Supporting Information - B904622D

Details of preparation

$[Ni_{20}(R/S\text{-}2\text{-}MG)_{20}(H_2O)_8].20H_2O$ **(1)**: $NiSO_4{\cdot}6H_2O$ (0.608 g), 2-methylglutaric acid (R/S) (0.507g), NaOH, and water in the molar ratio 1/1.5/2/180 were heated together for 5 days at 180°C. The pale green powder was washed with water.

$[Co_{20}(R/S\text{-}2MG)_{20}(H_2O)_8]{\cdot}16H_2O$ **(2)**: $CoSO_4{\cdot}7H_2O$, (1.302 g), (R/S)2-methylglutaric acid (1.014 g), NaOH and water in the molar ratio 1/1.5/2/90 were heated together for five days at 180°C. After cooling (pH = 5), pink crystals were recovered by filtration.

$[Co_{20}(S\text{-}2\text{-}MG)_{12}(3\text{-}MG)_8(H_2O)_8]{\cdot}20H_2O$, **(3)** and $[Co_{20}(R\text{-}2\text{-}MG)_{12}(3\text{-}MG)_8(H_2O)_8]{\cdot}20H_2O$, **(4)**, crystallise under hydrothermal conditions from a reaction mixture of 1 $CoSO_4.7H_2O$ (1.302 g)/ 1 R or S-2-methylglutaric acid (0.608 g)/ 0.5 3-methylglutaric acid (0.406 g)/ 2 NaOH, and 90 H_2O. Reactants were sealed in a Teflon-lined 23 mL autoclave and heated at 180°C for eight days.

X-ray Crystallography

Compound (1)

$[Ni_{20}(R/S\text{-}2\text{-}MG)_{20}(H_2O)_8].20H_2O$ **(1)**: X-ray powder diffraction data were collected, at room temperature, on a Bruker D-8 diffractometer using $CuK\alpha_1$ radiation (λ = 1.5406 Å); step size 0.02° (2θ); angular range 5-95° (2θ)]. Calculations were performed with the EXPO[1] package for pattern matching and direct methods, and by using SHELXL-97[2] for successive difference Fourier maps. Hydrogen atoms were not located. $C_{30}H_{54}Ni_5O_{27}$, cubic, space group $P4_132$, a=16.5347(3) Å, V=4520.5(1) Å^3, Z=4, d_{calc}=1.73 g cm^{-3}. The final Rietveld refinement (502 I_{int}), performed by using FullProf[3] integrated in WinPLOTR[4], converged to R_F = 0.082 and R_{WP} = 0.128.

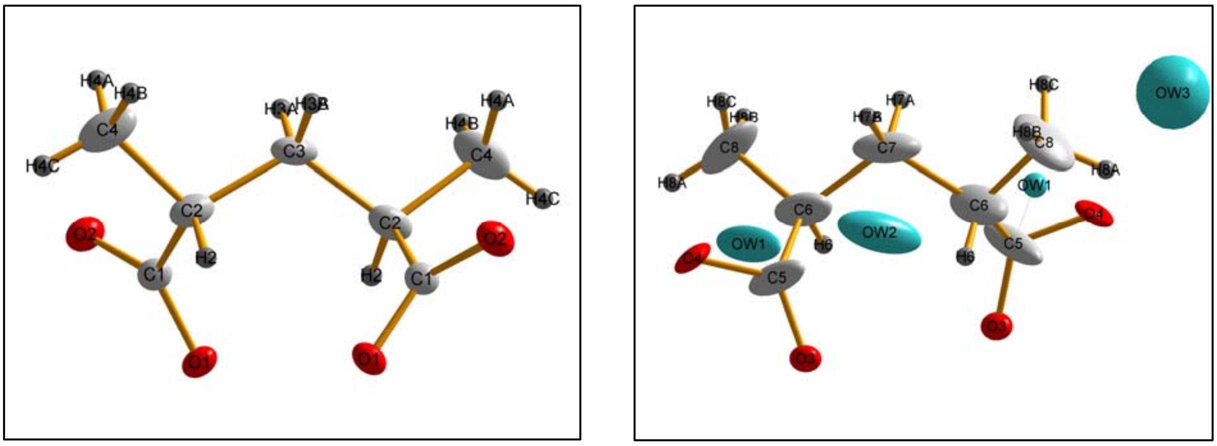
Compound (2)

