



This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Crystal Growth & Design*, © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <http://dx.doi.org/10.1021/cg1000842>

(Article begins on next page)

A family of isorecticular chiral metal-organic frameworks based on coordination and hydrogen bonds in $[M[Co(ethylenediamine)(oxalato)_2]_2]$

Cédric Borel,^a Kate Davies,^b Paul Handa,^a Gustav Hedberg,^a Clive L. Oliver,^b Susan A. Bourne,^b

*Mikael Håkansson,^c Vratislav Langer,^a and Lars Öhrström^{*a}*

^a Dept. of Chemical and Biological Engineering, Chalmers University of Technology, SE-412 96

Gothenburg, Sweden. ^b Department of Chemistry, University of Cape Town, Rondebosch 7701,

Republic of South Africa ^c Dept. of Chemistry, University of Gothenburg, SE-412 96 Gothenburg,

Sweden.

ohrstrom@chalmers.se

From the parent compound $[Ca[Co(ethylenediamine)(oxalato)_2]_2]_n \cdot 4H_2O$, **1**, a series of framework compounds was prepared via the soluble sodium salt and crystal growth with the divalent metal ions Cd^{2+} , Mn^{2+} , and Sr^{2+} , (**2-4**). These compounds have the same general formula $[M[Co(ethylenediamine)(oxalato)_2]_2]_n \cdot xH_2O$ and they all form the same four- and eight-connected 3D net having **scu** topology (and are thus isorecticular) with water filled channels of variable size running in one direction of the crystals. However, they crystallize in two different space groups, the chiral $P2_1$ (**3**, **4** and the low temperature form of **1**) and the non-centrosymmetric P^- (**1**, **2**). The potential voids upon water removal are 18-20% of the unit cell. Preliminary gas sorption measurements at 298 K and 8 bar

show substantial CO₂ and N₂O uptake (12-14% and 15-16% by mass respectively) while the H₂ uptake was 0.18%, a relatively high value considering the low pressure and high temperature.

Introduction

The preparation of porous materials based on coordination compounds continues to attract attention as the scope of possible applications increase¹⁻⁵ and commercial actors are taking an interest.⁶ We have recently reported that [Ca[Co(ethylenediamine)(oxalato)₂]₂]_n·4H₂O (Figure 1) gives a 3D-net based on Ca(oxalato)₄ 8-connected nodes and Co(en)(oxalato)₂ 4-connected nodes resulting in a compound that retains its structure and 19% void volume even after residual solvent has been evacuated by vacuum at 160°C.⁷ The network in this compound is of the relatively rare (4⁴.6²)₂(4¹⁶.6¹²)-**scu** topology^{8,9} (Figure 1), and in this communication we present three more similar compounds that are not all *isostructural*, but form the same network, thus they are said to be *isorecticular*¹⁰.

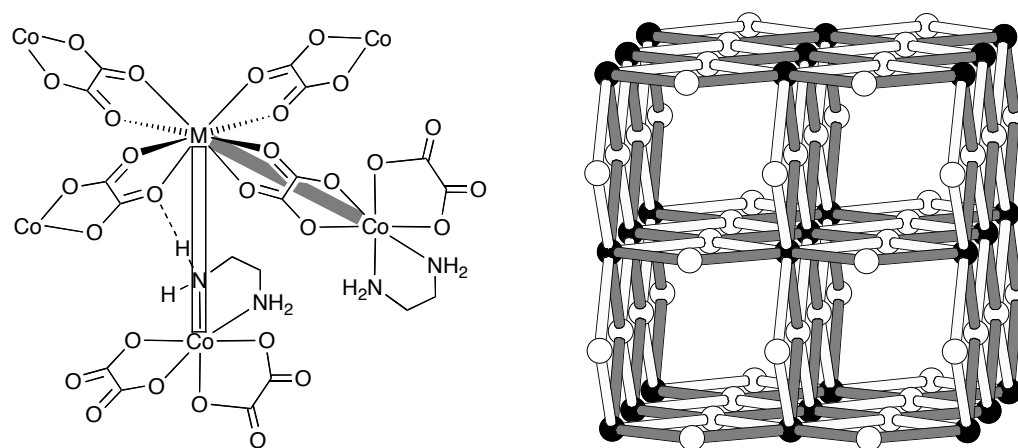


Figure 1. Left: Molecular units in [M[Co(ethylenediamine)(oxalato)₂]₂]_n·4H₂O and the oxalate and hydrogen bond bridges. Right: The resulting four- and eight-connected **scu**-net in M=Ca with oxalate links in grey and hydrogen bond links in white. Black spheres represent calcium ions and white spheres represent cobalt ions. The water molecules are situated in the channels and have been omitted.

There are several reasons why the expansion of the parent structure to a whole series of compounds is important: From a synthetic point of view it is valuable to test the usefulness of the supramolecular synthons employed, and while the metal-oxalate-metal bridge is well known the hydrogen bonds that expand the (4,4)-grid to a 3D net (Figure 1) are weaker and could be more easily influenced by changes of metal ions and dimensions of the network. From an applications point of view, narrower channels are preferable for gas sorption, as it is not optimal to form more than a monolayer of the sorbed gas onto the surfaces of the pores. In addition, even if practical uses of the present materials are unlikely, a set of compounds with only small changes in pore volumes and sizes, but with a change of metal ions, may give valuable information on the factors controlling the gas sorption properties. Finally we noted that the parent compound crystallized in a non-centrosymmetric (but not chiral) space group, thus small changes in metal coordination configuration prompted by changes of the M^{2+} ions could very well lead to a lowering of symmetry and thus to a chiral porous material.

From the point of view of making networks and MOF compounds, the **scu**-net represents a strategy where nodes with higher connectivity are linked via nodes with lower connectivity to form 3D-nets. Compared to high-connectivity nets (higher than six) where increased connectivity will give more nearest neighbours for each node, more links traversing space and denser nets, the introduction of a second node with lower connectivity will help to ensure a certain degree of porosity to the network. One such example is the fluorite (CaF_2) or $(4^6)_2(4^{12}.6^{12}.8^4)$ -**flu** net, built from perfect tetrahedra and cubes, present in $[Cd_4(\text{tetrakis}(4\text{-carboxyphenyl)methane})_2(\text{DMF})_4]\cdot 4\text{DMF}\cdot 4\text{H}_2\text{O}$,¹¹ and recently other **scu**-nets have also been prepared^{12,13}.

A slightly more complicated network is also less prone to interpenetration, an effect that tends to plague designs based on high symmetry and low connectivity nets. One reason may be that such nets are rarely self dual; that is, creating a new network by adding nodes at the centres of the empty spaces in the first network does not generate the starting network (4,4 2D nets are typically self dual). Of the

26 self dual 3D nets in the Reticular Chemistry Structural Resource database (RCSR)^{8,9} only four are binodal and have mixed connectivity (**ftw**: 4- and 12-connected, **hms**: 3- and 5-connected, **mcf**: 3- and 5-connected, and **rtw**: 4- and 5-connected). Moreover, in their survey of the networks in the Cambridge Structural Database, Blatov et al. found a low frequency of binodal networks.¹⁴

Experimental

Materials and methods

All chemicals were reagent grade and used without further purification. IR analyses were made with a Perkin Elmer Instruments Spectrum One FT-IR spectrophotometer using KBr tablets. A Fisons EA1108 ₂CHNS-O Elemental Analyser was used to analyze compound **1** for carbon (C), hydrogen (H) and nitrogen (N) content. The analysis was performed in duplicate. TGA on compound **1** was performed on a Mettler Toledo TGA/SDTA851e under N₂ gas with a flow rate of 30 mL/min. Sample masses were between 3 and 5 mg and all runs were conducted from 25 to 400 °C at a heating rate of 10 °C/min. TGA on compound **2** and **4** was performed on a TG-DSC NETZSCH STA 409 PC Luxx simultaneous thermal analyser under a 20ml/min N₂ gas flow. The temperature was increased at a rate of 2°C/min with an additional 60 min isotherm at 400°C. The experiment was performed on a 15 mg sample for compound **2** and with 4 mg for **4**. Two additional measurements were performed on compound **4**: The first measurement consisted of heating the sample to 160°C at a rate of 10°C/min then cooling to room temperature and the sample is cooled down and the experiment redone. Both experiments were performed under a mixture of O₂ and N₂ with a flow rate for both of 10 ml/min. Compound **3** has not been analyzed by TGA because of impurity problems.

