

Assembly of a photoreactive coordination polymer containing rectangular grids†

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We describe the synthesis, crystal structure and solid state reactivity of cadmium fumarate dihydrate, which is made up of planar H-bonded metal–organic layers and undergoes, upon irradiation, a topochemical [2 + 2] cycloaddition reaction.

Square-grid architectures in infinite metal–organic frameworks, are constructed from the assembly of a metal cation, acting as a four-fold node and of an appropriate bifunctional organic ligand acting as spacer.¹ The organic ligands that are usually employed are pyrazines, bipyridine and its various analogues. Square-grid architectures based on terephthalic acid have also been published recently.² The construction of related rectangular grids is achieved by using two chemically different ligands but only a few examples have appeared in the literature.^{1,3} In these examples only aromatic ligands have been employed so far. However, bifunctional aliphatic, unsaturated organic acids may be interesting ligands for the construction of coordination network solids. In this case, the presence of $-C=C-$ or $-C\equiv C-$ groups in the structure may induce solid state reactions (by heating or upon exposure to appropriate irradiation) in the case of favorable metric properties of the crystal framework.^{4,5} Non-planar (4,4) networks based on di-cobalt units and fumaric acid have been published recently,⁶ but in this case the presence of bulky (phen) ligands in the coordination sphere prevents short $-C=C-$ contacts. A rhombohedral grid based on di-manganese units and bulky aromatic dicarboxylic acids is also known.⁷ We report herein a new planar rectangular framework constructed from the assembly of Cd(II) cations with fumaric acid, **1**, and show that the presence of short $-C=C-$ contacts induces a [2 + 2] photocycloaddition reaction.‡

The structure of **1** contains centrosymmetrically related pairs of Cd(II) cations (Fig. 1). Each metal centre is hepta-coordinated in a pentagonal bipyramidal coordination geometry. The basal plane of the coordination polyhedron is composed of five carboxylate oxygen atoms belonging to three centrosymmetric ligands, while the two axial positions are occupied by water molecules. Two types of ligand are present. The two paired metal centres are bridged by two ligands of the same type, acting in the chelating bridging mode.

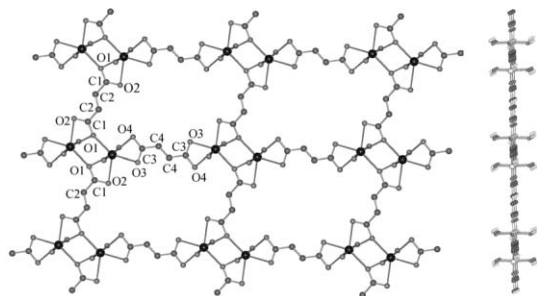


Fig. 1 Projection of one planar layer along *a* (left) and along *c* (right). The water molecules point above and below the layer plane.

† Electronic supplementary information (ESI) available: crystal structure representations and IR spectra of **1**. See <http://www.rsc.org/suppdata/cc/b4/b408522a/>

The other ligand type acts exclusively in the chelating mode. Each metal pair is connected to four neighbouring ones and the network thus formed is topologically equivalent to a (4,4) network (Fig. 1, left). The inner rectangular cavity has dimensions of $12.86 \times 8.64 \text{ \AA}$, as measured from the centres of the dimetallic units. The metal–organic layers are planar, with the two water molecules pointing above and below the plane respectively (Fig. 1). The layer sequence is of the $\cdots ABAB \cdots$ type with adjacent layers in a staggered arrangement. The result is that no significant channels or cavities remain in the structure. The layers are linked by strong hydrogen bonds in which the carboxylate oxygen atoms act as proton acceptors while the water molecules act as proton donors (Fig. 2). Interestingly, the presence of short contacts (3.378 \AA) between the $-C=C-$ bonds, belonging to adjacent layers, and the planarity of the network meet well the criteria for a [2 + 2] cycloaddition reaction to occur. Examination of the packing (Fig. 2) reveals that from the four possible tetracarboxylic isomers (Scheme 1) only isomer **a** is to be formed in the case of topochemical [2 + 2] cycloaddition reaction.