The data were collected with a MAR345 image plate on BM1A at the ESRF. The beamline delivers a focussed beam of approximately 0.5mm x 0.5mm spot size at the sample position. A Si(111) monochromator was used to selected radiation of wavelength 0.7000 Å, whereby sagittal bending of the second crystal provides horizontal focussing. Vertical focussing is achieved with Rh coated mirrors before and after the monochromator. The sample was selected from the batch as supplied and mounted in paraffin oil in a x-ray loop. The crystal was pink and had a polyhedra shape with maximum diameter of approximately 120 microns and many facets. The beam size was defined with slits to be 0.4mm x 0.4mm, and the sample was placed in the cold N_2 gas stream of an Oxford Cryostream at a temperature of 120K. A total of 64 rotation images were collected with a rotation per frame of 2deg and an exposure of approximately 5 seconds for each frame.

The sample-to-detector distance of 136 mm yielded a resolution on 0.80Å at the edge of the image. Total measuring time was approximately 2 hours for the complete data collection. The data were indexed and the intensities integrated using the CrysAlis software package from Oxford Diffraction. Absorption correction and scaling was performed with SADABS[5]. The total number of observed reflections was 21675, which reduced to 1726 independent reflections with an Rint of 0.0367. Structure solution was straightforward using SIR-92, and the refinement was carried out with SHELXL-97[2]. Oxygen atom of the interstitial disordered solvent molecule Ow3 was treated isotropically. The hydrogen atoms of the organic molecules were placed in calculated positions and refined by using a riding model. The hydrogen atoms were not located for the water molecules.

The second organic ligand, 2-methylglutarate, is disordered with statistic occupancy of 2/3. In this molecule, one oxygen atom coordinates through a mu2 manner (O3) and the other is non-coordinating (O4). To complete octahedral environment of the cobalt centers when the 2-methylglutarate is missing, the oxygen coordinating site is occupied by a bridging water molecule. Therefore, O3 oxygen atom belongs to a carboxylate for 2/3 and to a water molecule for 1/3. Moreover, when the organic molecule is missing, two other water molecules are present, Ow1 and Ow2, with of course an occupancy of 1/3. Therefore, since the second 2-methylglutarate and two water molecules "share the same space", distances between them appear to be short. The refinement of the occupancy with PART in SHELX[2] leads to the same disorder; 2/3 of organic and 1/3 water molecules.

The structure was also solved and refined in tetragonal sub-group, P4(1)2(1)2, and in triclinic P1. However, the reduction in symmetry did not help to resolve the disorder, and the introduction of twinning did not improve the refinement. Therefore it seems that the disorder is a "real" disorder and not an artifact due to the cubic symmetry.



(a) **(b)**

Compound 2: Ellipsoids representation of ; (a) 2-methylglutarate 1 and (b) 2-methylglutarate 2 and water molecules.