[Ca[Co(ethylenediamine)(oxalato)₂]₂]_n·4H₂O **1** was prepared according to the literature¹⁵ and re-crystallised from water to give X-ray diffraction quality purple crystals. The bulk phase was tested by comparing the room temperature powder diffraction pattern with the calculated powder diffraction

pattern from the room temperature crystal structure and was found to be identical. Calculated: C, 20.52; H, 3.44; N, 7.98, Found: C, 20.60; H, 3.75; N 7.78.

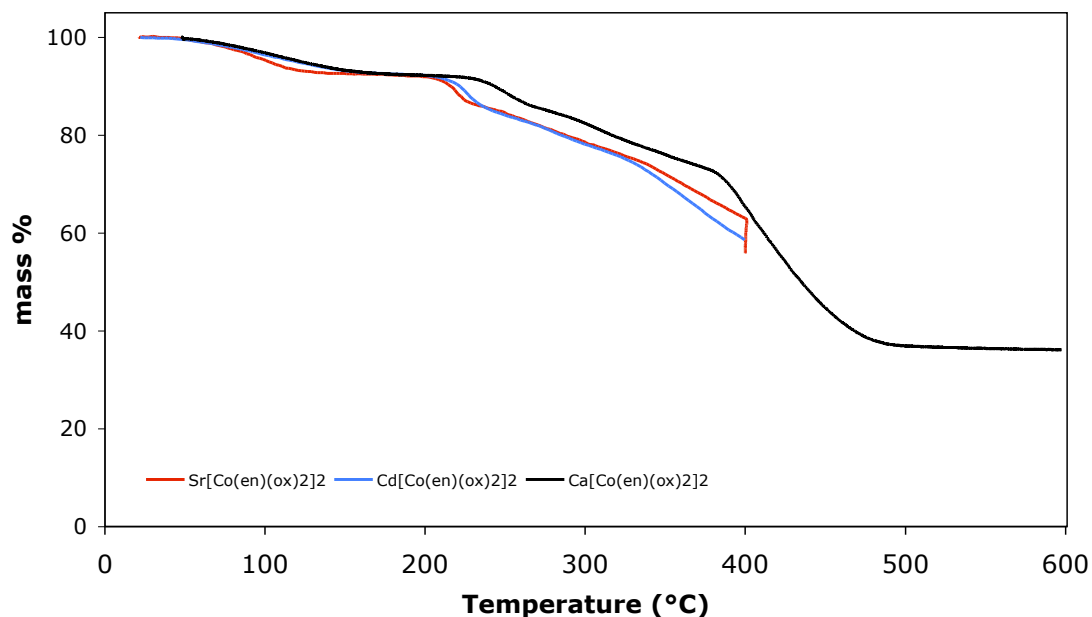
Thermogravimetric analysis (TGA) showed a 10.36% average weight loss from 65 °C to 160 °C, which corresponds to the loss of 4 water molecules (calculated 10.26%). Upon heating at 160 °C for over 4 hours¹ another TGA was performed which still showed a mass loss of 8.73% over the same temperature range (Figure S1). This corresponds to the loss of 3.4 water molecules (8.86%). This means that, although 4 water molecules may be removed under vacuum, 3.4 water molecules are present in the complex when the TGA is performed despite efforts to transfer the sample from vacuum oven to TGA as quickly as possible.

Preparation of a [Na[Co(ethylenediamine)(oxalato)₂]] solution: 1 g (1.56 mmol) of Ca[Co(ethylenediamine)(oxalato)₂]₂·4H₂O and 0.345 g (1.87 mmol) of sodium oxalate were dissolved in 160 ml of water and heated up till 80°C. A white precipitate of calcium oxalate appeared and was filtered out. The purple solution was cooled down to room temperature and the volume was adjusted to 160 ml in order to reach a concentration in [Co(ethylenediamine)(oxalato)₂]⁻ of 10⁻² mol/l.

Preparation of [Cd[Co(ethylenediamine)(oxalato)₂]₂]₂·xH₂O: 48 mg (20 mmol) of Cd(NO₃)₂ was dissolved in a small amount of water. The mixture was added to 40 ml of a 10⁻² mol/l [Na[Co(ethylenediamine)(oxalato)₂]] solution (0.39 mmol). The resulting mixture was slowly evaporated and after a week prismatic purple crystals appeared. The crystals were collected by filtration and washed with a small amount of cold water. TGA showed a 7.4 % weight loss from 65 °C to 160 °C, which corresponds to the loss of 3.2 water molecules.

Preparation of [Mn[Co(ethylenediamine)(oxalato)₂]₂]₂·xH₂O: 3 mg (20 mmol) of MnSO₄ was dissolved in a small amount of water. The mixture was added to 40 ml of a 10⁻² mol/l [Na[Co(ethylenediamine)(oxalato)₂]] solution (0.39 mmol). The solvent was slowly evaporated till dry. The resulting purple crystals were separated by hand from the byproducts.

Preparation of $[\text{Sr}[\text{Co}(\text{ethylenediamine})(\text{oxalato})_2]_2 \cdot 4\text{H}_2\text{O}$: 3 mg (20 mmol) of SrCO_3 was dissolved in a small amount of diluted hydrochloric acid. The mixture was added to 40 ml of a 10^{-2} mol/l $[\text{Na}[\text{Co}(\text{ethylenediamine})(\text{oxalato})_2]]$ solution (0.39 mmol). The resulting mixture was slowly evaporated and after a week prismatic purple crystals appeared. The crystals were collected by filtration and washed with a small amount of cold water. TGA showed a 7.3 % weight loss from 65 °C to 160 °C, which corresponds to the loss of 3.0 water molecules.



