Electronic Supporting information

2D and 3D Mixed M^{II}/Cu^{II} metal-organic frameworks (M = Ca and Sr) with *N,N'*-2,6-pyridinebis(oxamate) and oxalate: preparation and magneto-structural study

Tamires S. Fernandes,[a] Wanessa David Canêdo Melo,[a] Lucas H. G. Kalinke,[a,b] Renato Rabelo,[a,c] Ana K. Valdo,[a] Cameron C. da Silva,[a] Felipe T. Martins,[a] Pedro Amorós,[d] Francesc Lloret,[c] Miguel Julve*[c] and Danielle Cangussu*[a]

[a]*Universidade Federal de Goiás, Instituto de Química, Campus Samambaia, CP 131, CEP 74001-970 Goiânia, GO, Brazil. E-mail:daniellecangussu@gmail.com.*

[b]*Instituto Federal Goiás, IFG, Anápolis, Av. Pedro Ludovico, s/n, Reny Cury, 75131-457, Anápolis, GO, Brazil.*

[c]*Departament de Química Inorgànica/Instituto de Ciencia Molecular (ICMol), Facultat de Química de la Universitat de València, C/ Catedrático José Beltrán 2, 46980 Paterna (València), Spain. E-mail: Miguel.julve@uv.es.*

[d]*Institut de Ciència dels Materials (ICMUV), Universitat de València, C/ Catedrático José Beltrán 2, 46980 Paterna (València), Spain*

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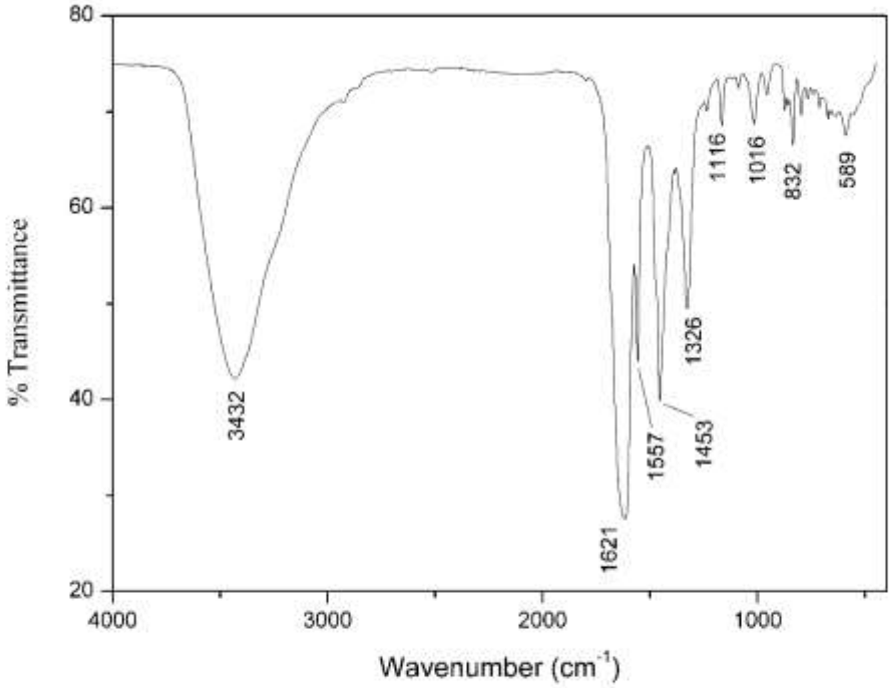

Figure S1. IR spectrum of **1**.

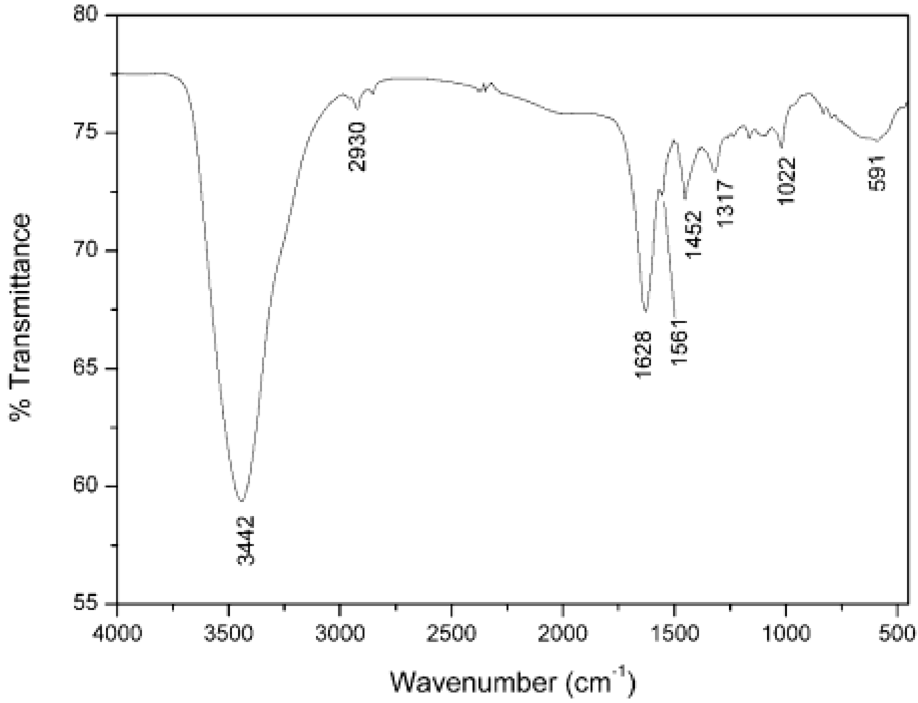

Figure S2. IR spectrum of **2**.

