Electronic Supplementary Information (ESI) for the manuscript:

Influence of the Alkaline Earth Cations on the Topology of M^{II}/Cu^{II} Mixed-Metal-Organic Frameworks (M = Ca, Sr and Ba)

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Experimental Section

Materials. All chemicals were of reagent grade quality, and they were purchased from commercial sources and used as received.

2,6-dimethyl-*N*-phenyloxamate (Me₂pma). The proligand HEt-Me₂pma [L = 2,6-dimethyl-*N*-phenyloxamate)] was prepared as previously reported.[1]

(*n*Bu₄N)₂{[Cu(Me₂pma)₂} · 4H₂O. The tetrabutylammonium salt of the copper(II) precursor was prepared by following a similar synthetic procedure to that reported previously for the analogue $Na_2[Cu(Me_2pma)_2] \cdot 4H_2O$.[1] In a typical experiment, the proligand HEt-Me₂pma (0.442 g, 2 mmol) was reacted with $CuCl_2 \cdot 2H_2O$ (0.17 g, 1 mmol) using a 1.0 M methanol solution of *n*-Bu₄NOH (4 mL, 4 mmol) as a base in water, and it was isolated as its tetrahydrated tetrabutylammonium salt (0.83 g, 83 %). Elemental analysis calculated. (%) for $C_{52}H_{98}CuN_4O_{10}$ (1002.9): C 62.27, H 9.85, N 5.59; found: C 62.28, H 9.01, N 5.61; IR (KBr): ν = 3007, 2969, 2935 (C–H), 1645cm^{-1} (C–O).

(*n*-Bu₄N)₂[Ca₂Cu₃(Me₂pma)₆(dmso)₂] · 3dmso · 2H₂O (1), (*n*-Bu₄N)₂[SrCu₂(Me₂pma)₄] · 2dmso (2), and (*n*-Bu₄N)₂[BaCu₂(Me₂pma)₄] · 2dmso (3). Well-formed blue cubes of **1** and deep green rectangular prisms of **2** and **3** suitable for single-crystal X-ray diffraction with synchrotron radiation were obtained by reaction in hot DMSO by following the next procedure: In a typical experiment, 0.02 mol of the corresponding metal salt [CaCl₂ (**1**), Sr(NO₃)₂ (**2**) and Ba(NO₃)₂ (**3**)] were dissolved in hot DMSO (5 mL) and added dropwise to a solution of (*n*Bu₄N)₂{[Cu(Me₂pma)₂} · 4H₂O (0.1 g, 0.1 mmol) dissolved in hot DMSO (5 mL) at 70 °C. The resulting dark green solutions were allowed to stand at room temperature. After several days, green (**1**) and blue (**2/3**) crystals appeared. They were collected by filtration and air-dried and finally, separated mechanically. Analysis calculated for **1** (2329.5) C, 52.59; H, 6.92; N, 4.81. Found: C, 52.62; H, 7.02; N, 4.92; IR (KBr) 2961 and 2917 (CH), 1628, 1608 and 1584 (CO), 1030 (SO) cm^{-1}. Analysis calculated for **2** (1620.6) C, 56.32; H, 7.46; N, 5.19. Found: C, 55.98; H, 7.56; N, 5.22; IR (KBr) 2961 and 2929 (CH), 1634, 1606 and 1583 (CO), 1033 (SO) cm^{-1}. Analysis calculated for **3** (1670.3) C, 54.65; H, 7.24; N,

[1] E. Pardo, R. Ruiz-García, F. Lloret, J. Faus, M. Julve, Y. Journaux, M. A. Novak, F. S. Delgado, C. Ruiz-Pérez, *Chem. Eur. J.* 2007, **13**, 2054.

5.03. Found: C, 54.28; H, 7'78; N, 5.34; IR (KBr) 2960 and 2939 (CH), 1631, 1606 and 1583 (CO), 1032 (SO) cm^{-1}.

Physical Techniques. Elemental analyses (C, H, N and S) were carried out by the Microanalytical Service of the Universitat de València. IR spectra were recorded on a Perkin-Elmer 882 spectrophotometer as KBr pellets. Variable-temperature direct current (dc) magnetic susceptibility measurements were carried out on powdered samples with a Quantum Design SQUID magnetometer. The susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder.

