^{-1} .

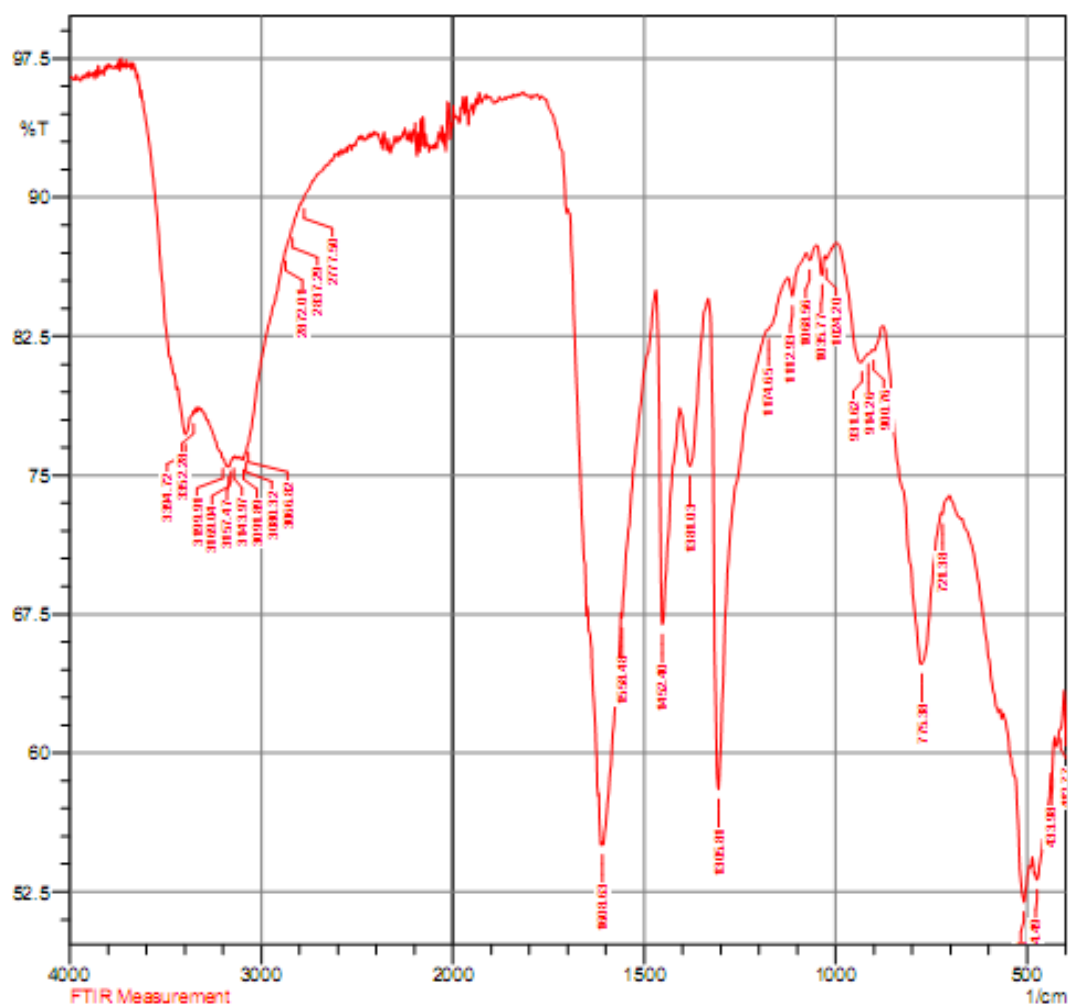


Figure S1: FT-IR spectrum of $\text{-}\{\text{Co}(\text{amp})_3\text{Cr}(\text{ox})_3 \cdot 6\text{H}_2\text{O}\}$

Structural analysis of Catena-{Co(amp)₃Cr(ox)₃.6H₂O} (I)

The crystal structure of the compound was solved by single crystal analysis. A 0.18 mm x 0.12 mm x 0.10 mm single crystal of I was chosen under an optical microscope and coated with grease before being mounted on a glass fiber. Data were collected at 100K on a Bruker AXS D8 Venture diffractometer equipped with a Mo microfocus source ($\lambda = 0.71073 \text{ \AA}$), multilayer optics, a Photon 100 CMOS detector and an Oxford Cryosystems nitrogen gas flow device (700 series Cryostream). The determination of the unit cell parameters, the integration of raw diffraction images and the multi scan absorption correction, frame to frame scaling, merging of reflections was conducted with the APEX 2 Program package (Bruker AXS, 2010). The structure was solved by direct methods using SIR 92 (Altomare et al., 1994) and refined on F^2 by full matrix least-squares procedures within the independent atom model (IAM) by using SHELXL-97 (Sheldrick, 1997). All non-H atoms were refined anisotropically. Hydrogen atoms of water molecules and those of the amino group (amp ligand) were located from iterative examination of difference F maps following least-squares refinements and the remaining (aromatic and methyl) were calculated. All of these hydrogen atoms were included as riding atoms with isotropic displacement parameters ADPs such as $U_{iso}^H = 1.2U_{eq}^C$; $U_{iso}^H = 1.2U_{eq}^N$; $d_{Ow-H} = (0.96 \pm 0.02) \text{ \AA}$, $U_{iso}^{Hw} = 1.5U_{eq}^{Ow}$. The structure was examined using the Addsym subroutine PLATON (Spek, 1990) to ensure that no additional symmetry could be applied to the model. Crystal structure view was obtained using Diamond 3.0 software (Klaus, 2004).