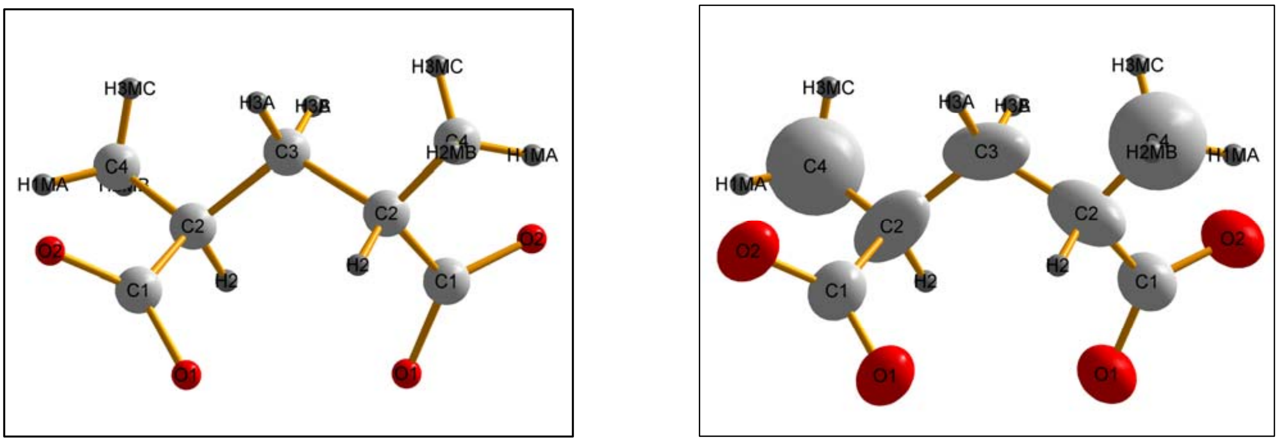
The carbons of the methyl groups present a high thermal factor for two reasons: first each molecule is located on a two-fold axis whereas the methyl is only present on half of the molecule (two crystallographic sites for one carbon), secondly methyl groups are always more agitated then the rest of the molecule due to a higher degree of freedom (rotation). Oxygen atom of the interstitial disordered solvent molecule Ow3 was treated isotropically.

Refinement for **(2)**: $C_{30}H_{52}Co_5O_{26}$, cubic, space group $P4_132$, a=16.6130(1) Å, V=4585.0(5) Å^3, Z=4, d_{calc}=1.63 g cm^{-3}, μ(MoKα)=1.856 mm^{-1}, F(000)=2300, θ_{max}=25.9°; 21639 reflections collected of which 1561 unique (R_{int}=0.035). Final R indices (1557 observed reflections, $I>2\sigma I$): $R(F)$ = 3.7%, $wR(F^2)$ = 11.9%, GOF = 1.18 for 114 parameters. Highest residual electron density 0.60 e Å^{-3}.

Compound (3)

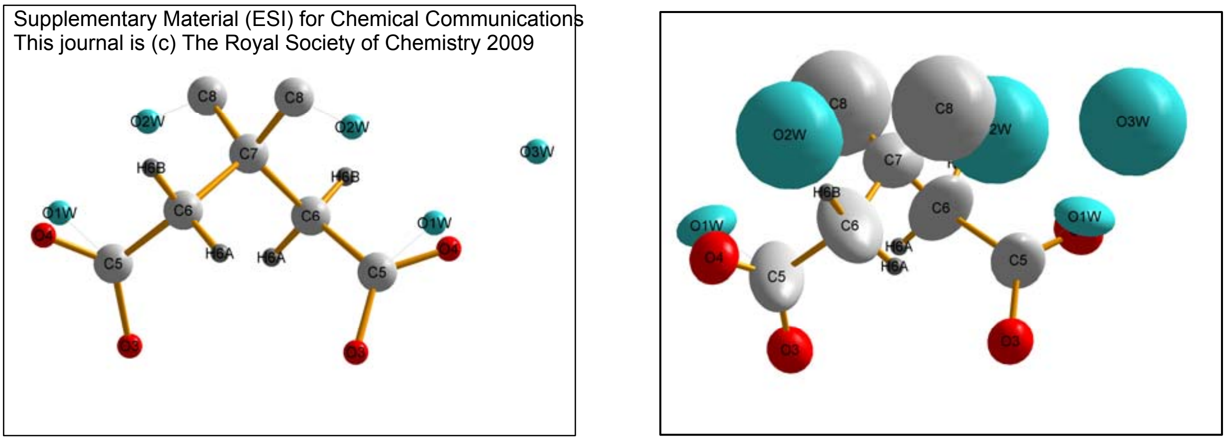
Intensity data collection was carried out at room temperature with a Bruker X8-APEX equipped with a normal-focus molybdenum-target X-ray tube (λ = 0.71073 Å). An empirical absorption correction was applied (SADABS program based on Blessing's method)[5]. The structures were solved by direct methods and refined by the full-matrix least-squares procedure (SHELX-TL package)[2]. Heavier atoms were initially located by direct methods. The remaining non-hydrogen atoms were located from Fourier differences maps and were refined with anisotropic thermal parameters except for methyl group of the methylglutarate ions and two solvent molecules (OW2 and OW3). Hydrogen atoms were not placed for the water molecules and for the methyl group of the 3-methylglutarate (2/3 occupancy). All the other hydrogen atoms were placed in calculated positions and refined by using a riding model.