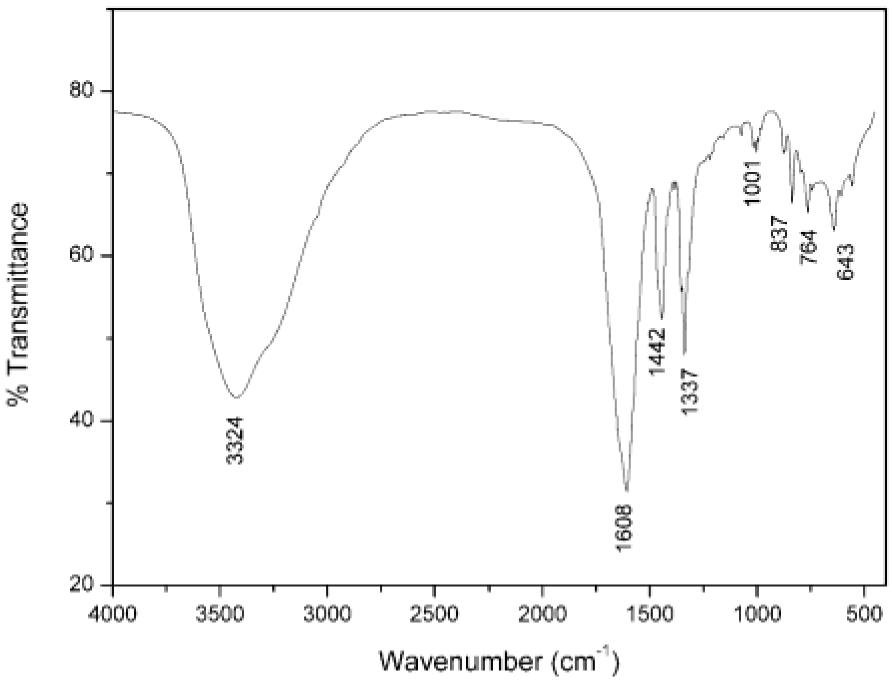

Figure S3. IR spectrum of **3**.

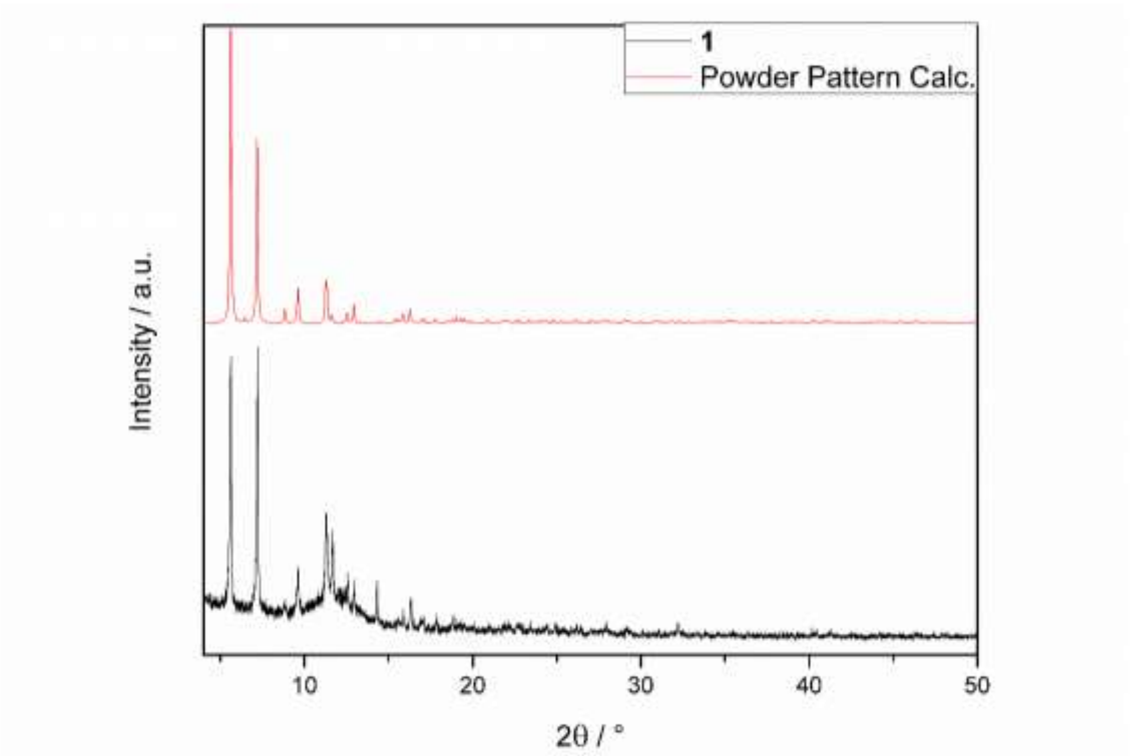

Figure S4. PXRD pattern for **1**.

