Supporting Information

A 3-D coordination network constructed from an angular bis-oxamato tecton and calcium ions

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1- Experimental

All reagents were purchased from Aldrich and Tedia. Infrared (IR) spectra were recorded with Bruker ALPHA spectrophotometer. Gel crystallization was performed using gelatin from bovine skin Type B (Aldrich). Elemental Analysis was performed with a Flash E1112 Thermofinnigan. The metal percentage in the gelatin was determined using ICP/AES Spectro cirus CCD by the Analysis service of the Universidade de São Paulo.

Synthesis

The compound **$H_2Et_2L_2$** was synthesized according with the procedure described in the literature.[1] Single crystals were obtained when the hot solution of this compound in ethyl acetate was slowly cooled to room temperature.

H_4L

To an aqueous solution of sodium hydroxide 0.1 M (70 mL) was added (0.75 g, 1.7 mmol) of H_2Et_2L under vigorous stirring. After the complete dissolution, HCl (1 M) was added and a white precipitate formed which was filtered under reduced pressure and washed with distilled water. This compound was recrystallized in 2-propanol. The solid was filtered out and single crystals were formed by slow evaporation of the solvent at room temperature. (0.34g, 46%). IR (cm^{-1}) = 3563(w), 3499 (w), 3405(w), 3306(m), 3100(w), 3065(w) 2903(w), 2815(w), 2650(w), 2525(w), 1793(m), 1604(vs), 1589(s), 1583(s), 1494(w), 1433(w), 1402(w) 1292(s), 1272(s), 1249(m), 1178(s), 1147(vs), 1120(m), 1106(s), 980(m,br), 926(m), 855(m), 844(s), 831(s), 820(m), 751(m), 714(s), 685(vs), 668(s), 628(m), 582(vs), 542(s), 529(s), 503(vs), 472(s), 434(w), 388(s). (0.34 g, 46%); ^{1}H-NMR: (300 MHz, DMSO, ppm) δ = 7.95(m, 8H), 11.06(s, 2H). ^{13}C-NMR (DMSO, ppm): 120.55, 125.36, 136.39, 142.17, 157.39, 161.55; m. p. = (199-201)°C; Elemental analysis calculated for $C_{16}H_{16}N_2O_{10}S$ ($H_4L.2H_2O$): C =44.86, H = 3.76, N = 6.54, found: C = 44.64, H = 3.84, N = 6.47.

[Ca(H$_2$L)(H$_2$O)].2H$_2$O

At first, we tried to synthesize this compound by adding an aqueous solution of $CaCl_2$ to an alkali solution of H_4L and a precipitate was formed immediately when the solution was diluted or not. In order to obtain single crystals suitable for X-ray diffraction studies, crystallization using gel was performed. Two different kinds of gel were tested: gelatin and agarose with the best result obtained with gelatin. Since gelatin is a biological material, it is expected to have some metal ions in its constitution, therefore the elemental analysis of the K(I), Na(I) and Ca(II) was carried out using ICP/AES in order to quantify the amount of these ions in the gelatin. The concentration of these ions were 9.88, 2724.61 and 744.07 ppm for K(I), Na(I) and Ca(II), respectively. The crystallization using calcium chloride dissolved in the gelatin medium did not result in good quality crystals. However, it is known that some heterogeneous additives have improved the crystal quality even if they do not participate effectively in the reaction.[2] In order to evaluate the influence of transition metal ions in the crystallization of the **[Ca(H$_2$L)(H$_2$O)].2H$_2$O** compound, $FeSO_4.7H_2O$, $Mn(CH_3COOH)_2.4H_2O$ and $Zn(CH_3COOH)_2.2H_2O$ were added to the gel solution. White single crystals were formed into the gel in all cases with the same crystalline structure, however, bigger crystals and better yield were obtained when iron(II) sulfate was used.