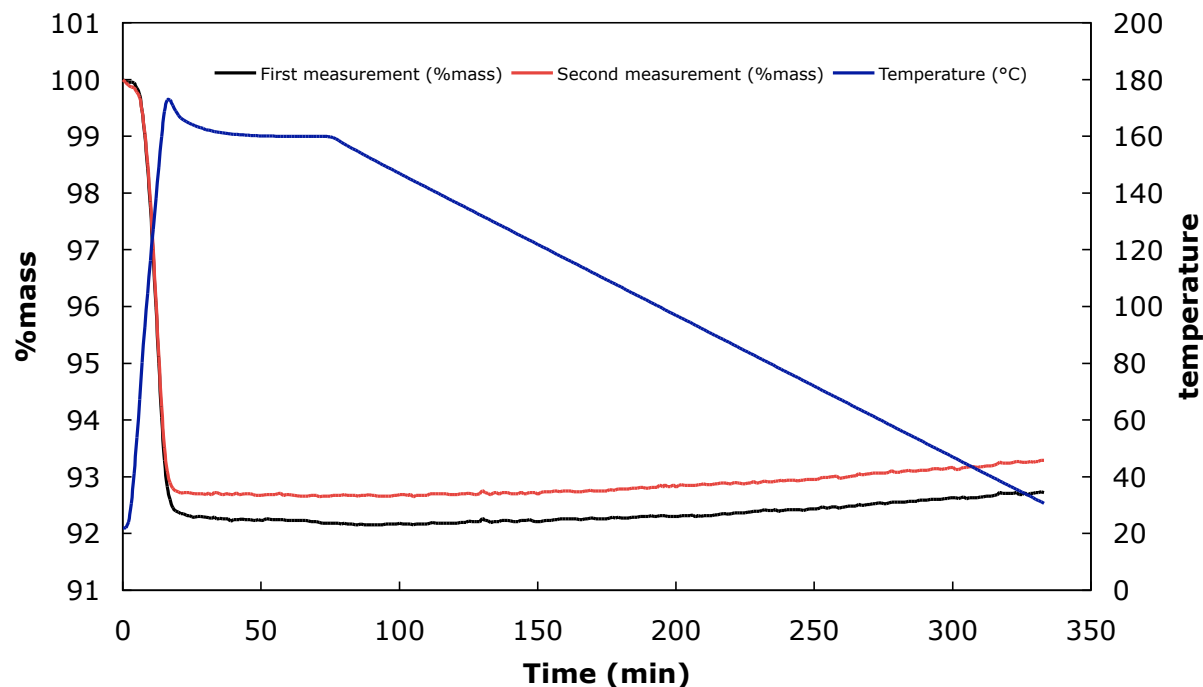


Figure 2. TGA measurements on **1**, **2** and **4** (top) and two consecutive measurements on **1** (bottom).

X-ray crystallography

Compounds **1-4** were analyzed at room temperature using a Rigaku R-Axis IIC image plate system with graphite-monochromated MoK α radiation ($\lambda = 0.7107 \text{ \AA}$) from a RU-H3R rotating anode operated at 50 kV, 90 mA. Ninety oscillation photographs with a rotation angle of 2° were collected and processed using the *CrystalClear* software package.¹⁶ Empirical corrections were applied for the effects of absorption using the *REQAB* program within *CrystalClear*. Low temperature structures of [Ca[Co(ethylenediamine)(oxalato)₂]₂]_n·4H₂O **1** LT and [Sr[Co(ethylenediamine)(oxalato)₂]₂]_n·4H₂O **4** LT were obtained using a Bruker SMART CCD diffractometer and MoK α radiation. CCD data were integrated with the *SAINT* package¹⁷ and a multi-scan absorption correction was applied using *SADABS*.¹⁸ All structures were solved by direct methods (*SIR-97*¹⁹) and refined against all F^2 data by full-matrix least-squares (*SHELXL97*²⁰), including anisotropic displacement parameters for all non-H

atoms. H atoms were placed in calculated positions (unless otherwise stated) and allowed to ride during subsequent refinement. The crystallographic data are summarized in Table 1.

Network analysis

The short (Schläfli) symbol gives the number of smallest rings found in the net and also the stoichiometry and the connectivity (p) of the nodes, through the relation $p = \frac{1}{2} + (\frac{1}{4} + 2 \cdot (\text{sum of superscripts}))^{\frac{1}{2}}$, and thus gives a rough idea of the type of network in question. The short (Schläfli) symbol, the vertex (or long) symbol, and the C10 (td10) value were calculated using *TOPOS*.^{21,22}

Gas sorption studies

A schematic view of the apparatus used for the gas sorption studies is shown in Figure 3.²³ Chamber A is left empty as a control while chamber B contains the sample of a known weight with a plug of cotton wool. The entire system is heated to 65 °C and kept at that temperature, under vacuum, for 4 hours to remove the guest water. 65 °C is the maximum temperature attainable with this apparatus. The system is then cooled to 25 °C while still under vacuum. Valves 2 and 3 are then closed while approximately 20 bar of gas is released into chamber A. Valve 1 is closed and gas pressures in chambers A and B are monitored using the program *Absorbance*.²⁴ Valve 2 is then opened and quickly closed again and *Absorbance* is left running overnight to allow equilibrium in chamber B.

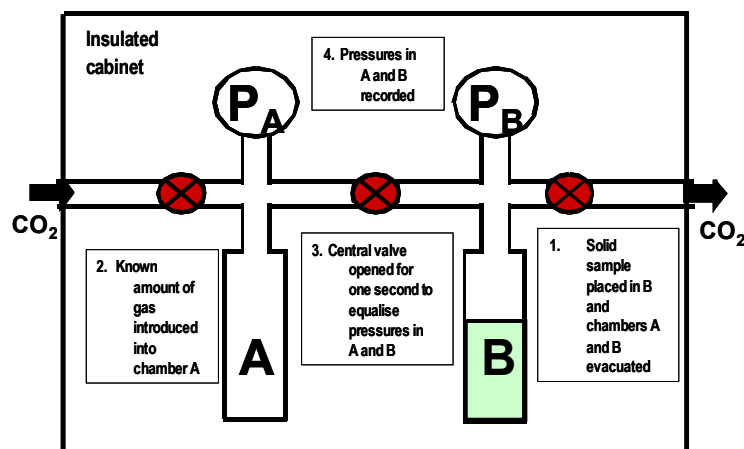


Figure 3. A schematic view of the apparatus for recording gas sorption isotherms.²³

Table 1. Crystallographic data for **1-4** including the low temperature data for **1** and **4**. Formulas and densities are based on the modeling of the X-ray data and include various amounts of solvent waters.

	1	1LT	2	3	4	4LT
Chemical formula	C ₁₂ H ₁₆ CaCo ₂ N ₄ O ₁₆	C ₁₂ H ₂₄ CaCo ₂ N ₄ O ₂₀	C ₁₂ H ₁₆ CdCo ₂ N ₄ O ₁₆	C ₂₄ H ₃₂ Co ₄ Mn ₂ N ₈ O ₃₉	C ₁₂ H ₂₂ Co ₂ N ₄ O ₂₀ Sr	C ₁₂ H ₁₇ Co ₂ N ₄ O _{19.26} Sr
Formula weight	630.23	702.29	772.599	1402.18	741.77	730.92
Temperature/K	293(2)	153(2)	293(2)	293(2)	293(2)	153(2)
Crystal system	Tetragonal	Monoclinic	Tetragonal	Monoclinic	Monoclinic	Monoclinic
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Space group	P [−]	P2 ₁	P [−]	P2 ₁	P2 ₁	P2 ₁
a/ \AA	8.898(3)	8.9518(12)	8.918(3)	8.842(2)	9.0785(17)	9.0325(14)
b/ \AA	8.898(3)	15.455(2)	8.918(3)	30.394(6)	15.666(3)	15.476(2)
c/ \AA	7.679(3)	8.9934(12)	7.690(3)	8.823(2)	9.1321(17)	9.1107(15)
$\alpha/^\circ$	90	90	90	90	90	90
$\beta/^\circ$	90	92.910(3)	90	92.158(8)	92.57(8)	92.883(3)
$\gamma/^\circ$	90	90	90	90	90	90
Volume/ \AA^3	608.0(3)	1242.6(3)	611.7(4)	2369.2(8)	1297.5(4)	1272.0(3)
Z	1	2	1	2	2	2
$\rho_{\text{calc}}/\text{Mg m}^{-3}$	1.721	1.877	1.907	1.965	1.899	1.908
μ/mm^{-1}	1.654	1.640	2.28	1.864	3.406	3.47
Reflections col.	3741	13508	3614	17729	8813	13813
Indep. reflections	1053	4411	1045	9973	4420	4492
R(int)	0.045	0.0551	0.051	0.0573	0.031	0.044
Obs. ref.(I>2 σ (I))	991	4034	1014	8239	4231	3800
Param./restraints	82/0	376/9	81/0	684/1	352/1	359/1
GOF	1.11	1.022	1.16	1.035	1.11	1.02
R1(I>2 σ (I))	0.069	0.0538	0.0690	0.0965	0.045	0.055
wR2 (all data)	0.182	0.0587	0.187	0.1047	0.121	0.150
Largest peak/e. \AA^{-3}	0.49	1.630	1.20	3.860	2.13	1.78
Largest hole/e. \AA^{-3}	−0.88	−0.504	−2.53	−1.564	−0.83	−0.62

Flack parameter	0.01(6)	0.02(2)	0.07 (10)	0.03(3)	−0.003(9)	−0.015(11)
-----------------	---------	---------	-----------	---------	-----------	------------

Results

Synthesis

[Ca[Co(ethylenediamine)(oxalato)₂]₂]_n·4H₂O was dissolved in hot water and transformed to its soluble sodium salt by precipitation of the calcium ions by sodium oxalate. The dissolved complex ion was then reacted with water solutions of Cd(NO₃)₂, Mn(NO₃)₂ and SrCO₃, and crystals of the corresponding network solids [M[Co(ethylenediamine)(oxalato)₂]₂]_n·xH₂O were obtained by slow evaporation. Reaction with Fe²⁺ ions results in the decomposition of the complex and with Co²⁺ and Zn²⁺ no products were been obtained. Ba²⁺ ions have not yet yielded any suitably crystalline material.