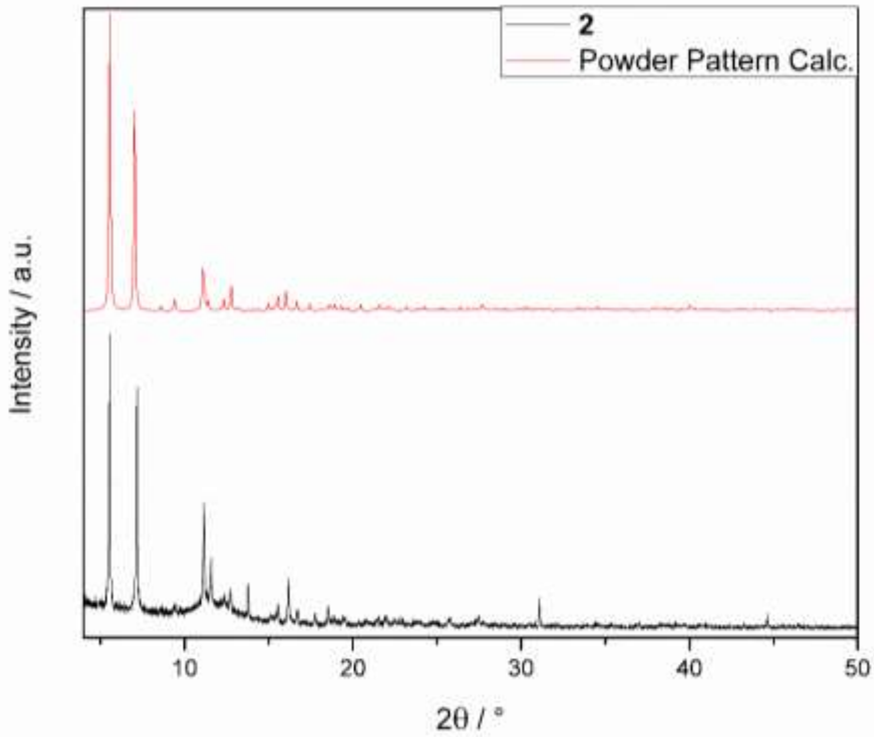

Figure S5. PXRD pattern for **2**.

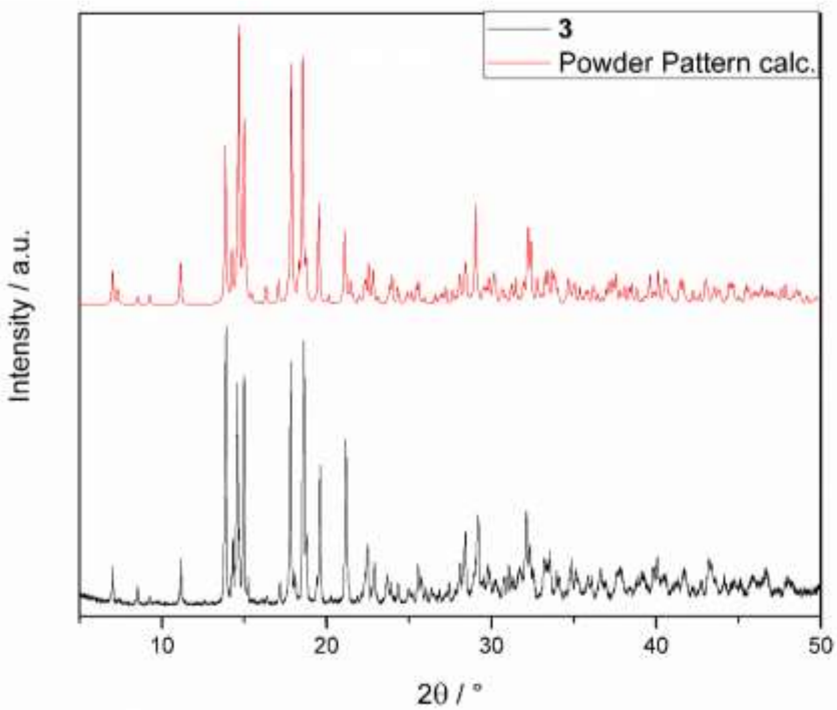

Figure S6. PXRD pattern for **3**.

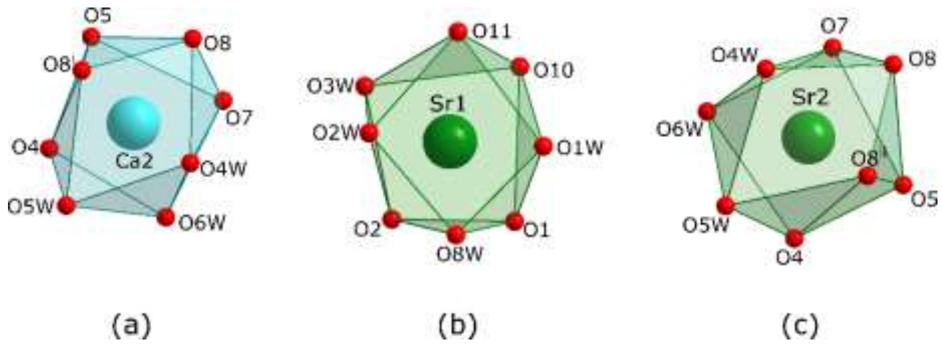

Figure S7. Polyhedra of the Ca2 (**1**), Sr1 (**2**) and Sr2 (**2**) atoms.