Crystallographic data of the compound are summarized in table S1. The coordinated polyhedra of Co^{3+} and Cr^{3+} ions in I are slightly distorted octahedra and the $\text{Co}^{3+}\text{-N}$, $\text{Cr}^{3+}\text{-O}$ bond lengths mean values, $(1.946 \pm 0.015 \text{ \AA})$ and $(1.969 \pm 0.022 \text{ \AA})$ (Table S2) respectively are in agreement with the mean $\text{Co}^{3+}\text{-N}$ $(1.962 \pm 0.035) \text{ \AA}$ and $\text{Cr}^{3+}\text{-O}$ $(1.969 \pm 0.027 \text{ \AA})$ values observed in the CSD (Allen, 2002). Indeed, the Co^{3+} ion lies $0.015 (1) \text{ \AA}$ from the (N2, N3, N6, and N5) equatorial plane which forms a dihedral angle of $86.66(7)^\circ$ with the (N1, Co, N4) plane in apical position (Fig 1). While the Cr^{3+} ion exactly lies in the (O2, O3, O4 and O6) equatorial plane which forms with the (O1, Cr, O5) plane in apical position, a dihedral angle of $86.27 (5)^\circ$.

Table S1: Crystal data and structure refinement of I.

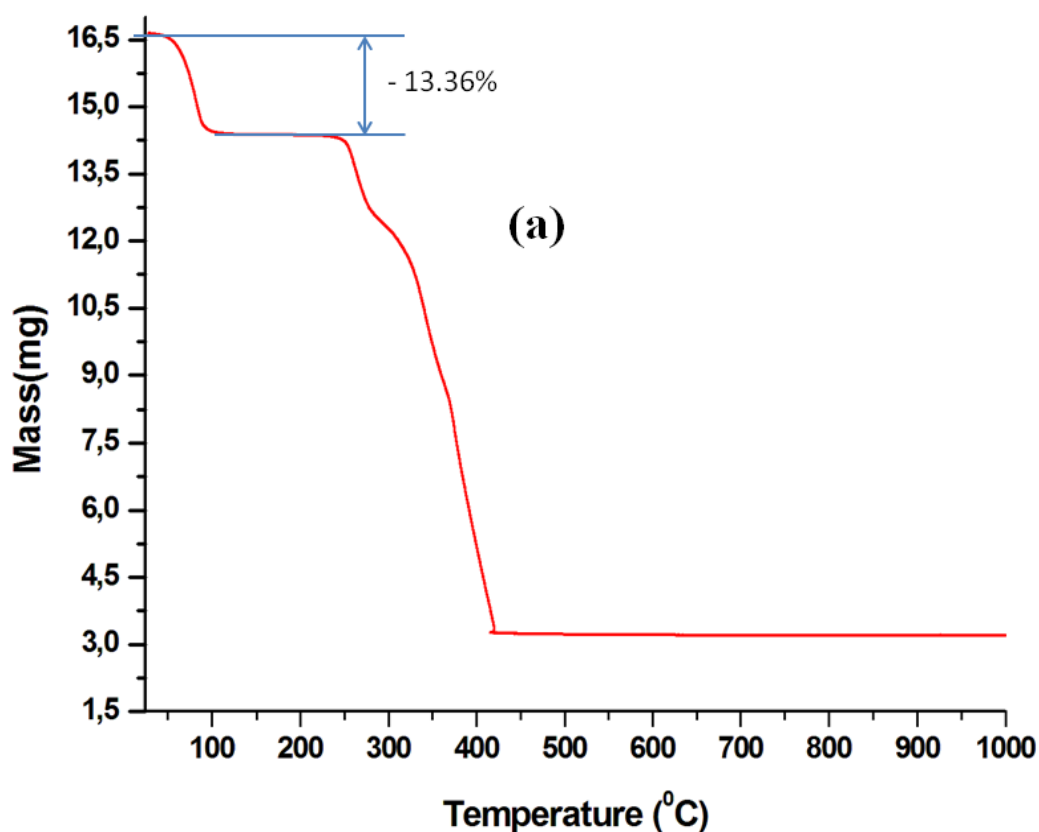
Co(amp) ₃ Cr(ox) ₃ .6H ₂ O	
Crystal data	
Chemical formula	Co(C ₆ H ₈ N ₂) ₃ Cr(C ₂ O ₄) ₃ .6H ₂ O
<i>M_r</i>	807.52
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.1923 (8), 18.0299 (10), 14.1801 (9)
β (°)	99.357 (2)
<i>V</i> (Å ³)	3327.9 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.91
Crystal size (mm)	0.18 × 0.12 × 0.10
Data collection	
Diffractometer	D8 Venture Photon, Bruker AXS diffractometer
Absorption correction	Multi-scan <i>APEX2</i> v2013.4-1 (Bruker AXS, 2010) Empirical absorption correction using spherical harmonics, implemented in <i>SCALE3</i> <i>ABSPACK</i> scaling algorithm.
<i>T_{min}</i> , <i>T_{max}</i>	0.693, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	100946, 10353, 8042
<i>R_{int}</i>	0.054
(sin θ/λ) _{max} (Å ⁻¹)	0.738
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.041, 0.094, 1.05
No. of reflections	10353
No. of parameters	505
No. of restraints	18
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.70, -0.56