Structures

Crystallographic data are summarized in Table 1 and important parameters for the networks are presented in Table 2. The general features of structures of **1-4** are very similar: an approximately square antiprism around M²⁺ (except perhaps for M²⁺ = Mn) and an octahedral geometry at Co³⁺ with all M-O and M-N distance in accordance with similar structures in the Cambridge Crystallography Database²⁵.

Table 2. Relevant structural data for the network and channels in **1-4**.

M^{2+}		M-Co distance [Å]	Void [%] ^a	Channel diameter ^b [Å]	Ionic radius ^{26,27} [Å]	T [K]	Space group
Mn ²⁺	3	5.52	18	3.7	0.96	293	P2 ₁
Cd ²⁺	2	5.59	18	3.8	1.10	293	P [−]
Ca ²⁺	1	5.64	19	3.9	1.12	293	P [−]
Ca ²⁺	1LT	5.63	18	3.8	1.12	173	P2 ₁
Sr ²⁺	4	5.79	20	4.1	1.26	293	P2 ₁
Sr ²⁺	4LT	5.79	20	4.0	1.26	153	P2 ₁

^a Calculated with PLATON²⁸ (solvent waters removed) ^b Calculated as the square root of the void volume divided by the unit cell length in the channel direction.

The room temperature structure of [Ca[Co(ethylenediamine)(oxalato)₂]₂]_n·4H₂O **1** has already been reported in a short communication⁷ and this structure will be described only briefly. The network node at Ca²⁺ propagates through the four oxalate bridges and via four strong N-H...O hydrogen bonds (N...O 2.939(3) Å, 162.9(4)°) as is schematically shown in Figure 1. This results in a four (at Co) and eight (at Ca) connected 3D-net with the **scu** topology⁷. Relevant bond- and network data are shown in Table 2 and the structure with waters omitted is plotted in Figure 4a.

The N-H...H-N distances are always the shortest atom-atom distances across the channels, however this distance will not give a good representation of the diameter of the channels across the series of compounds as the ethylenediamine configuration is slightly different between each compound and small shifts in the torsion angles may give large difference in N-H...H-N distances. Instead, we assume that the channels are square shaped, and divide the calculated void volume with the unit cell length in the channel direction to obtain the cross-section area. An approximate measure of the diameter is then

obtained by taking the square root of this area, giving a consistent series of measurements for all compounds.

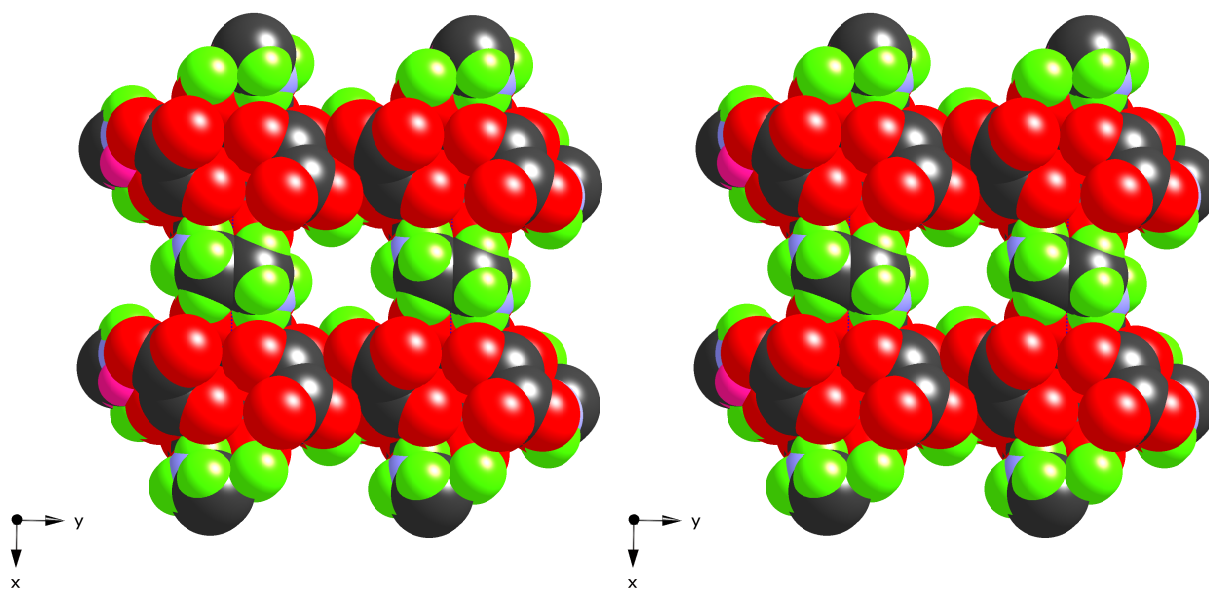


Figure 4. $[\text{Ca}[\text{Co}(\text{ethylenediamine})(\text{oxalato})_2]_2]_n$ in its room temperature P^- polymorph (a, left **1**) and low temperature $P2_1$ form (b, right, **1LT**). The space filling models have been plotted using van der Waal's radii and the water molecules in the channels have been omitted. The scale is identical in the two plots.

The water molecules in the channels are disordered at room temperature and could not be refined; therefore a low temperature structure determination was also performed. Surprisingly, the 173 K data show an unambiguous symmetry lowering, from the space group P^- to the chiral space group $P2_1$. The structure with waters omitted is plotted in Figure 4b where it can be directly compared to the room temperature structure in Figure 4a (no difference is actually visible!). The chirality can be traced back to the configuration of the oxalates around calcium, in the room temperature structure there is an S_4 axis present that has disappeared in the low temperature form, see Figure 5. The difference is hardly noticeable to the eye, but clear from the symmetry.

As oxalate bridges connect all the calcium ions, the integrity of the network cannot be preserved unless all complexes change conformation in the same way, and thus a chiral structure is generated. The complete network can be compared with the room temperature form in Figures 4a and 4b.

Note that the cobalt complex unit is present as a racemate, and that this is also a requirement for the construction of the network.