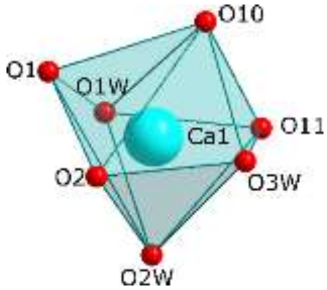

Figure S8. Polyhedron of the Ca1 atom in **1**.

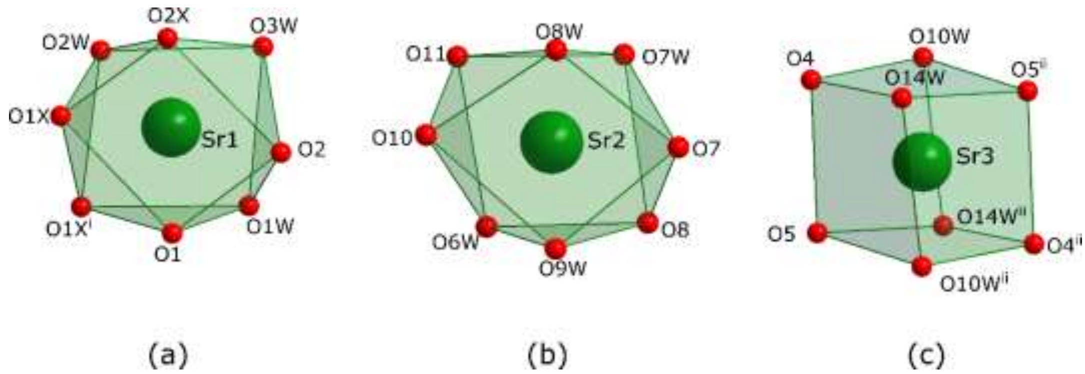

Figure S9. Polyhedra of the Sr1, Sr2 and Sr3 atoms in **3**.

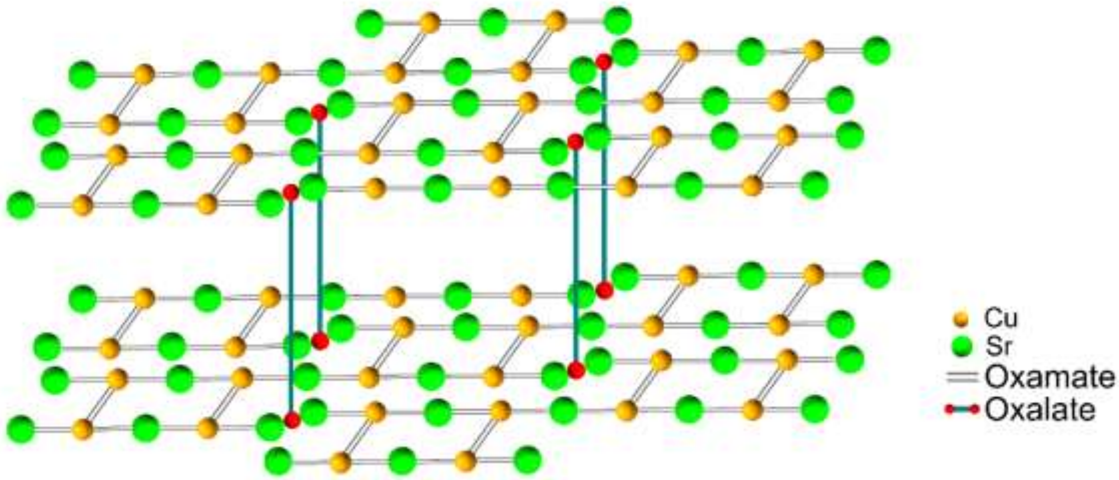

Figure S10. Schematic drawing of a fragment of the 3D structure of **3** mediated by the oxamate and oxalate bridges.

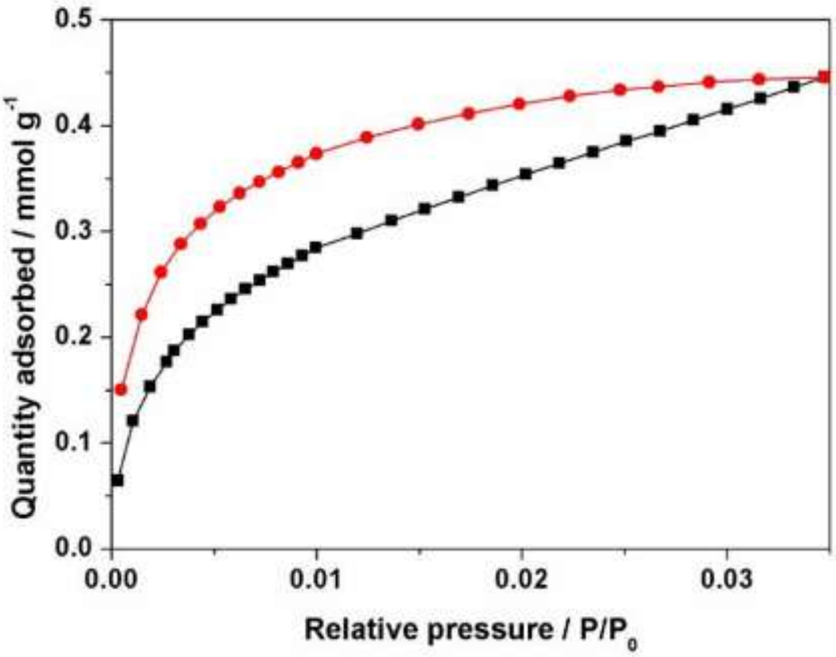

Figure S11. CO_2 adsorption isotherm of a solid sample of **1**.