During irradiation of a powder sample of **1**, the colour of the

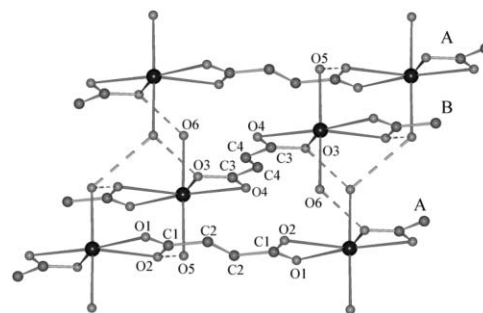
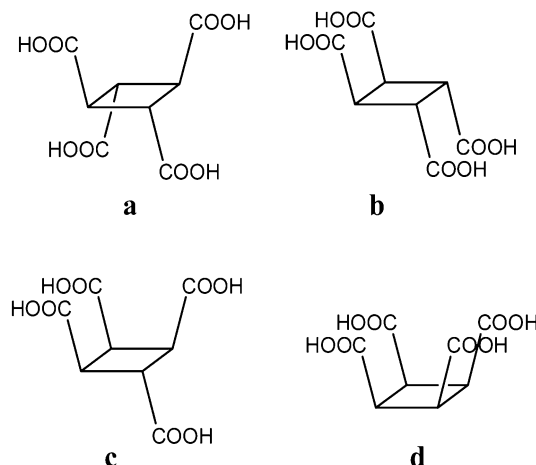


Fig. 2 Part of three adjacent layers A, B, A. Dashed lines represent H-bonds. Double bonds $C2=C2$ and $C4=C4$ (3.378 \AA apart), participate in the photochemical reaction.



Scheme 1

sample gradually changed from white to light grey with a simultaneous reduction of its volume. The progress of reaction was monitored by Thermal Analysis (TG/DTA), FT-IR and NMR spectroscopies. The TG/DTA carried out on a non-irradiated sample (Fig. 3a) shows an endothermic peak between 112 and 136 °C corresponding to loss of two water molecules (theoretical 13.82%, experimental 13.25%). The dehydrated sample is not photoreactive and remains stable up to 385 °C beyond which decomposition occurs. The irradiated sample (Fig. 3b and c) is characterized by the appearance of an endothermic peak centred at about 75 °C and an exothermic peak centered at about 385 °C.

These peaks increase with irradiation time while the initial ones decrease gradually. No further evolution is observed after 25 h of irradiation. TG/DTA analysis (Fig. 3) shows that only half of the initial water content remains in the sample after completion of the reaction (theoretical 6.91%, experimental 7.31%). This is easily explained by considering that the [2 + 2] photocycloaddition reaction proceeds by pairs of reacting metal–organic layers. As two reacting layers approach each other the coordinated water molecules located between them (half of the total) (Fig. 2) are eliminated. The departure of the remaining water molecules is accompanied by a large endothermic peak in the range 25–150 °C, characteristic of lattice water, escaping without phase transition (“solvent evaporation” process).⁸ We therefore conclude that during reaction both coordinated water molecules are removed from the coordination sphere of the metal, but only those located between the two reacting layers are also removed from the sample. The remaining water molecules are probably located in small cavities accounting for the “solvent evaporation” observed.

These observations are in line with spectroscopic results. In the FT-IR spectra we observed that the ν_{C-C} (1660 cm^{-1}) gradually decreases with irradiation time, while a new band, which is not possible to assign with certainty, appears at 1280 cm^{-1} . The similarity between the vibrational spectra, suggests that only a minimum structural rearrangement has occurred during photolysis. Especially, the similarity in the region of the stretching vibration of the carboxylate group ($\approx 1400\text{--}1650\text{ cm}^{-1}$) indicates that no major modification occurs in the carboxylate mode of coordination.⁹ The solution $^1\text{H-NMR}$ spectra (Fig. 4), show that the singlet at 6.57 ppm, which is attributed to the C–H of fumaric acid, decreases gradually with irradiation time. This is followed by increase of the singlet at 3.31 ppm. This peak is attributed to the C–H of the cyclobutane ring of isomer **a** (Scheme 1), because it is very close to the value of 3.33 ppm observed in the case of its methyl ester analogue.¹⁰ The singlet for isomers **b** or **d**, both possessing vicinal hydrogen atoms, is expected at higher fields (0.4–0.6 ppm).^{10,11} Finally, isomer **c** is excluded since multiplets are expected in this case. These conclusions are also consistent with the IR spectroscopy results because formation of isomers **b**, **c** and **d** would induce severe modifications in the coordination mode of the carboxylate group.