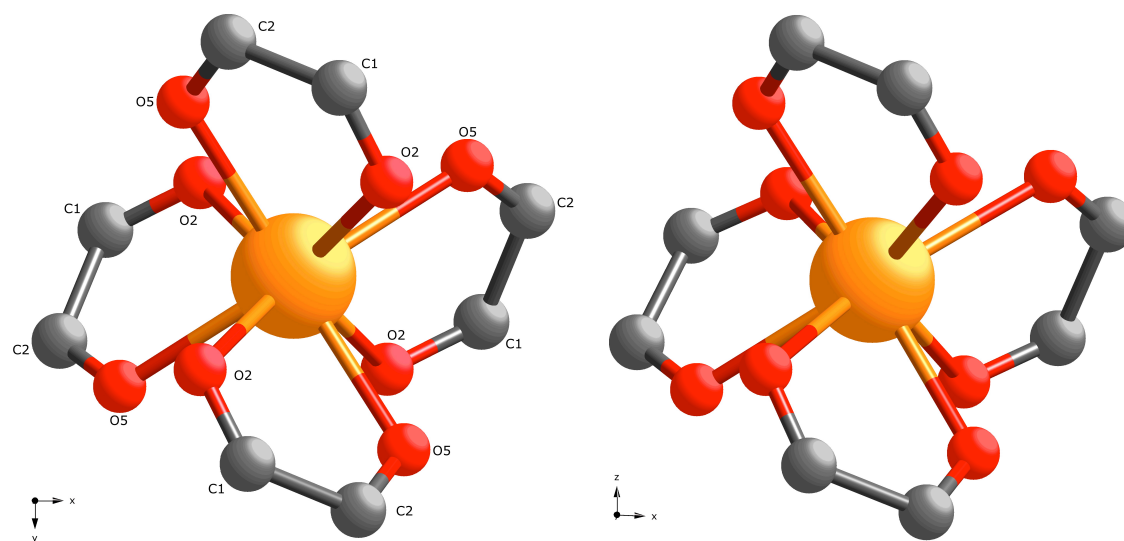


Figure 5 $[\text{Ca}[\text{Co}(\text{ethylenediamine})(\text{oxalato})_2]_2]_n$ showing the coordination environment around calcium in its room temperature P^- polymorph (a, left, **1**) and low temperature $P2_1$ form (b, right, **1LT**). The labels in the left figure help us to identify the S_4 axis that proves that this conformation is not chiral. In 5b there are no symmetry equivalent atoms as the S_4 axis is not present and by the β -angle is no longer exactly 90.0° . The scales are identical in the two plots.

The hydrogen bonds of the low temperature structure are summarized in Table 3.

Table 3 Hydrogen bonds in **1LT** [Ca[Co(ethylenediamine)(oxalato)₂]₂]_n·4H₂O

D	H	A	D-H [Å]	H...A [Å]	D...A [Å]	D-H...A [°]
<i>net</i>						
N4E	H4E1	O1C	0.88(2)	2.17(3)	3.004(7)	158(7)
N4F	H4F1	O2A	0.87(2)	2.05(2)	2.909(6)	173(7)
N1F	H1F1	O2D	0.88(2)	2.22(4)	3.018(7)	149(6)
N1E	H1E2	O2B	0.87(2)	2.14(3)	2.978(7)	161(6)
<i>intra-net</i>						
N1F	H1F1	O4D	0.88(2)	2.34(4)	3.101(7)	145(6)
<i>net-water</i>						
N1F	H1F2	O2W	0.88(2)	1.95(2)	2.829(8)	176(7)
N1E	H1E1	O2W	0.87(2)	1.99(3)	2.849(8)	168(7)
N4E	H4E2	O1W	0.88(2)	2.18(5)	2.923(8)	142(7)
N4F	H4F2	O4W	0.87(2)	2.31(6)	2.975(8)	133(7)
O1W	H1W1	O3C	0.83	1.95	2.758(7)	162.9
O4W	H4W2	O3D	0.93	2.28	2.846(7)	119.1
O3W	H3W1	O1A	0.84	2.07	2.873(7)	158.9
O3W	H3W2	O4B	0.87	2.17	2.882(7)	139.0
<i>water-water</i>						
O1W	H1W2	O3W	0.82	1.93	2.702(8)	156.6
O2W	H2W1	O1W	0.83	1.86	2.639(9)	155.7
O2W	H2W2	O4W	0.82	1.88	2.681(8)	166.6

O4W	H4W1	O3W	0.83	1.93	2.760(8)	175.9
-----	------	-----	------	------	----------	-------

Compound **2**, $[\text{Cd}[\text{Co}(\text{ethylenediamine})(\text{oxalato})_2]_n \cdot 4\text{H}_2\text{O}$ is isostructural with the room temperature form of **1**, not surprising given the close resemblance of the calcium and cadmium ions (i.e. ionic radii 1.12 Å vs 1.10 Å for an 8-coordinated Ca^{2+} and Cd^{2+} respectively. Relevant data are found in Table 2.

Mn^{2+} , although quite small (six-coordinated Mn^{2+} having a high spin radius of 0.83 Å), can also be seven or eight coordinated (then the radius increase to 0.96 Å), and in compound **3** the M^{2+} sites (Mn1 and Mn2) are approximately bicapped trigonal prismatic with six shorter Mn-O distances in the range 2.21-2.42 Å, and two longer Mn-O interactions at 2.41-2.55 Å. Disregarding these differences in bond lengths, the complex ion may still be regarded as a square antiprism. Displacement ellipsoid plots are found in Figure 6 and the complete network has been plotted in Figure 7. Relevant data are found in Table 2.

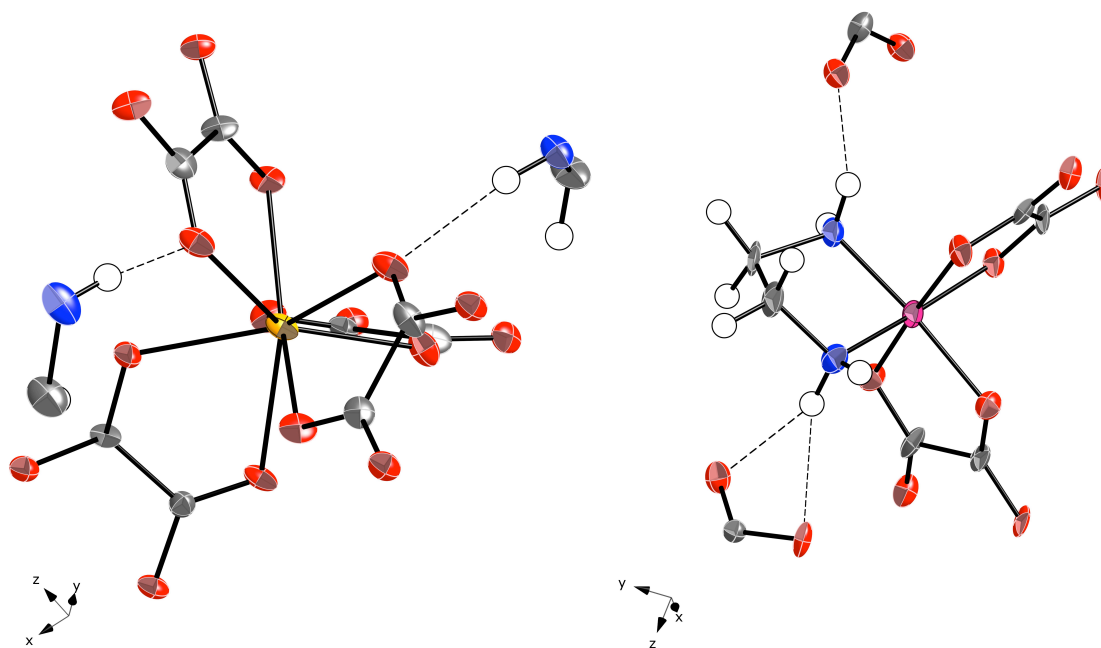


Figure 6. Displacement ellipsoid drawings of one of the Mn, and one of the Co centers, and their respective coordination environment in **3**.