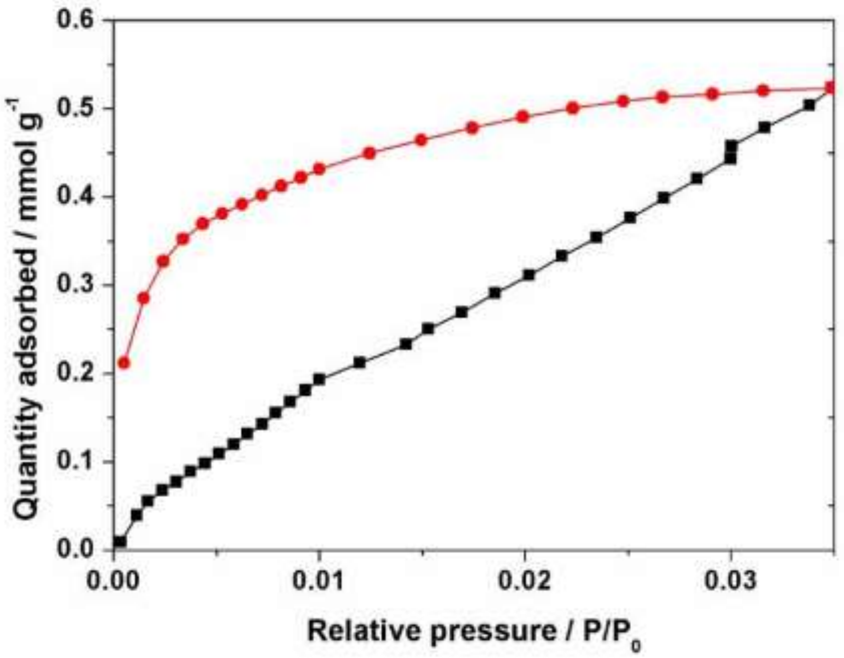

Figure S12. CO_2 adsorption isotherm of a solid sample of **2**.

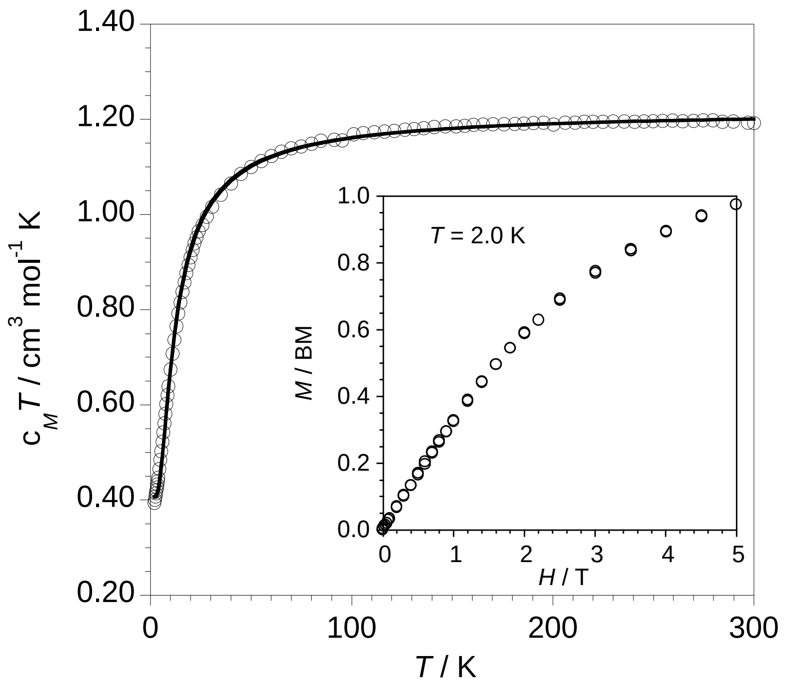

Figure 13. Thermal dependence of the $\chi_M T$ product for **2**: (o) experimental; (—) best-fit curve through eq (2) (see text). The inset shows the field dependence of the magnetization for **2** at 2.0 K.