Crystal Structure Data Collection and Refinement. Data collection for **1**, **2** and **3** compounds were carried out in the BM16 Spanish beamline of ESRF(Grenoble, France) the data were indexed, integrated, and scaled using the HKL2000 program. All the measured independent reflections were used in the analysis. The structure was solved by direct methods and refined with full-matrix least-squares technique on F^2 using the SHELXS-97 and SHELXL-97 programs.[2] Anisotropic thermal parameters were used to refine all non-H atoms. The treatment of the hydrogen atoms was constrained for all samples: it were set on calculated positions and refined with isotropic thermal parameters. Some restrains were added to fix the distances and angles in the case of compound **1**. These restrains involve mainly distances between carbon atoms in the tails of the n-Bu$_4$N$^+$ cations and also distances and angles in the free DMSO molecules. Due to these disorders, the inclusion in the model of the H atoms in the molecules anchored in the cavities (n-Bu$_4$N$^+$ and DMSO) have no great accuracy, even if these have been constrained on the reported model. The main crystallographic data and some experimental details are shown in Table S1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-838956 (**1**), CCDC-838957 (**2**) and CCDC-838958 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[2] Sheldrick, G. M. *SHELX97*, release 97-2; Institüt für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, **1998**.

Table S1. Crystal data and details of structure determination of compounds **1-3**.

Compound	1	2	3
T(K)	100(2)	100(2)	100(2)
Formula	$C_{202}H_{324}Ca_4Cu_6N_{16}O_{49}S_{10}$	$C_{76}H_{120}Cu_2N_6O_{14}S_2Sr$	$C_{76}H_{120}BaCu_2N_6O_{14}S_2$
M	4614.95	1620.60	1670.32
Crystal System	Monoclinic	Orthorhombic	Orthorhombic
Space Group	$P2_1/c$	$P b c a$	$P b c a$
a, Å	16.125(3)	17.731(4)	18.512(4)
b, Å	25.632(5)	15.981(3)	15.920(3)
c, Å	30.125(6)	28.505(6)	27.967(6)
β, (°)	95.55(3)	-	-
V, Å^3	12393(4)	8077(3)	8242(3)
Z	2	4	4
Index ranges	$-20 \leq h \leq 20$ $-30 \leq k \leq 32$ $-37 \leq l \leq 38$	$-22 \leq h \leq 21$ $-20 \leq k \leq 20$ $-36 \leq l \leq 36$	$-23 \leq h \leq 23$ $-20 \leq k \leq 20$ $-35 \leq l \leq 35$
ρ_{calc} (Mg m^{-3})	1.245	1.333	1.346
λ (Mo-K$_\alpha$ Å)	0.73790	0.73790	0.73790
μ (Mo-K$_\alpha$ mm^{-1})	0.743	1.295	1.097
$R_1{}^a$, $I > 2\sigma(I)$ (all)	0.1131 (0.1236)	0.0551 (0.0579)	0.0849 (0.0933)
$wR_2{}^b$, $I > 2\sigma(I)$ (all)	0.3590 (0.3768)	0.1576 (0.1602)	0.2494 (0.2585)
Measured reflections (R_{int})	146548 (0.0810)	64883 (0.0465)	68000 (0.0589)
Independent reflections ($I > 2\sigma(I)$)	25945 (21675)	8844 (8113)	9021 (7539)
Parameters (Restraints)	1350 (29)	459 (0)	459 (0)
Crystal size (mm)	0.09 x 0.06 x 0.05	0.1 x 0.08 x 0.07	0.09 x 0.08 x 0.08

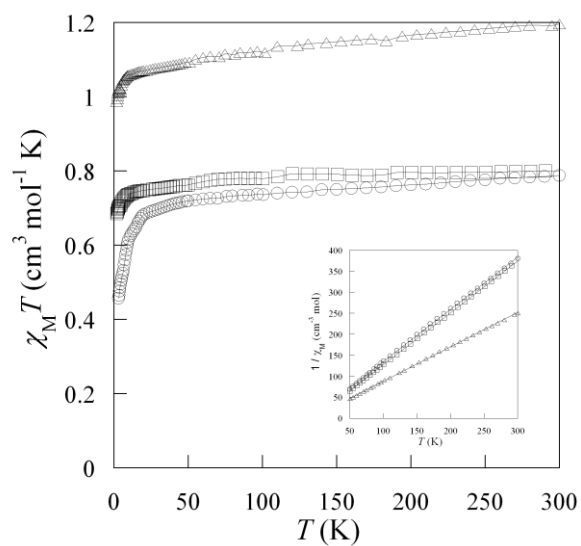^{a} $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

Fig. S1 Temperature dependence of $\chi_M T$ of **1** (Δ), **2** (□) and **3** (○) (under an applied magnetic field of 1 T ($T \geq 50$ K) and 100 G ($T <$ 50 K). The inset shows the χ_M^{-1} *vs.* T plot for **1** (Δ), **2** (□) and **3** (○) and the solid line is the best fit to Curie Weiss law.