The gelatin (11.00 g) was dissolved in 880 mL of hot mili-Q water followed by the addition of 0.70 g of $Fe(SO_4)_2.7H_2O$. The solution was transferred to test tubes and kept at 5°C for 24 hours. Then, 0.45 g ($1.1x10^{-3}$ mols) of H_4L dissolved in 225 mL of 0.1 M potassium hydroxide solution was layered on the gel and kept at 5°C for two weeks. White single crystal formed into the gel were manually separated from the yellow precipitate formed on the bottom of the test tube.

Crystallographic studies

Single crystal X-ray diffraction data were collected on an Oxford Xcalibur 3 for **H$_4$L** and on a Xcalibur 3 Atlas Gemini Ultra diffractometers for **[Ca(H$_2$L)(H$_2$O)].2H$_2$O** using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) and CuK_α radiation (λ = 1.54184 Å), respectively. The unit cell parameters were determined using all the collected reflections; the absorption correction and the integration of the collected reflections were performed using the CRYSALISPRO software.[3] Empirical multi-scan absorption corrections using equivalent reflections were performed with the SCALE3 ABSPACK program.[4] Single crystal X-ray diffraction data were collected on a Nonius Kappa-CCD diffractometer for **H$_2$Et$_2$L** using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). Data integration and scaling of the

reflections were performed with the HKL Denzo and Scalepack.[5] The structures were solved by direct methods using the SHELXS program and the atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2 using the SHELXL program.[6] Hydrogen atoms were placed in calculated positions and refined isotropically using a riding model, except for those atoms on water molecules which could be found in the difference Fourier map. The sulfonyl group and oxygen atoms of water molecules in the **[Ca(H$_2$L)(H$_2$O)].2H$_2$O** structure are disordered over two positions and were refined with partial occupancy. Selected bond lengths and angles for **[Ca(H$_2$L)(H$_2$O)].2H$_2$O** are given in table S3.

2- Chart of H_2Et_2L

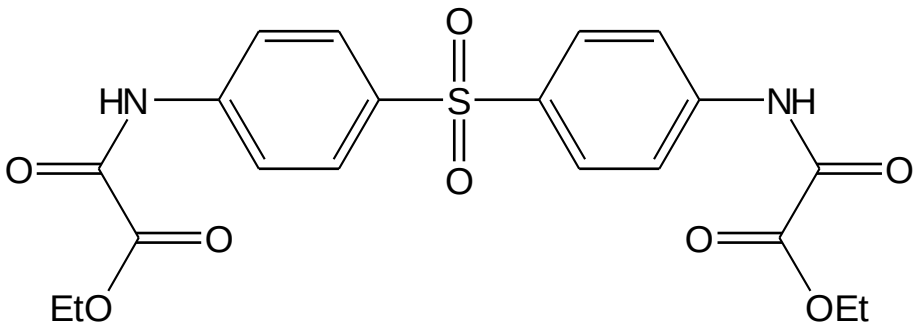


Chart 1: 4,4'-sulfonylbis(phenylamine)bis(ethyl-2-oxoacetate) (H_2Et_2L)

3- Crystallographic data

Table S2 : Hydrogen bonds parameters of **H_4L**:

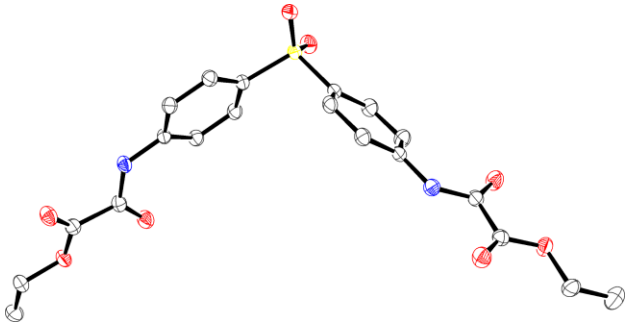
D-H---A	D-H (Å)	H----A (Å)	D---A (Å)	D-H---A (º)
O4-H4···OW1	0.820	1.865	2.623	153.08
O1W-H7···O2^{i}	0.833	2.059	2.862	161.78
O1W-H8···O2W^{ii}	0.833	1.806	2.638	175.38
N1-H1···O5^{iii}	0.860	2.153	2.934	150.90

Symmetry codes: i = -0.5-*x*, 1-*y*, 0.5+*z*; ii = -0.5+*x*, *y*, 0.5-*z*; iii = -*x*, 1-*y*, 1-*z*.