The second organic ligand, 3-methylglutarate, is disordered with statistic occupancy of 2/3. In this molecule, one oxygen atom coordinates through a mu2 manner (O3) and the other is non-coordinating (O4). To complete octahedral environment of the cobalt centers when the ligand is missing, the oxygen coordinating site is occupied by a bridging water molecule. Therefore, O3 oxygen atom belongs to a carboxylate for 2/3 and to a water molecule for 1/3. Moreover, when the organic molecule is missing, two other water molecules are present, Ow1 and Ow2, with an occupancy of 1/3. The structure was also solved and refined in triclinic P1. However, the reduction in symmetry did not help to resolve the disorder, and the introduction of twinning did not improve the refinement. Therefore it seems that the disorder is a “real” disorder and not an artifact due to the cubic symmetry.



(a) (b)

Compound 3: Representation of the 2-methylglutarate; (a) ball and sticks, (b) ellipsoids.



(a) **(b)**

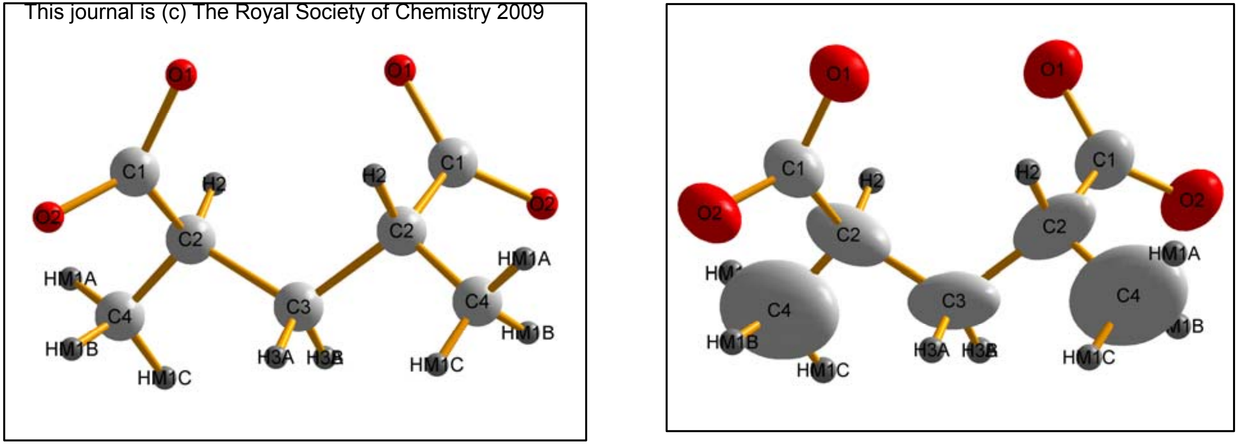
Compound 3: Representation of the 3-methylglutarate and the water molecules, (a) ball and sticks, (b) ellipsoids.