Table S2: Selected bond lengths (Å) and angles (°) for I.

Co-N(1)	1.9601(2)	Cr-O(1)	1.9483(2)
Co-N(2)	1.9339(2)	Cr-O(2)	1.9607(2)
Co-N(3)	1.9425(2)	Cr-O(3)	1.9619(2)
Co-N(4)	1.9451(2)	Cr-O(4)	1.9678(2)
Co-N(5)	1.9358(2)	Cr-O(5)	1.9820(2)
Co-N(6)	1.9574(2)	Cr-O(6)	1.9934(2)
<hr/>			
N(2)-Co-N(5)	94.62(6)	O(1)-Cr-O(2)	83.44(6)
N(2)-Co-N(3)	84.99(6)	O(1)-Cr-O(3)	91.56(6)
N(5)-Co-N(3)	175.20(6)	O(2)-Cr-O(3)	92.95(6)
N(2)-Co-N(4)	89.96(6)	O(1)-Cr-O(4)	90.06(6)
N(5)-Co-N(4)	84.48(6)	O(2)-Cr-O(4)	171.77(6)
N(3)-Co-N(4)	90.73(6)	O(3)-Cr-O(4)	82.16(6)
N(2)-Co-N(6)	175.80(6)	O(1)-Cr-O(6)	94.59(5)
N(5)-Co-N(6)	88.40(6)	O(2)-Cr-O(6)	93.81(5)
N(3)-Co-N(6)	92.24(6)	O(3)-Cr-O(6)	171.34(6)
N(4)-Co-N(6)	93.23(6)	O(4)-Cr-O(6)	91.72(5)
N(2)-Co-N(1)	93.42(6)	O(1)-Cr-O(5)	175.45(5)
N(5)-Co-N(1)	95.17(6)	O(2)-Cr-O(5)	93.42(6)
N(3)-Co-N(1)	89.64(6)	O(3)-Cr-O(5)	91.90(5)
N(4)-Co-N(1)	176.61(6)	O(4)-Cr-O(5)	93.35(6)
N(6)-Co-N(1)	83.39(6)	O(6)-Cr-O(5)	82.31(5)

Thermogravimetric analysis

The thermogravimetric analysis (TGA) was performed from 25 to 1000 °C on a METTLER TOLEDO TGA/DSC 1 instrument at a heating rate of 5 °C/ min under air and N₂ (100mL/min) by using 16.659 mg of the sample for analysis in air and 15.377 mg in N₂. The both curves obtained shows that the dehydration proceeds around 77° in one single step [Weight loss: 13.36 % (anal.) Vs 13.38 % (exp, air) and 13.15 % (exp, N₂)] and the compound does not decompose. The stability is kept until 250°C where its decomposition begins (see Fig.S2).