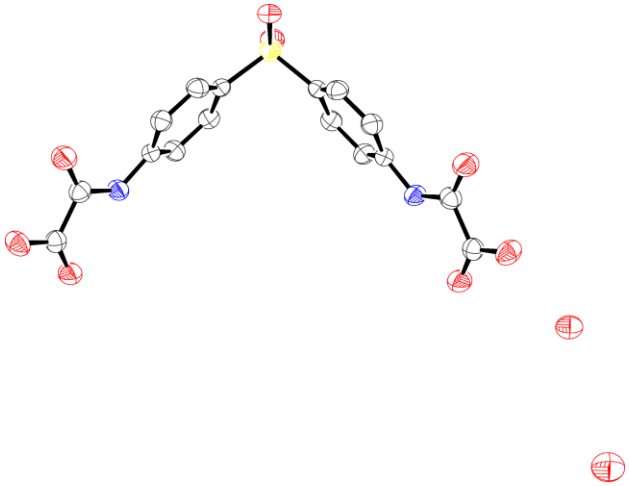
Table S3: Selected bond lengths (Å) and bond angles (º) for **[Ca(H$_2$L)(H$_2$O)].2H$_2$O**.

Bond length			
Ca^{i}-O5	2.440(5)	Ca-O1W	2.429(5)
Ca^{ii}-O5	2.458(5)	Ca^{iv}-O1	2.470(5)
Ca^{ii}-O4	2.561(5)	Ca-O1	2.500(5)
Ca^{iii}-O6	2.403(6)	Ca^{iv}-O3	2.515(5)
Bond angles			
O6^{iii}-Ca-O1W	82.23(19)	O1W-Ca^{i}-O5	102.70(19)
O1W-Ca^{ii}-O5	77.35(18)	O6^{iii}-Ca^{iv}-O1	75.75(18)
O5^{i}-Ca^{iv}-O1	80.82(18)	O6^{iii}-Ca-O1	72.24(19)
O5^{i}-Ca-O1	70.74(17)	O1^{iv}-Ca-O1	77.95(18)
O1W-Ca^{iv}-O3	145.43(19)	O5^{ii}-Ca^{iv}-O3	74.34(17)
O1-Ca^{iv}-O3	139.43(18)	O1W-Ca^{ii}-O4	78.82(18)
O5^{i}-Ca^{ii}-O4	66.18(17)	O1-Ca^{ii}-O4	146.82(18)
O6^{iii}-Ca^{i}-O5	139.42(18)	O6^{iii}-Ca^{ii}-O5	147.93(18)
O5^{i}-Ca^{ii}-O5	70.05(19)	O1W-Ca^{iv}-O1	148.38(18)
O5^{ii}-Ca^{iv}-O1	131.61(18)	O1W-Ca-O1	73.85(17)
O5^{ii}-Ca-O1	123.80(18)	O6^{iii}-Ca^{iv}-O3	112.87(19)
O5^{i}-Ca^{iv}-O3	85.91(18)	O1^{iv}-Ca^{iv}-O3	65.60(17)
O6^{iii}-Ca^{ii}-O4	85.87(19)	O5^{i}-Ca^{ii}-O4	134.71(17)
O1^{iv}-Ca^{ii}-O4	121.16(18)	O3^{iv}-Ca^{ii}-O4	71.88(18)

Symmetry codes: i = 0.5+*x*, 0.5+*y*, 1+*z*; ii = -0.5-*x*, 0.5+*y*, 0.5-*z*; iii = -0.5-*x*, 1.5-*y*, -*z*; iv = -*x*, 2-*y*, 1-*z*.



(a)



(b)

Figure S1: Perspective views for **H_2Et_2L** (a) and **H_4L** (b). Color code: grey, red, blue, yellow stand for carbon, oxygen, nitrogen and sulfur, respectively.

4- References

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