Carbon atoms of the two methyl groups were left isotropic for two reasons: first each molecule is located on a two-fold axis leading to two crystallographic equivalent sites for one carbon; secondly methyl groups are always more agitated then the rest of the molecule due to a higher degree of freedom (rotation). Oxygen atom of the interstitial disordered solvent molecules Ow2 and Ow3 were treated isotropically.

Refinement for **(3)**, $C_{30}H_{54}Co_5O_{27}$, cubic, space group $P4_332$, a=16.7176(2) Å, V=4672.2(1) $Å^3$, Z=4, d_{calc} =1.62 g cm^{-3}, μ(MoKα)=1.824 mm^{-1}, F(000)=2340, θ_{max}=30.0°; 33850 reflections collected of which 2299 unique (R_{int}=0.119). Final R indices (1467 observed reflections, $I>2\sigma I$): $R(F)$ = 6.2%, $wR(F^2)$ = 15.1%, GOF = 1.107 for 98 parameters. Highest residual electron density 0.22 e $Å^{-3}$.

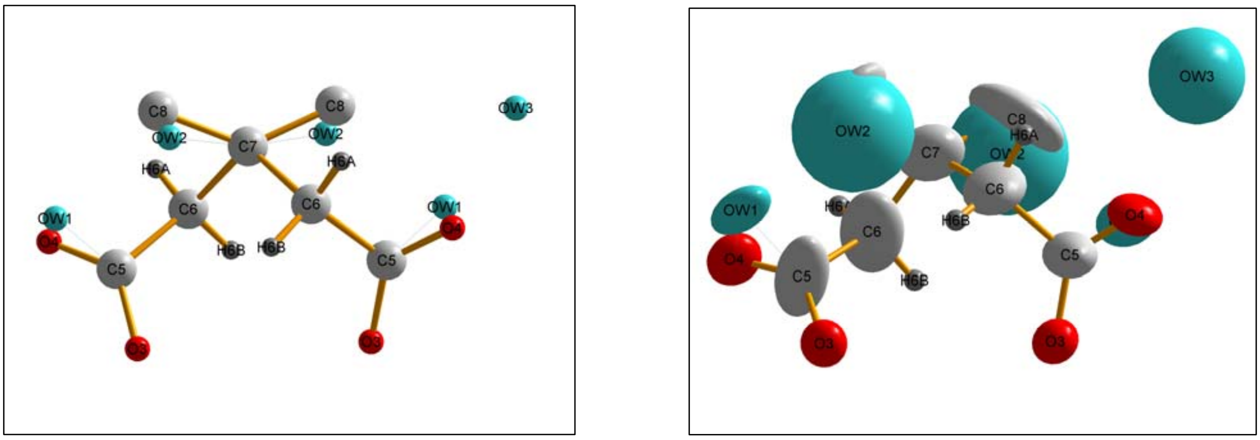
Compound (4)

Intensity data collection was carried out at room temperature with a Bruker X8-APEX diffractometer equipped with a normal-focus molybdenum-target X-ray tube (λ = 0.71073 Å). An empirical absorption correction was applied (SADABS program based on Blessing's method)[5]. The structures were solved by direct methods and refined by the full-matrix least-squares procedure (SHELX-TL package)[2]. Heavier atoms were initially located by direct methods. The remaining non-hydrogen atoms were located from Fourier differences maps and were refined with anisotropic thermal parameters except two solvent molecules (OW2 and OW3). Hydrogen atoms were not located for the water molecules and for the methyl group of the 3-methylglutarate (2/3 occupancy). All the other hydrogen atoms were placed in calculated positions and refined by using a riding model. Compound (4) presents the same type of disorder as compound (3), and since the second 2-methylglutarate and two water molecules “share the same space”, distances between them appear to be short.



(a) (b)

Compound 4: Representation of the 2-methylglutarate; (a) ball and sticks, (b) ellipsoids.