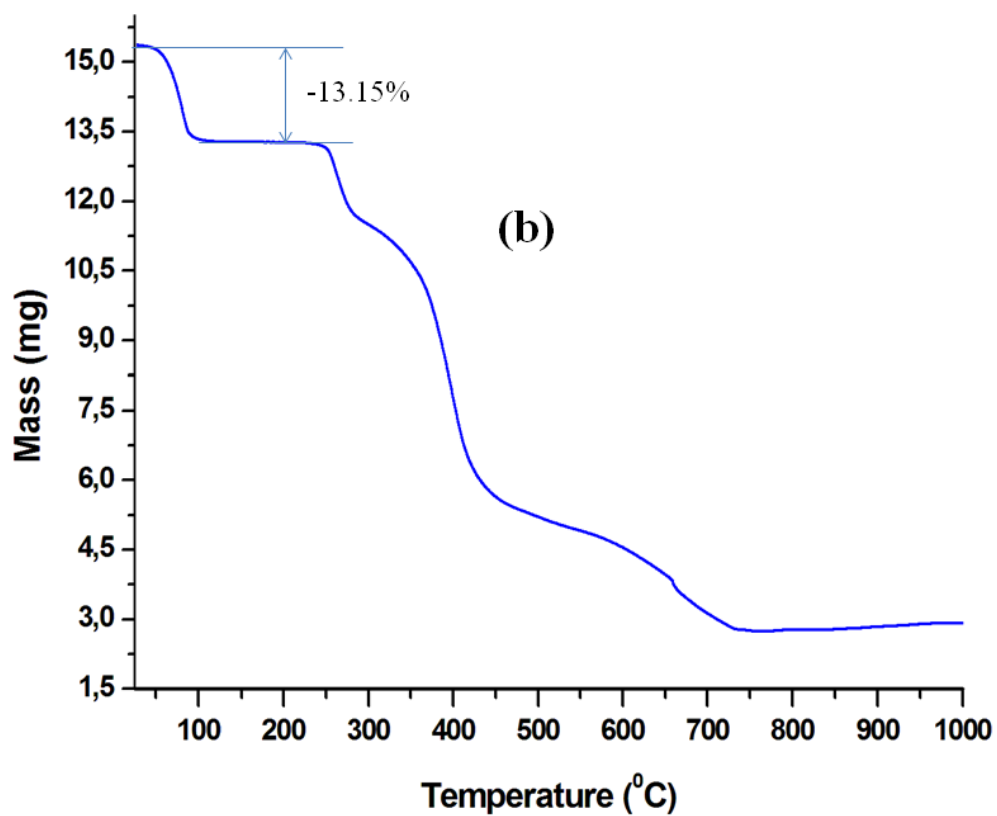


Figure S2: Curve of the Thermogravimetric Analysis (TGA) of I performed: (a) in air and (b) in N_2 ; heating rate: $5^\circ/\text{min}$.

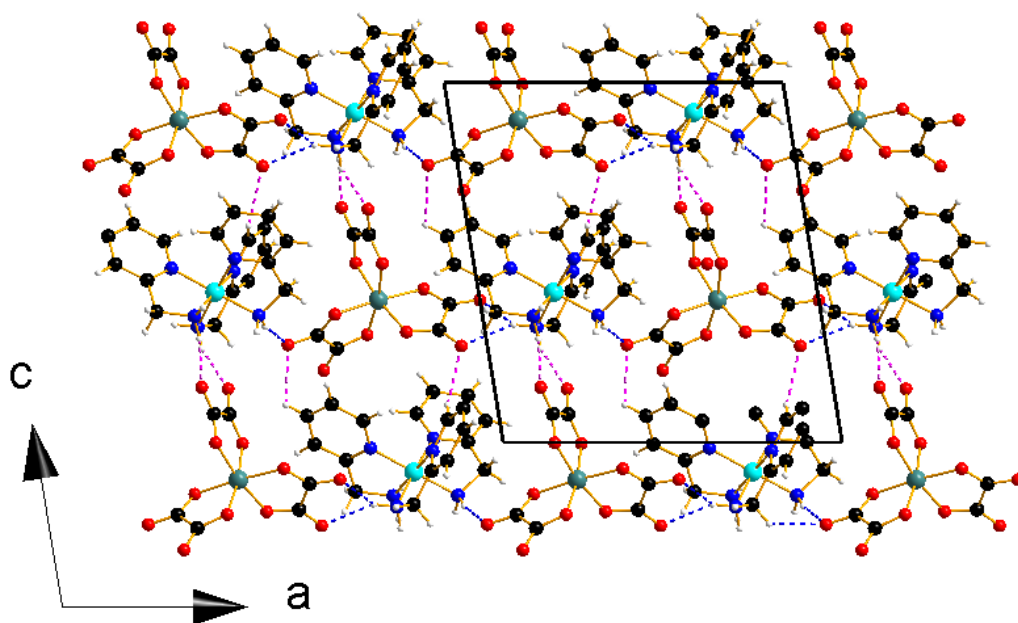


Figure S3: View of the infinite zigzag chains of $\text{Co}(\text{amp})^{3+}$ and $\text{Cr}(\text{ox})^{3-}$ connected by hydrogen bonds both along the a axis (drawn in blue) and c axis (drawn in pink) in I.