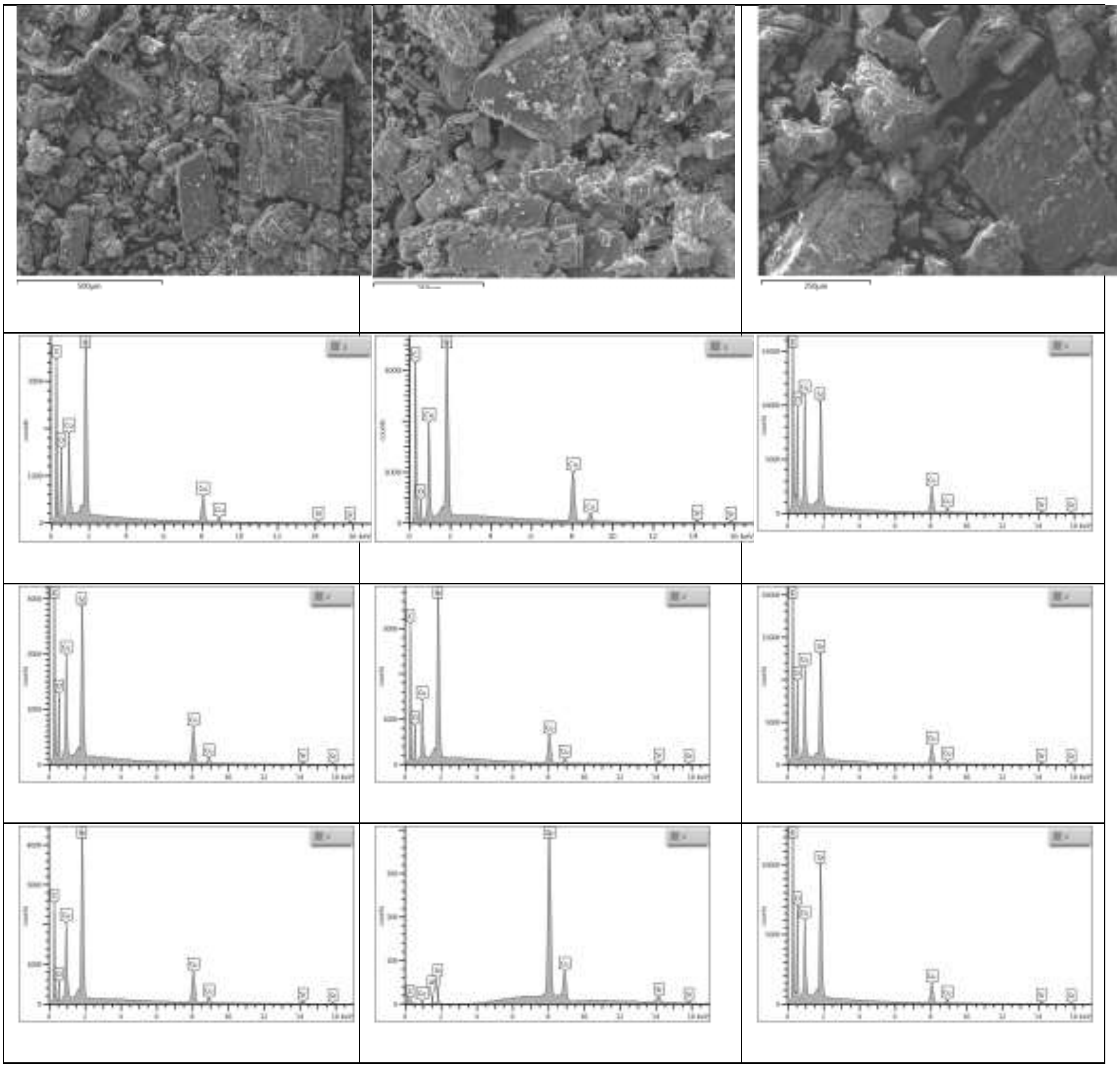

Figure 14. SEM images and EDS spectra of three selected areas of **3** (Fig. S14)

Table S1. Selected bond lengths (Å) and angles (°) around the alkaline-earth cations of **1-3**[a].

				1			
Ca1-O1^{i}	2.402(4)	Ca1-O3W^{i}	2.375(6)	Ca2-O4	2.463(4)	Ca2-O8^{ii}	2.397(4)
Ca1-O2^{i}	2.435(4)	Ca1-O10	2.402(4)	Ca2-O5	2.467(4)	Ca2-O4W	2.489(5)
Ca1-O1W^{i}	2.370(7)	Ca1-O11	2.430(4)	Ca2-O7	2.410(4)	Ca2-O5W	2.563(5)
Ca1-O2W^{i}	2.369(6)			Ca2-O8	2.482 (4)	Ca2-O6W	2.423(5)
O1-Ca1-O2	66.88(12)	O1W-Ca1-O10	91.2(2)	O4-Ca2-O5W	68.54(16)	O8-Ca2-O8^{ii}	67.02(13)
O1-Ca1-O1W	76.81(18)	O1W-Ca1-O11	79.9 (2)	O4-Ca2-O6W	77.82(17)	O8-Ca2-O4W	73.45(14)
O1-Ca1-O2W	123.1(3)	O2W-Ca1-O3W	89.0(4)	O5-Ca2-O7	84.42(14)	O8^{ii}-Ca2-O4W	81.17(15)

O1-Ca1-O3W	124.6(2)	O2W-Ca1-O10	153.0(3)	O5-Ca2-O8	78.28(12)	O8-Ca2-O5W	134.44(16)
O1-Ca1-O10	82.63(14)	O2W-Ca1-O11	85.7(3)	O5-Ca2-O8^{ii}	78.16(13)	O8^{ii}-Ca2-O5W	77.24(15)
O1-Ca1-O11	141.52(14)	O3W-Ca1-O10	81.412)	O5-Ca2-O4W	149.67(14)	O8-Ca2-O6W	130.35(16)
O2-Ca1-O1W	130.2(2)	O3W-Ca1-O11	75.59(18)	O5-Ca2-O5W	121.69(15)	O8^{ii}-Ca2-O6W	149.16(19)
O2-Ca1-O2W	85.0(2)	O10-Ca1-O11	67.58(13)	O5-Ca2-O6W	126.45(19)	O4W-Ca2-O5W	73.82(17)
O2-Ca1-O3W	73.60(18)	O4-Ca2-O5	65.60(12)	O7-Ca2-O8	65.50(12)	O4W-Ca2-O6W	81.39(19)
O2-Ca1-O10	115.59(16)	O4-Ca2-O7	111.93(14)	O7-Ca2-O8^{ii}	131.85(13)	O5W-Ca2-O6W	73.68(19)
O2-Ca1-O11	147.90(15)	O4-Ca2-O8	143.73(13)	O7-Ca2-O4W	93.61(17)		
O1W-Ca1-O3W	155.5(2)	O4-Ca2-O8^{ii}	100.97(13)	O7-Ca2-O5W	146.97(17)		
O1W-Ca1-O2W	87.5(3)	O4-Ca2-O4W	140.73(15)	O7-Ca2-O6W	74.29(18)		