(a) (b)

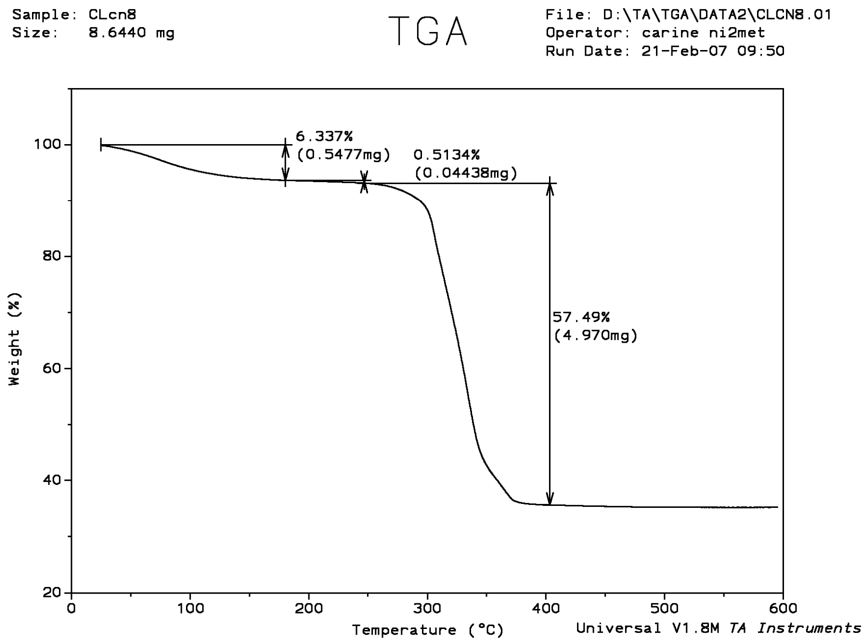
Compound 4: Representation of the 3-methylglutarate and the water molecules, (a) ball and sticks, (b) ellipsoids.

Carbon atom of the methyl groups of the 3-methylglutarate presents a high thermal displacement for two reasons: first this molecule is located on a two-fold axis leading to two crystallographic equivalent sites for one carbon; secondly methyl groups are always more agitated then the rest of the molecule due to a higher degree of freedom (rotation). Due to the agitation of this methyl group the distance between C6 and C8 is too short. Oxygen atom of the interstitial disordered solvent molecules Ow2 and Ow3 were treated isotropically.

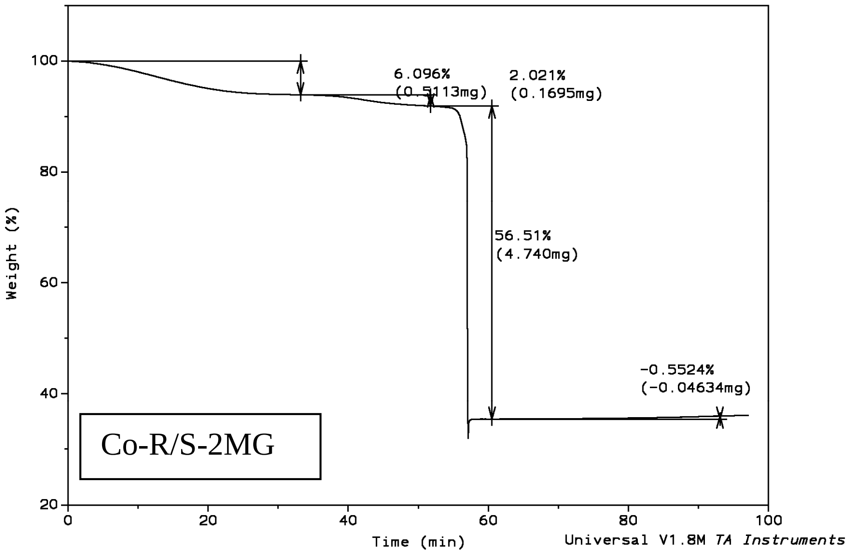
Refinement for **(4)**, $C_{30}H_{54}Co_5O_{27}$, cubic, space group $P4_132$, a=16.7268(1) Å, V=4679.92(5) Å^3, Z=4, d_{calc}=1.62 g cm^{-3}, μ(MoKα)=1.821 mm^{-1}, F(000)=2340, θ_{max}=30.0°; 98330 reflections collected of which 2302 unique (R_{int}=0.072). Final R indices (1965 observed reflections, $I > 2\sigma\ I$): R(F) = 4.9 %, $wR(F^2)$ = 12.8 %, GOF = 1.19 for 131 parameters. Highest residual electron density 0.80 e Å^{-3}.