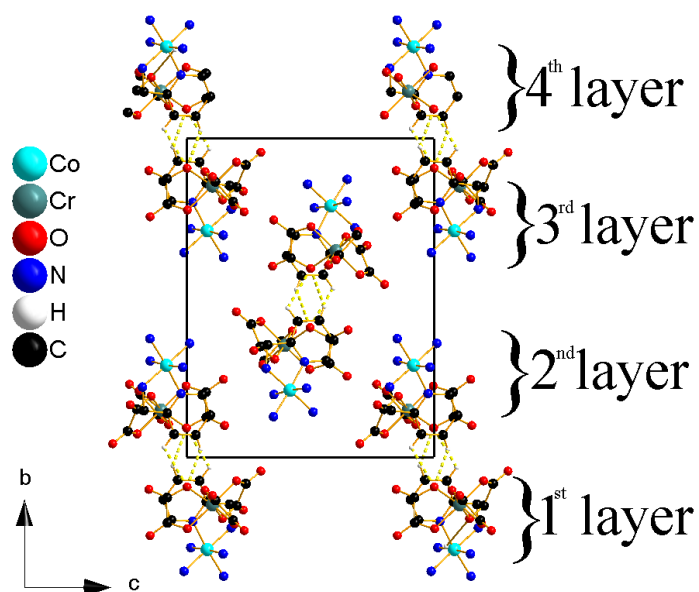


Figure S4: Projection down [100] direction of the crystal packing of I showing the layered arrangement connected around the (0 0 0) and $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ inversion centers of the cell. The empty space is filled with the water cluster. Carbon atoms of amp ligand have not been drawn for clarity.

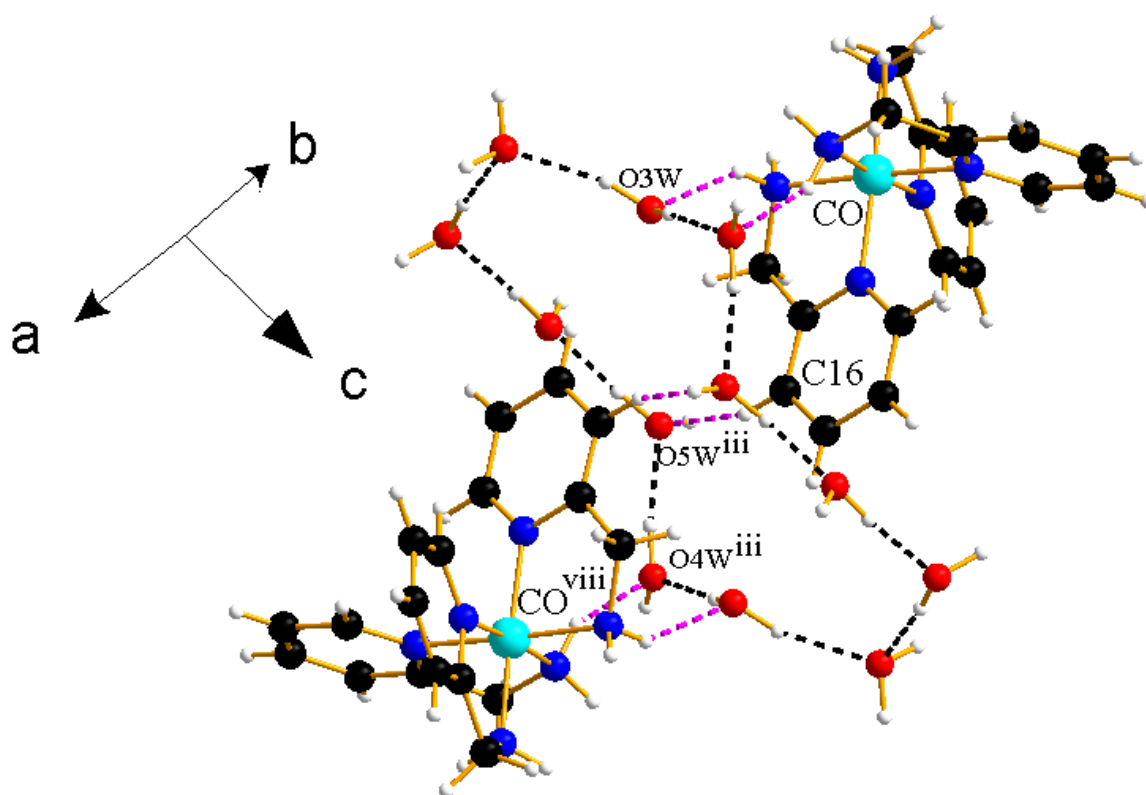


Figure S5: Perspective view of H-bonded assembly of the dodecameric cluster with two D ions belonging to two consecutive layers. For symmetry code, see table S3.