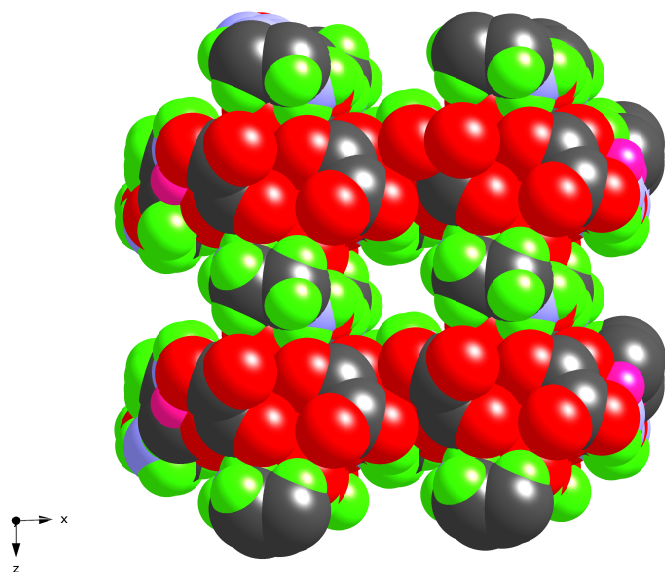


Figure 7. $[\text{Mn}[\text{Co}(\text{ethylenediamine})(\text{oxalato})_2]_2]_n$. The space filling model has been plotted using van der Waal's radii and the water molecules in the channels have been omitted.

Compound **4** contains the larger strontium ion (1.26 \AA for eight coordinated Sr^{2+}), and consequently the network is somewhat expanded, see Table 2. Moreover, $[\text{Sr}[\text{Co}(\text{ethylenediamine})(\text{oxalato})_2]_2]_n \cdot 4\text{H}_2\text{O}$ crystallizes in the chiral space group $P2_1$ and this space group is also found at low temperature. A displacement ellipsoid plot is found in Figure 8a. In this compound the water molecules (but not the hydrogens) can be identified and refined, and the hydrogen bonded water chain is plotted in Figure 8b. The coordination and hydrogen bond network is identical to those in **1-3** and has not been plotted.

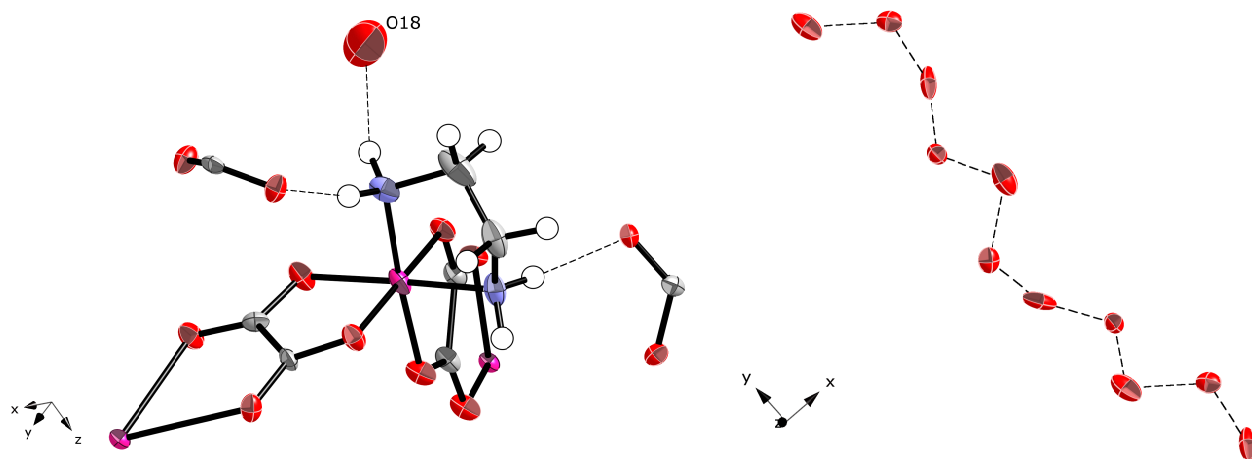


Figure 8. Left: coordination bonds and hydrogen bonds around one cobalt ion in **4** (O18 is solvent water in the channels) Right: chains of solvent water in the channels.

Thermogravimetric and powder X-ray measurements

The calcium and strontium derivatives (**1** and **4**) were subject to repeated thermogravimetric measurements. These experiments both show that although approximately four water molecules are lost from each compound, more than three water molecules are easily and rapidly resorbed from air. This means that the powder X-ray diffractogram obtained on the "dry" phase of **1** is really a diffractogram of a partially rehydrated sample. Nevertheless, this diffractogram proved more or less identical to the product "as synthesized" and also agreed well with the powder X-ray peaks calculated from the single crystal data.

Gas sorption measurements

Gas sorption studies were performed despite TGA evidence not being able to confirm that the channels are empty before sorption. In order to remove water before gas sorption, the entire apparatus was held under vacuum at 65°C for 4 hours before each run. Experiments were carried out using CO₂, N₂O and H₂. All experiments were performed twice on the same sample under the identical conditions,

and although the second experiment generally showed slightly higher absorption the values corresponded well as shown in Table 4.

Table 4. Percentage absorption by mass of the gases CO₂, N₂O and H₂ by [Ca[Co(ethylenediamine)(oxalato)₂]₂]_n·xH₂O^a **1**.

Gas	Run 1	Run 2
CO ₂	12.37%	14.00%
N ₂ O	15.50%	16.47%
H ₂	0.16%	0.18%

^a Before each run the entire apparatus was heated to 65 °C and kept at that temperature, under vacuum, for 4 hours to remove the guest water. We thus expect x to be close to zero.

Discussion

There are a number of examples of coordination polymers of general formula $[M^{II}[M'^{III}(N,N\text{-bidentate})(\text{oxalato})_2]_2]$ where M is a large divalent cation such as Ba^{2+} or Mn^{2+} , M' is a smaller Cr^{3+} or Co^{3+} and the bidentate ligand is bipyridine or phenanthroline.²⁹ These all lack hydrogen bond abilities from the nitrogen ligands and form 1D chains, see Figure 9.

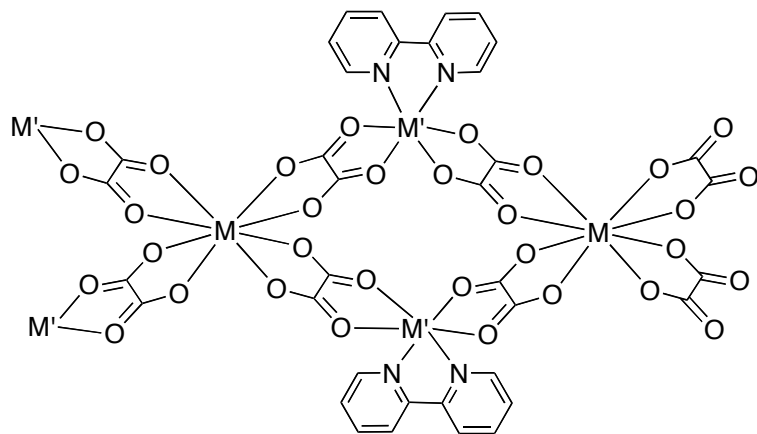


Figure 9. Coordination polymers of general formula $[M^{II}[M'^{III}(N,N\text{-bidentate})(\text{oxalato})_2]_2]$ where M is a large divalent cation such as Ba^{2+} or Mn^{2+} , M' is a smaller Cr^{3+} or Co^{3+} and the bidentate ligand is bipyridine or phenanthroline form 1D chains.²⁹

However, the presence of the strong hydrogen bond donor N-H in the ethylenediamine ligand clearly changes this. The only available acceptors are the oxalate oxygens, and of these the ones bonded to the M^{2+} ions will probably be the most accessible as the $\text{M}^{2+}\text{-O}$ distances are 20-25% longer and the ethylenediamine is blocking one face of the cobalt site, even though the coordination number is higher on this atom. The consistent formation of the same net in compounds **1-4** clearly shows the structure directing ability of this interaction, and the stability of the structure upon heating and solvent removal show the robustness of this synthon.