Thermogravimetry

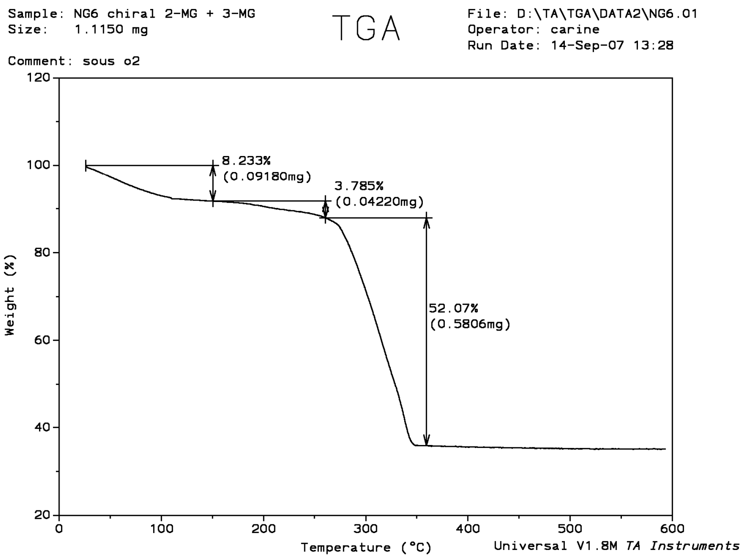
(1) Mixture of $[Ni_{20}(R\text{-}2MG)_{12}(S\text{-}2MG)_8(H_2O)_8].20H_2O$ and $[Ni_{20}(S\text{-}2MG)_{12}(R\text{-}2MG)_8(H_2O)_8].20H_2O$



(2) Mixture of $[Co_{20}(R\text{-}2MG)_{12}(S\text{-}2MG)_8(H_2O)_8].16H_2O$ and $[Co_{20}(S\text{-}2MG)_{12}(R\text{-}2MG)_8(H_2O)_8].20H_2O$



(3) $[Co_{20}(S\text{-}2MG)_{12}(3\text{-}MG)_8(H_2O)_8].20H_2O$



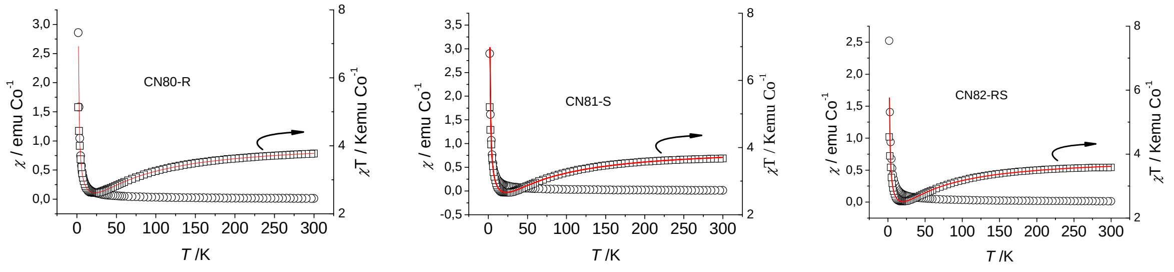
Magnetic properties

Experimental

The magnetic measurements were carried out by using a Quantum Design MPMS-XL SQUID magnetometer in the ranges 1.8-300 K, ± 5 T. The experimental values were corrected from diamagnetism of the sample and the sample holder.