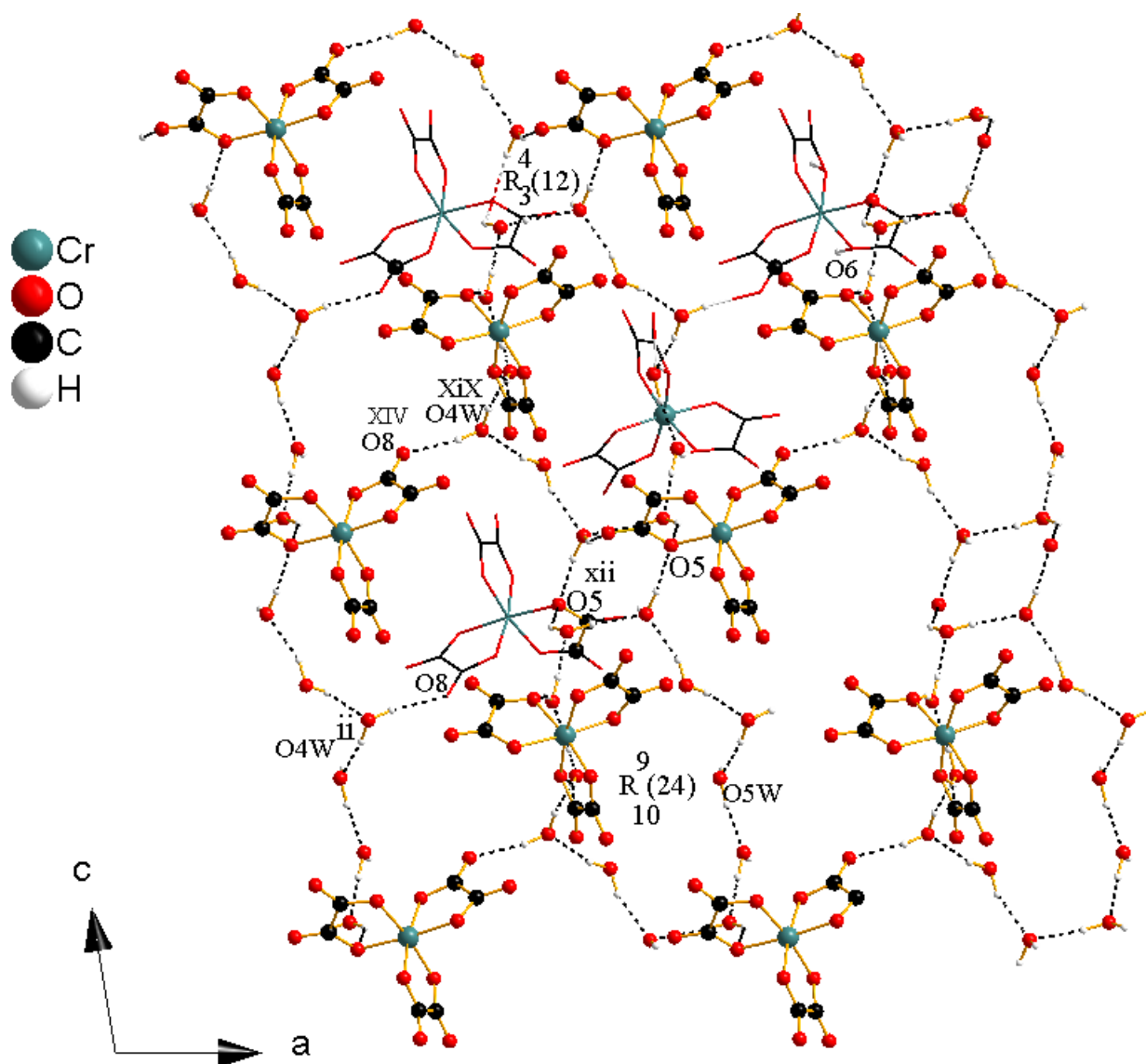


Figure S6: Perspective view of H-bonded assembly of the dodecameric cluster ($R_{10}^3(24)$) and A ions within and between two consecutive layers. For distinction A ions of the first layer have been drawn in ball and stick while for the second, the wires were used. For symmetry code, see Table S3. R12 water cluster is named $R_{10}^3(24)$ (see table S4) by using Bernstein nomenclature.