2

Sr1-O1^{i}	2.567(5)	Sr1-O3W^{i}	2.485(8)	Sr2-O4	2.574(5)	Sr2-O8^{ii}	2.547(5)
Sr1-O2^{i}	2.593(6)	Sr1-O8W^{i}	2.685(12)	Sr2-O5	2.609(5)	Sr2-O4W	2.658(6)
Sr1-O1W^{i}	2.602(8)	Sr1-O10	2.570(5)	Sr2-O7	2.547(5)	Sr2-O5W	2.680(7)
Sr1-O2W^{i}	2.495(9)	Sr1-O11	2.590(5)	Sr2-O8	2.604(5)	Sr2-O6W	2.579(9)
O1-Sr1-O2	63.33(16)	O1W-Sr1-O3W	152.4(3)	O4-Sr2-O5	62.56(15)	O7-Sr2-O8^{ii}	127.83(17)
O1-Sr1-O1W	80.2(2)	O1W-Sr1-O8W	63.3(4)	O4-Sr2-O7	115.32(19)	O7-Sr2-O4W	93.7(2)
O1-Sr1-O2W	142.7(3)	O1W-Sr1-O10	81.9(2)	O4-Sr2-O8	140.24(16)	O7-Sr2-O5W	149.9(2)
O1-Sr1-O3W	121.5(3)	O1W-Sr1-O11	76.3(2)	O4-Sr2-O8^{ii}	98.53(17)	O7-Sr2-O6W	77.3(3)
O1-Sr1-O8W	77.6(4)	O2W-Sr1-O3W	73.8(5)	O4-Sr2-O4W	143.9(2)	O8-Sr2-O8^{ii}	66.77(17)
O1-Sr1-O10	82.35(17)	O2W-Sr1-O8W	69.5(5)	O4-Sr2-O5W	69.3(2)	O8-Sr2-O4W	71.61(19)
O1-Sr1-O11	140.11(17)	O2W-Sr1-O10	135.7(2)	O4-Sr2-O6W	83.0(3)	O8^{ii}-Sr2-O4W	77.5(2)
O2-Sr1-O1W	134.8(3)	O2W-Sr1-O11	73.6(2)	O5-Sr2-O7	83.87(19)	O8-Sr2-O5W	135.1(2)
O2-Sr1-O2W	95.3(3)	O3W-Sr1-O8W	133.5(5)	O5-Sr2-O8	78.00(16)	O8^{ii}-Sr2-O5W	77.6(2)
O2-Sr1-O3W	72.0(3)	O3W-Sr1-O10	84.4(3)	O5-Sr2-O8^{ii}	77.84(17)	O8-Sr2-O6W	129.2(3)
O2-Sr1-O8W	84.0(3)	O3W-Sr1-O11	76.2(3)	O5-Sr2-O4W	146.51(19)	O8^{ii}-Sr2-O6W	148.7(4)
O2-Sr1-O10	115.0(2)	O8W-Sr1-O10	142.1(4)	O5-Sr2-O5W	121.0(2)	O4W-Sr2-O5W	74.8(2)
O2-Sr1-O11	148.06(19)	O8W-Sr1-O11	117.9(3)	O5-Sr2-O6W	128.3(4)	O4W-Sr2-O6W	83.0(4)
O1W-Sr1-O2W	99.7(4)	O10-Sr1-O11	62.90(16)	O7-Sr2-O8	61.75(16)	O5W-Sr2-O6W	73.7(3)