Results

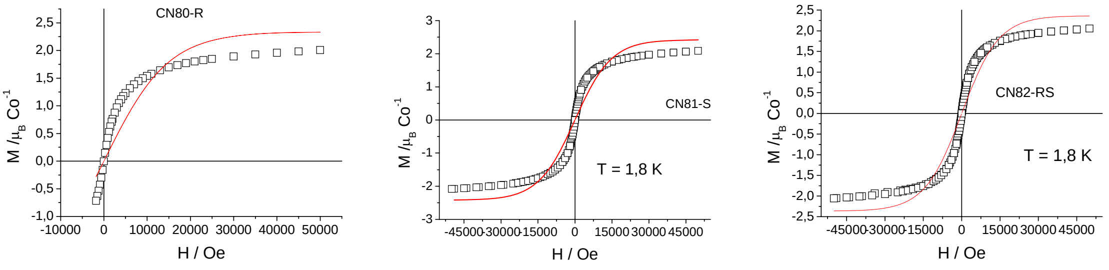
The three compounds **(2)**, **(3)** and **(4)** exhibit very similar magnetic behaviors:



(4) **(3)** **(2)**

Figure 1: Temperature variation of the magnetic susceptibility χ (circles) and corresponding χT product (squares) of **(4)**, **(3)** and **(2)**.

Above 150 K, the magnetic susceptibility obeys the Curie-Weis law. The Curie constants deduced from the fit of the inverse susceptibility as a function of temperature are given in Table 1. All the values are in agreement with high spin Co^{2+} ions in octahedral sites. The decrease of χT with temperature is consistent with the negative values of the Weiss temperatures θ. It can either be due to spin-orbit coupling effect or antiferromagnetic interactions. The latter is inferred in the present case from the occurrence of a minimum in the χT curves at 22 K followed by a divergence down to 1.8 K, which is characteristic of ferrimagnetic systems. However, no long-range ordering was observed above 1.8 K. The magnetization versus field curves recorded at 1.8 K (Fig. 2) exhibit saturation values Ms of ca 2 μ_B per cobalt, in the expected range for high spin octahedral species. Comparison with the Brillouin function shows that M increases much steeper than expected for a simple paramagnet, confirming the existence of ferrimagnetic-like correlations.



(4) **(3)** **(2)**

Figure 2: Magnetization versus field curves of **(4)**, **(3)** and **(2)** recorded at 1.8 K. The full lines correspond to the Brillouin function scaled to Ms.

Compounds	*C* / K cm^3 per Co mol	*θ* /K	*Ms* / μ_B	
Co-2-MG – R **(4)**	4.09	-25.8	2.01	
Co-2-MG – S **(3)**	3.89	-18.1	2.09	
Co-2-MG- RS **(2)**	3.80	-17.4	2.05	

Table 1: Characteristic magnetic data for **(4)**, **(3)** and **(2)**

Optical properties

Optical circular dichroïsm (ODC) was measured in absorption mode with a JASCO 810 spectrometer on powder samples embedded in KBr pellets. The experimental data were corrected from the signal recorded for a KBr pellet with similar dimensions.

[1] A. Altomare, M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Rizzi, *J. Appl. Crystallogr.* **1999**, *32*, 339.
[2] G. M. Sheldrick, *SHELXS97 and SHELXL97: Software package for the Crystal Structure Determination, University of Göttingen, Germany*, **1997**.
[3] J. Rodriguez-Carvajal, *In "Collected Abstracts of Powder Diffraction Meeting", Toulouse, France* **1990**, 127.
[4] T. Roisnel, J. Rodriguez-Carvajal, *In "Abstracts of the 7th European Powder Diffraction Conference", Barcelona, Spain* **2000**, 71.
[5] G. M. S. Sheldrick, Version 2.06; Empirical Absorption Correction Program; University of Göttingen: Göttingen, Germany,, **2002**.