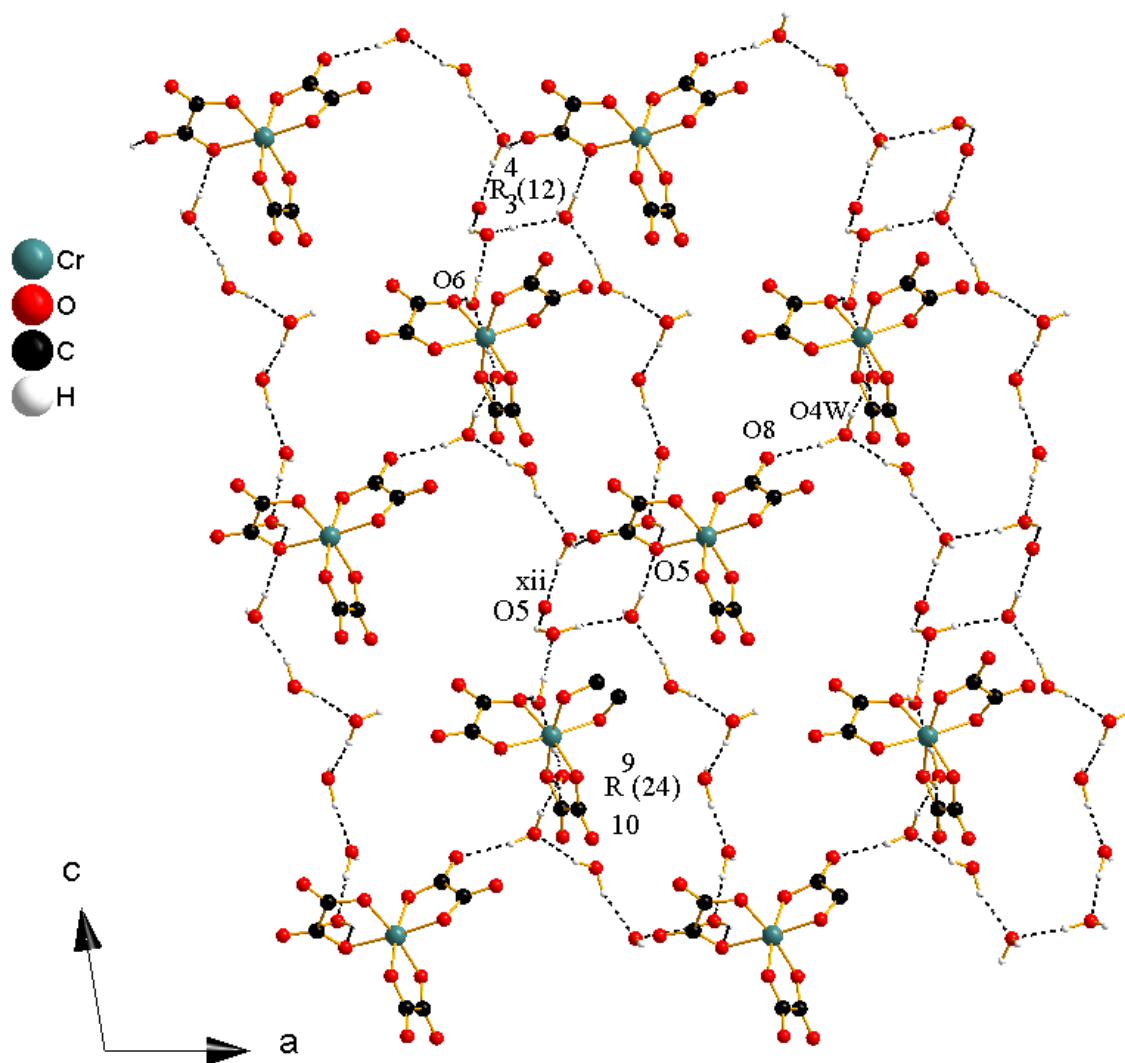


Figure S7: Perspective view of H-bonded assembly of the dodecameric cluster ($R_{10}^9(24)$) and A ions within the layer to form tapes along the c axis and connected in the [100] direction by O8 - - O4w hydrogen bond.

Table S3: Hydrogen bonds, Ow- -Ow distances and Ow- -Ow - -Ow angle for I.

D-H...A	d(D-H) Å	d(H...A) Å	d(D...A) Å	<(DHA) °
Hydrogen bonds within the cluster, mean D- -A value: 2.810 (2) Å				
O(5W)-H(10W)...O(6W)	0.950(9)	1.797(12)	2.728(3)	166(2)
O(4W)-H(8W)...O(5W)	0.954(9)	1.816(10)	2.760(2)	170(2)
O(6W)-H(11W)...O(1W) ^{vi}	0.950(10)	1.829(10)	2.777(3)	175(2)
O(3W)-H(5W)...O(4W) ^{iv}	0.939(9)	1.922(11)	2.834(2)	163(2)
O(1W)-H(1W)...O(2W) ^v	0.950(9)	1.952(10)	2.899(2)	174(3)
O(3W)-H(6W)...O(2W) ⁱ	0.936(9)	1.957(12)	2.859(2)	161(2)
Hydrogen bonds between the cluster and D ions, mean D- -A value: 3.037 (2) Å				
N(3)-H(3B)...O(4W) ^{iv}	0.88(3)	2.07(3)	2.872(2)	152(2)
N(6)-H(6A)...O(3W)	0.87(3)	2.08(3)	2.882(2)	153(2)
C(16)-H(16A)...O(5W) ⁱⁱⁱ	0.95	2.48	3.357(2)	152.7
Hydrogen bonds between the cluster and A ions, mean D- -A value: 2.981 (2) Å				
O(2W)-H(4W)...O(11) ^y	0.944(9)	1.891(12)	2.791(2)	159(2)
O(2W)-H(3W)...O(5)	0.946(9)	1.938(10)	2.8751(19)	171(2)
O(6W)-H(12W)...O(6)	0.949(9)	1.970(10)	2.903(2)	167(2)
O(4W)-H(7W)...O(8) ^{vii}	0.949(9)	1.978(13)	2.876(2)	157(2)
O(5W)-H(9W)...O(4)	0.945(9)	2.082(15)	2.957(2)	153(2)
O(1W)-H(2W)...O(5)	0.939(2)	2.40(2)	3.172(2)	139(2)
O(5W)-H(9W)...O(10)	0.945(9)	2.450(4)	3.295(3)	149(2)
Hydrogen bonds between A and D ions along the [100] direction, mean D- -A value: 3.114 (2) Å				
N(6)-H(6B)...O(7) ⁱⁱⁱ	0.91(3)	2.06(3)	2.959(2)	172(2)
N(4)-H(4B)...O(12) ⁱⁱ	0.89(3)	2.21(3)	3.021(2)	151(2)
N(4)-H(4B)...O(11) ⁱⁱ	0.89(3)	2.40(3)	3.065(2)	132(2)
C(21)-H(21A)...O(10) ⁱⁱ	0.95	2.50	3.368(3)	151.2