We should perhaps emphasize that this is not a simple a case of one of many types of isostructural Mn(II) , Ca(II) , Cd(II) and Sr(II) compounds, a comprehensive search of the CSD²⁵ reveals that there

are, to date, no such isostructural systems reported in the database. For six coordinated metal ions there a number of isostructural triplets, i.e. for Cd(II), Ca(II) and Mn(II), but for eight coordinated M^{2+} there are only a few isostructural pairs, i.e. Ca(II) and Sr(II). Examination of the Mn(II), Ca(II), Cd(II) and Sr(II) oxalates reveal no other close relations except for catena-[tetrakis(m2-Oxalato)-octa-aqua-calcium-di-potassium-zirconium(iv)] CSD code WENSIS, that is described to be isostructural with its cadmium analogue.³⁰

Thus, it is not just the question of easily changing one M^{2+} for another; the supramolecular synthon needs to be sufficiently persistent in order to impose the same structure on all the different metal ions. To date, this synthon has not proved to be strong enough to impose eight-coordination on the otherwise typically six- or four-coordinated Fe(II), Co(II) and Zn(II) ions.

Bridging oxalate ions forming extended 3D structures are not uncommon, including both bimetallic compounds and tetrakis complexes.³¹⁻³⁷ The three-connected **srs**-nets formed by some of the tris-oxalate complexes have, in principle, relatively large channels, but all existing examples contain cationic templates in these voids. More links (four-connected) make the nets based on tetrakis complexes denser, and even with the large Ba^{2+} ion these network compounds do not form any accessible voids.³⁸ However, with an additional node of lower connectivity porous compounds may be obtained as shown by **1-4**.

The **scu**-net in these compounds is one of the nets formed by the linking of two different geometrical shapes, in this case perfect squares and perfect cubes, giving nets with two kinds of nodes (vertices) and one kind of link (edge). $[Ca[Co(ethylenediamine)(oxalato)_2]]_n \cdot 4H_2O$ was likely first example of this net in the literature,⁷ and has been followed by others.^{12,13}

In this context we note that classification and nomenclature are becoming increasingly important issues as more and more examples of 3D-nets are found, or deliberately synthesised.^{14,39-50} The network topology of the nets in this study were established by computing (see experimental part) the vertex

symbol⁵¹ (extended Schläfli or long symbol) and comparing both the symbol and the experimental net with the ideal **scu**-net for which parameters can be found in for example the RCSR.^{8,9}

We would like to emphasise four important reasons for adhering to the practises of assigning and naming the network topology in this way: Firstly, it helps us to understand the structures of products we get. Second, it makes it easier to compare new materials to what others have already reported if we all use the same system. Moreover, the description of a network in terms of individual motifs as ladder, chains, helices etc. depends too much on what the individual researcher sees in the structure and is as best tedious and at it's worst misleading. It thus also helps us in communicating our results to our colleagues, the third reason. Finally, these ideal nets make good blueprints for metal-organic frameworks and other network compounds, thus they help us creating new materials.

By changing the divalent metal ion the idea was to modify the size of the channel by increasing or decreasing the size of the ion. We were thus expecting a correlation between the radii of the cation and the size of the channels and this seems also to be the case, see Figure 11.

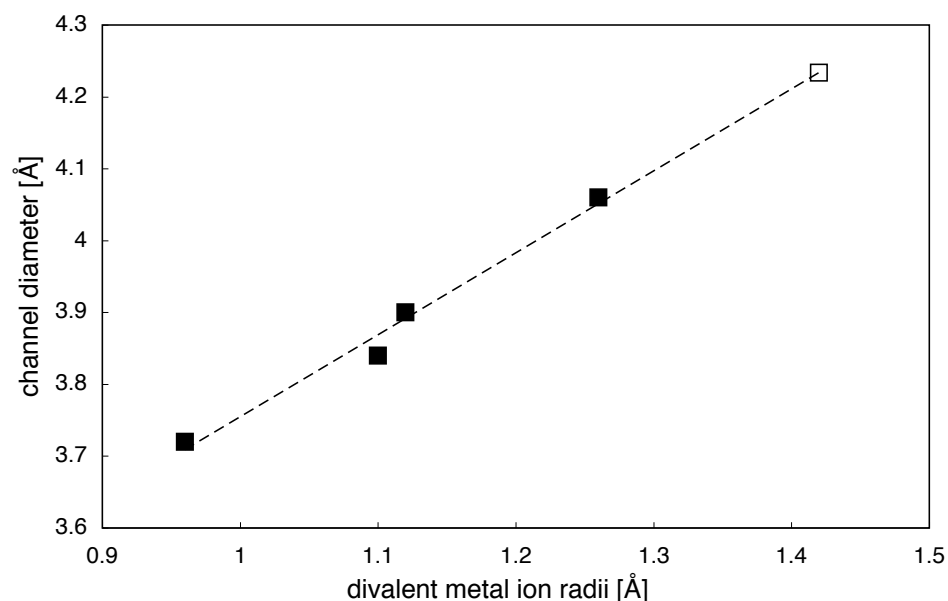


Figure 11. The channel diameter calculated from diffraction data at 298 K (see Table 2) plotted against the M^{2+} ionic radii (8-coordinated) ■. An extrapolated value for Ba^{2+} has been added □.

The preliminary gas sorption measurements on compound **1**, which have been realised only at room temperature (see Table 3), reveal a relatively low capacity of carbon dioxide absorption compare to the experiments done by other groups, such as the results obtain by Arstad et al. in 2008⁵². They reported capacities for this specific gas as high as 10% by weight already at 1 atm, and up to 30% at 10 atm. Nor is it likely that more elevated pressures would significantly increase the CO₂ sorption of **1** as the pores are likely already close to saturation (the limit of carbon dioxide sorption is probably not far from the water sorption which seems to be around 10%).

On the other hand, regarding the results obtained for the hydrogen absorption, the [Ca[Co(ethylenediamine)(oxalato)₂]₂]_n **scu-net** compare well to other well-known framework compounds. For example, "MOF-177" obtained by Yaghi and co-workers, shows three times lower absorption capacities at room temperature and modest pressures according to the work reported by Li et al. in 2007⁵³. However, it has to be emphasized that this is a single point measurement only, and the performance of this materials needs to be judged based on sorption data from a wide range of pressures and temperatures. The value of 0.17% by weight for **1** (mean of two measurements) corresponds roughly to one hydrogen atom per calcium ion.

The possibility of these compounds to adsorb larger molecules can be judged from the diameter of the channels and the kinetic diameters of possible small molecules. For **1** we have a shortest atom-atom distance across the channels of 4.9 Å, and subtracting the van der Waals radius for hydrogen (1.2 Å) we get a conservative measure of the pore diameter as 3.7 Å. This is in qualitative agreement with the 3.9 Å obtained from the PLATON void analysis in Table 2. Both values can be compared to the kinetic diameters of the following small molecules: H₂O, 2.64 Å; H₂, 2.89 Å; N₂O, 3.3 Å; CO₂, 3.30-3.94 Å; methane, 3.76 Å; ethane, 4.44 Å, n-butane, 4.69 Å.⁵⁴ Thus, while even methane might possibly be absorbed in **1**, straight chain small hydrocarbons will be too big. However, we predict (Figure 11) that

the corresponding barium compound will have a pore diameter of over 4.2 Å and if this material is also chiral, which seems likely, it would be interesting to test the possible interaction between the channels and the small chiral 2-butanol molecule.

Conclusions

The synthesis of compounds **2-4** indicate that the supramolecular synthons earlier proven to give a Metal-Organic Framework with a **scu**-net in $[\text{Ca}[\text{Co}(\text{ethylenediamine})(\text{oxalato})_2]_2]_n \cdot 4\text{H}_2\text{O}$ are reliable and can be used to prepare similar MOF:s with other cations. The gas sorption capacities are quite low for carbon dioxide but it is significant at room temperature and slightly above normal pressure in the case of hydrogen. Complementary analyses, such as hydrogen sorption isotherms, have to be performed to check if the remarkable absorption is still available at higher pressures and also at lower temperatures.