3

Sr1-O1	2.546(5)	Sr1-O2W	2.562(6)	Sr2-O11^{iv}	2.637(6)	Sr3-O4^{iv}	2.781(6)
Sr1-O2	2.650(6)	Sr1-O3W	2.604(8)	Sr2-O6W	2.602(7)	Sr3-O5^{iv}	2.677(7)
Sr1-O1X^{iii}	2.602(5)	Sr2-O7	2.617(5)	Sr2-O7W	2.571(7)	Sr3-O10W	2.587(16)
Sr1-O2X	2.503(5)	Sr2-O8	2.654(5)	Sr2-O8W	2.547(7)	Sr3-O14W	2.56(3)
Sr1-O1W	2.655(7)	Sr2-O10^{iv}	2.631(5)	Sr2-O9W	2.499(7)		
O1-Sr1-O2	62.95(18)	O1x^{iii}-Sr1-O3W	137.8(3)	O10-Sr2-O6W	82.7(2)	O4^{iv}-Sr3-O5	120.21(19)
O1-Sr1-O1x	78.27(17)	O2x-Sr1-O1W	145.81(19)	O10-Sr2-O7W	133.0(2)	O4^{iv}-Sr3-O5^{iv}	59.79(19)
O1-Sr1-O1x^{iii}	73.10(18)	O2x-Sr1-O2W	87.9(3)	O10-Sr2-O8W	71.57(19)	O4^{iv}-Sr3-O10W	72.9(5)
O1-Sr1-O2x	102.2(2)	O2x-Sr1-O3W	79.1(3)	O10-Sr2-O9W	79.4(2)	O4^{iv}-Sr3-O10W^{iv}	107.1(5)
O1-Sr1-O1W	79.0(0)	O1W-Sr1-O2W	110.6(2)	O11-Sr2-O6W	78.5(2)	O4^{iv}-Sr3-O14W	113.9(5)
O1-Sr1-O2W	145.3(2)	O1W-Sr1-O3W	76.5(3)	O11-Sr2-O7W	74.8(2)	O4^{iv}-Sr3-O14W^{iv}	66.1(5)
O1-Sr1-O3W	134.3(3)	O2W-Sr1-O3W	80.0(3)	O11-Sr2-O8W	84.8(2)	O5-Sr3-O5^{iv}	180
O2-Sr1-O1x	117.06(19)	O7-Sr2-O8	62.25(16)	O11-Sr2-O9W	139.0(2)	O5-Sr3-O10W	71.0(4)
O2-Sr1-O1x^{iii}	131.38(17)	O7-Sr2-O10	131.03(17)	O6W-Sr2-O7W	107.2(3)	O5-Sr3-O10W^{iv}	109.0(4)
O2-Sr1-O2x	78.19(19)	O7-Sr2-O11	143.8(2)	O6W-Sr2-O8W	153.7(2)	O5-Sr3-O14W	96.9(7)
O2-Sr1-O1W	72.1(2)	O7-Sr2-O6W	131.5(2)	O6W-Sr2-O9W	83.7(3)	O5-Sr3-O14W^{iv}	83.1(7)
O2-Sr1-O2W	151.4(2)	O7-Sr2-O7W	76.3(2)	O7W-Sr2-O8W	87.4(3)	O5^{iv}-Sr3-O10W	109.0(4)
O2-Sr1-O3W	73.0(3)	O7-Sr2-O8W	72.40(19)	O7W-Sr2-O9W	146.1(3)	O5^{iv}-Sr3-O10W^{iv}	71.0(4)
O1x-Sr1-O1x^{iii}	70.11(17)	O7-Sr2-O9W	72.8(2)	O8W-Sr2-O9W	96.3(3)	O5^{iv}-Sr3-O14W	83.1(7)
O1x-Sr1-O2x	63.42(16)	O8-Sr2-O10	147.08(19)	O4-Sr3-O4^{iv}	180	O5^{iv}-Sr3-O14W^{iv}	96.9(7)

O1x^{iii}-Sr1-O2x	133.13(17)	O8-Sr2-O11	129.04(18)	O4-Sr3-O5	59.79(19)	O10W-Sr3-O10W^{iv}	180
O1x-Sr1-O1W	146.89(18)	O8-Sr2-O6W	71.7(2)	O4-Sr3-O5^{iv}	120.21(19)	O10W-Sr3-O14W	70.9(9)
O1x^{iii}-Sr1-O1W	80.42(17)	O8-Sr2-O7W	75.8(2)	O4-Sr3-O10w	107.1(5)	O10W-Sr3-O14W^{iv}	109.1(9)
O1x-Sr1-O2W	77.0(2)	O8-Sr2-O8W	134.09(19)	O4-Sr3-O10w^{iv}	72.9(5)	O10W^{iv}-Sr3-O14W	109.1(9)
O1x^{iii}-Sr1-O2W	75.8(2)	O8-Sr2-O9W	77.6(3)	O4-Sr3-O14w	66.1(5)	O10W^{iv}-Sr3-O14W^{iv}	70.9(9)
O1x-Sr1-O3W	136.2(3)	O10-Sr2-O11	62.04(17)	O4-Sr3-O14w^{iv}	113.9(5)	O14W-Sr3-O14W^{iv}	180

[a]Symmetry code: (i) = *x*, 1-*y*, -1/2+*z*; (ii) = 1/2-*x*, 1/2-*y*, 1-*z*; (iii) = -*x*, 2-*y*, -*z*; (iv) = -*x*, 1-*y*, -*z*.

Table S2. Results of the *SHAPE* analysis for the Ca(II) and Sr(II) cores in **1-3**

Compound	Atom	CU-8*	SAPR-8*	TDD-8*	JBTPR-8*	BTPR-8*
1	Ca2	8.639	3.618	**1.249**	2.827	2.193
2	Sr1	8.692	**1.878**	1.980	2.930	2.389
	Sr2	9.329	3.990	**1.733**	3.079	2.233
3	Sr1	11.189	1.509	**1.385**	2.681	1.913
	Sr2	9.434	2.076	2.017	2.144	**1.479**
	Sr3	**0.999**	11.515	8.545	12.571	12.464
Compound	Atom	PBPY-7**	COC-7**	CTPR-7**	JPBPY-7**	JETPY-7**
1	Ca1	5.001	2.081	**0.699**	8.058	19.482

*CU-8, Cube; SAPR-8, Square antiprism; TDD-8, Triangular dodecahedron; JBTPR-8, Biaugmented trigonal prism J50; BTPR-8 Biaugmented trigonal prism. **PBPY-7, Pentagonal bipyramid; COC-7, Capped octahedron; CTPR-7, Capped trigonal prism; JPBPY-7, Pentagonal bipyramid J13; JETPY-7, Elongated triangular pyramid J7.