Hydrogen bonds between A and D ions along the [001] direction, mean D- -A value:

2.941 (2) Å

N(4)-H(4A)...O(10) ⁱ	0.85(3)	1.95(3)	2.754(2)	158(2)
N(3)-H(3A)...O(9) ⁱ	0.89(3)	1.98(2)	2.831(2)	159(2)
C(21)-H(21A)...O(7)	0.95	2.43	2.968(2)	115.6
C(7)-H(7A)...O(12)	0.95	2.44	3.211(2)	138.4

Hydrogen bonds between two consecutive layers ([010] direction), mean D- -A value:

3.055 (2) Å

C(9)-H(9A)...O(3) ^{vi}	0.95	2.45	3.017(2)	118.1
C(10)-H(10A)...O(3) ^{vi}	0.95	2.59	3.091(2)	113.1

Characteristics of the chair R₁₂ water cluster hosted in I

Ow –Ow—Ow angles	value	Ow –Ow—Ow angles	value
O2w ^{xi} ...O3w ^{vi} ...O4w	131.31(1)°	O3w ^{vi} ...O4w ... O5w	109.14(2)°
O4w ...O5w ...O6w	131.05(3)°	O5w ... O6w ... O1w ^{vi}	135.23(3)°
O6w ^x ...O1w ^{ix} ...O2w ^{xi}	117.02(1)°	O1w ^{ix} ...O2w ^{xi} ... O3w ^{vi}	104.32(1)°

Symmetry transformations used to generate equivalent atoms:

i) x, y, z-1 ii) x-1/2, -y+1/2, z-1/2 iii) x+1/2, -y+1/2, z-1/2 iv) -x+1/2, y-1/2, -z+3/2 v) -x+1, -y, -z+2 vi) -x+1/2, y+1/2, -z+3/2 vii) x+1/2, -y+1/2, z+1/2 viii) -x+1, -y, -z+1 ix) x-1/2, -y+1/2, z+1/2 x) -x, -y+1, -z+2 xi) -x+1/2, y+1/2, -z+5/2 xii) 1-x, -y, 2-z

Table S4: Graph set analysis nomenclature of hydrogen bonds between water cluster and A ions in I

Motifs	Acceptor and donor atoms involved in the different motif
R₁₀⁹(24)	O2w ⁱⁱ , O1w ^{vi} , O6w, O5w, O4w, O3w ^{vi} , O2w ^{xi} , O1w ^{ix} , O6w ^x , O5w ^x , O4w ^x , O3w ^{ix}
R₃⁴(12)	O1w, O5, O2w, O1w ^{xii} , O5 ^{xii} , O2w ^{xii}

For symmetry codes see Table S3.

Table S5: Comparison of key structural characteristics of dodecameric water clusters

Dodecameric clusters form	Average value Ow- Ow length (Å)	Average Ow-Ow-Ow Angle (°)	Number of hydrogen bonded within the cluster	References
Discrete dodecameric ring (R12)				
Dish-like	2.761	121.65	Not given	Dai et al., 2008
Chair-like	2.757	131.38	12	Barr et al. 1993
Chair-like	2.810	121.34	12	This study
Cuboid geometries (Theoretical studies)	2.823-2.835	88.74 – 93.65	18 or 20	Maheshwary et al., 2001 Shi et al, 2005
Cubane shape water tape of 16 water molecules having characteristics close to the Fused cuboid geometry dodecameric water cluster	2.818	89.99	16	Gawronski et al, 2006
Others forms of dodecameric cluster				
Hexagonal prismatic	2.829	98.15	18	Li et al., 2012
Cage-like	2.780	103.4	18	Wang et al. 2010
2D shell	2.000	121.63	12 & 11	Gu et al., 2008 & Kim et al. 2000
Chair-conformational hexamer	2.73	114.65	12	Song & Ma, 2007
Cyclic quasiplanar	2.801	111.16	12	Ghosh & Bharadwaj, 2004
Open-cube octamer buttressed	2.826	96.41	12	Neogi et al., 2004
Chair decamer with two handles	2.814	/	12	Fu et al. 2010
Impeller-like dodecameric cluster	2.844	103.22	6	Tseng et al. 2014

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