Acknowledgments

We thank the Swedish Research Council (VR), the Swedish Governmental Agency for Innovation Systems (VINNOVA) and the Swedish International Development Agency (SIDA) for financial support. KD thanks the University of Cape Town (UCT) and the UCT Department of Chemistry Equity and Development Program (EDP) for funding.

Supporting Information Available.

Crystallographic information files (CIF) for compounds **1-4**.

References

- (1) Sahaym, U.; Norton, M. G. *J. Mater. Sci.* **2008**, *43*, 5395.
- (2) Morris, R. E.; Wheatley, P. S. *Angew. Chem. Int. Ed.* **2008**, *47*, 4966.
- (3) Figueroa, J. D.; Fout, T.; Plasynski, S.; McIlvried, H.; Srivastava, R. D. *Int. J. Greenhouse Gas. Contr.* **2008**, *2*, 9.
- (4) van den Berg, A. W. C.; Arean, C. O. *Chem. Commun.* **2008**, 668.
- (5) Ferey, G. *Chem. Soc. Rev.* **2008**, *37*, 191.
- (6) Jacoby, M. *Chemical & Engineering News* 2008; Vol. 86, p 13.
- (7) Borel, C.; Håkansson, M.; Öhrström, L. *Crystengcomm* **2006**, *8* 666.
- (8) O'Keeffe, M.; Peskov, M. A.; Ramsden, S.; Yaghi, O. M. *Acc. Chem. Res.* **2009**, *41*, 1782.

- (9) O'Keeffe, M.; Yaghi, O. M.; Ramsden, S.; <http://rcsr.anu.edu.au/> Australian National University Supercomputer Facility: Canberra, accessed Jan 2010
- (10) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.
- (11) Chun, H.; Kim, D.; Dybtsev, D. N.; Kim, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 971.
- (12) Wu, J. Y.; Yang, S. L.; Luo, T. T.; Liu, Y. H.; Cheng, Y. W.; Chen, Y. F.; Wen, Y. S.; Lin, L. G.; Lu, K. L. *Chem. Eur. J.* **2008**, *14*, 7136.
- (13) Duan, X. Y.; Cheng, X.; Lin, J. G.; Zang, S. Q.; Li, Y. Z.; Zhu, C. J.; Meng, Q. J. *Crystengcomm* **2008**, *10*, 706.
- (14) Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *Crystengcomm* **2004**, *6*, 377.
- (15) Dwyer, F. P.; Garvan, F. L.; Reid, I. K. *J. Am. Chem. Soc.* **1961**, *65*, 1892.
- (16) CrystalClear; Molecular Structure Corporation & Rigaku, Rigaku Corporation, Tokyo, Japan, and MSC, The Woodlands, Texas, USA.
- (17) SAINT; Siemens analytical X-ray Instruments Inc.: Madison, Wisconsin, USA, 1995.
- (18) SADABS; Sheldrick, G. M.; University of Göttingen: Göttingen, Germany, 1996.
- (19) SIR-97; Altomare, A.; A. M. C. Burla; M. Camalli; G. L. Cascarano; C. Giacovazzo; A. Guagliardi; A. G. G. Moliterni; Polidori, G.; R. Spagna *J. Appl. Crystallogr.* **1999**, *32*, 115.
- (20) SHELXL97; Sheldrick, G. M.; Acta. Cryst. A **64**, 112-122 2008.
- (21) Blatov, V. <http://www.topos.ssu.samara.ru/>, A.; Ac.Pavlov St. 1, 443011 Samara, Russia 2004; Vol. 2007.

- (22) Blatov, V. A.; Shevchenko, A. P.; Serezhkin, V. N. *J. Appl. Cryst.* **2000**, 33, 1193.
- (23) Atwood, J. L.; Barbour, L. J.; Thallapally, P. K.; Wirsig, T. B. *Chem. Comm.* **2005**, 51.
- (24) *Absorbance* software, Barbour, L. J.; University of Stellenbosch.
- (25) Allen, F. H. *Acta Cryst. B* **2002**, 58, 380.
- (26) Shannon, R. D. *Acta Cryst.* **1976**, A32, 751.
- (27) Electronic Table of Shannon Ionic Radii,
<http://v.web.umkc.edu/vanhornj/shannonradii.htm>, Van Horn, J. D. 2001. accessed 02/18/2009
- (28) Spek, A. L.; *Acta Cryst. D* 65, 148-155: **2009**.
- (29) Larsson, K. *Acta Cryst. E* **2001**, 57, m195.
- (30) Yang, J.-Y.; Fu, Y.-L.; Ren, J.-L.; Ng, S. W. *Acta Crystallogr., E* **2006**, 62, m2424.
- (31) Trombe, J. C.; Mohanu, A. *Solid State Sciences* **2004**, 6, 1403.
- (32) Audebrand, N.; Jeanneau, E.; Bataille, T.; Raite, S.; Louer, D. *Solid State Sciences* **2004**, 6, 579.
- (33) Jeanneau, E.; Audebrand, N.; Le Floch, M.; Bureau, B.; Louer, D. *J. Solid State Chem.* **2003**, 170, 330.
- (34) Prasad, P. A.; Neeraj, S.; Vaidhyanathan, R.; Natarajan, S. *J. Solid State Chem.* **2002**, 166, 128.
- (35) Jeanneau, E.; Audebrand, N.; Louer, D. *J. Mater. Chem.* **2002**, 12, 2383.

- (36) Decurtins, S.; Schmalle, H. W.; Schneuwly, P.; Ensling, J.; Gütllich, P. *J. Am. Chem. Soc.* **1994**, *116*, 9521.
- (37) Armentano, D.; De Munno, G.; Lloret, F.; Julve, M. *Crystengcomm* **2005**, *7*, 57.
- (38) Borel, C.; Ghazzali, M.; Langer, V.; Öhrström, L. *Inorg. Chem. Commun.* **2009**, *12*, 105.
- (39) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176.
- (40) Delgado-Friedrichs, O.; Foster, M. D.; O'Keeffe, M.; Proserpio, D. M.; Treacy, M. M. J.; Yaghi, O. M. *J. Solid State Chem.* **2005**, *178*, 2533.
- (41) Delgado-Friedrichs, O.; O'Keeffe, M. *J. Solid State Chem.* **2005**, *178*, 2480.
- (42) Bonneau, C.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acta Cryst. A* **2004**, *60*, 517.
- (43) Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acta Cryst. A* **2003**, *59*, 515.
- (44) Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acta Cryst. A* **2003**, *59*, 22.
- (45) Delgado-Friedrichs, O.; Dress, A. W. M.; Huson, D. H.; Klinowski, J.; Mackay, A. L. *Nature* **1999**, *400*, 644.
- (46) Baburin, I. A.; Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *J. Solid State Chem.* **2005**, *178*, 2452.
- (47) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Crystengcomm* **2003**, *5*, 269.
- (48) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247.

- (49) Batten, S. R.; Robson, R. *Angew. Chem. Int. Ed.* **1998**, 37, 1461.
- (50) Batten, S. R. *CrystEngComm* **2001**, 1.
- (51) O'Keeffe, M.; Eddaoudi, M.; Li, H. L.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, 152, 3.
- (52) Arstad, B.; Fjellvåg, H.; Kongshaug, K. O.; Swang, O.; Blom, R. *Adsorption* **2008**, 14, 755.
- (53) Li, Y.; Yang, R. T. *Langmuir* **2007**, 23, 12937.
- (54) Sircar, S.; Myers, A. L. In *Handbook of zeolite science and technology* Auerbach, S. M., Carrado, K. A., Dutta, P. K., Eds.; M. Dekker: New York, 2003.