In conclusion, we showed that it is possible to prepare a reactive metal-coordination network solid. The strong H-bonds between

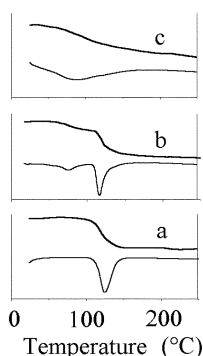


Fig. 3 TG/DTA curves of compound **1** before irradiation (a), at an intermediate stage of the reaction (b), and at the end of the reaction (c).

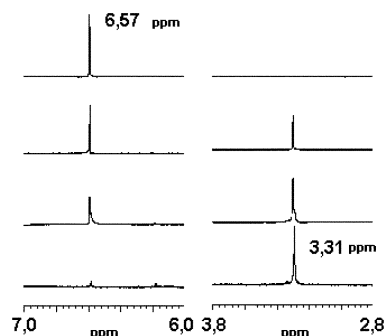


Fig. 4 $^1\text{H-NMR}$ spectra of acidified solutions of compound **1** at different irradiation times: before irradiation (top), intermediate stages of the reaction (intermediate curves) and at the end of the reaction (bottom).

successive layers appear to be the driving force for organising the olefinic double bonds to undergo [2 + 2] topochemical photodimerisation. Moreover, the departure of coordinated water molecules during dimerisation, allowed us to introduce TG analysis as a tool for monitoring the progress of the solid state reaction.

Notes and references

‡ Compound **1** was prepared by mixing of equal volumes (10 ml) of aqueous solutions of CdNO_3 0.1 M and fumaric acid 0.1 M, at pH 6. The precipitate was filtered and colourless crystals were formed from the supernate within a few days. C, H, analysis: calcd (%): C 18.02, H 2.30; found: C 17.85, H 2.10. Crystal data for **1**: $\text{CdC}_4\text{H}_6\text{O}_6$, $M = 262.50$, triclinic, space group P1, $a = 6.757(1)$, $b = 7.544(1)$, $c = 7.809(1)$ Å, $\alpha = 68.54(1)$, $\beta = 86.53(1)$, $\gamma = 69.96(1)^\circ$, $V = 347.08(8)$ Å³, $Z = 2$, $D_c = 2.512\text{ g cm}^{-3}$, $T = 293\text{ K}$, $\mu(\text{MoK}\alpha) = 3.126\text{ mm}^{-1}$, $\lambda(\text{MoK}\alpha) = 0.7107$ Å. Of 1512 reflections measured on a Bruker P4 diffractometer, 1183 were unique ($R_{\text{int}} = 0.021$). Structure solution and refinement with SHELX97. H-atoms refined isotropically. Final $R = 0.0296$, $wR2 = 0.0755$, $\text{GOF} = 1.099$. CCDC 168034. See <http://www.rsc.org/suppdata/cc/b4/b408522a/> for crystallographic data in .cif or other electronic format. Irradiation experiments were carried out on a sample of 1, crushed and spread between two quartz plates, with an OSRAM-400 W high-pressure mercury lamp, at room temperature. $^1\text{H-NMR}$ spectra were recorded in D_2O , on a Bruker AMX-400 MHz spectrometer. The product formation of *trans-trans-trans*-1,2,3,4-cyclobutanetetracarboxylic acid (CBTA) was determined by integration of the $^1\text{H-NMR}$ signals of the crude product in D_2O acidified with HCl. In these conditions the Cd(II) cations are decomplexed. Selected data, δ_{H} (ppm) (D_2O with drops of HCl, 400 MHz): 6.57 (s, 2H, fumaric-H), 3.31 (s, 4H, cyclobutyl-H).

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