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First Examples of DPDS-DPS in situ Transformation at Room Temperature via a 1,2-Nucleophilic Addition Mechanism

Noelia De la Pinta,a Ana B. Caballero,d Gotzon Madariaga,a José M. Ezpeleta,c Antonio Rodriguez-Dieguez,d Juan M. Salasd and Roberto Cortésb*

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A cleavage/reorganization reaction at room temperature has been detected in three metal organic coordination compounds synthesized from the DPDS [di(4-pyridyl) disulphide] ligand: Mn(NCS)2(DPS)4 (1), [Fe(NCS)2(DPS)2]·2H2O (2) and Zn(NCO)2(DPS) (3), [DPS = di(4-pyridyl)sulphide]. The in situ reorganization process is explained by a 1,2-nucleophilic addition mechanism.

The research interest on the well known 4,4’-dipyridine like ligands, characterized by their ability to arrange nets with large cavities, has grown rapidly in the last few years. Their structural flexibility converts them in excellent different-size spacers for Metal Organic Frameworks (MOFs),1 Coordination Polymers (CPs),2 Spin Crossover (SCO)3 and other technologically interesting systems whose structures and properties may be controlled by choosing appropriate bridging ligands, metal ions and counter ions. The structural motifs range from zero- to three-dimensional being the limiting factor the bridging ligand flexibility. In most cases the supra-molecular architecture is governed by intermolecular directed H-bonds which involve the bridging ligands, the counter-ions and, if present, guest molecules trapped in voids or channels.

The less studied ligands of this family are those where the outermost pyridine rings are connected through sulphur atoms of which the shortest ones correspond to di(4-pyridyl)sulphide (DPDS) and di(4-pyridyl)sulphide (DPS). DPDS shows a higher rigidity associated to the S-S bond that confers it a characteristic twisted shape (Figure S1†). Moreover it is known that in the resulting packing its two optical isomers are always present thus conforming achiral structures.4 DPS is a priori a more versatile ligand and therefore should let a richer variety of atomic arrangements. However, its presence is scarce although cleavage of S-S and S-C bonds has been reported under photochemical,5 electrochemical5 and chemical conditions.7 Above 100ºC, under solvothermal conditions, DPDS is also known to transform into DPS and other related ligands5 (Scheme S1†) throughout in situ disulphide cleavage reactions. The in situ ligand synthesis possesses a great attractive in fields like Organic and/or Coordination Chemistry as long as the understanding of such mechanisms would allow the discovery of new reactions and, as a consequence, the preparation of new complexes.9

What is rather unusual is the generation of this kind of organic frameworks in which the ligand DPDS shows an in situ rearrangement of its bonds to DPS during the assembly of a metal organic compound via a nucleophilic addition at room temperature. DPDS cleavage at room temperature has always been explained by means of radical mechanisms.10 However a nucleophilic reaction would be favoured, in contrast to a radical process, to form DPS by the chemical environment, the protic conditions of the solutions and the absence of extreme conditions.

With the aim of obtaining different DPDS compounds a synthesis with various transition metals [Mn(II), Fe (II) and
Zn(II) in combination with the pseudo-halides cyanate (NCO\(^{-}\)) and thiocyanate (NCS\(^{-}\)), was designed. Unexpectedly, since the process was driven under soft conditions, all the synthesized materials 1-3\(^{+}\) showed S-S cleavage bond and a further reorganization into DPS. Furthermore in collaboration with other group of investigation, another DPDS-DPS transformation using the biological ligand DMTP (anionic form of 4,6-dimethyl-1,2,3-triazolo[4,5-d]pyrimidin-5,7-dione\(^{11}\)) in combination with Zn (II) metal and DPDS was detected. However, given the reaction conditions (reflux) it was clear that the S-S cleavage and reorganization in this compound, [Zn(DPDS)\(_2\)(H\(_2\)O)\(_2\)][ClO\(_4\)\(_2\)]·H\(_2\)O (4), was produced by a radical mechanism.

Herein we report the syntheses and structures (see the ESI\(^{\dagger}\) for further details) of four new DPS based compounds showing arrangements of increasing dimensionality including porous frameworks. Three of them (1-3) are the first examples of an \textit{in situ} cleavage/reorganization of DPDS into DPS produced at room temperature. A mechanism for such synthetic process will be subsequently proposed.

The reaction of Mn(NO\(_3\))\(_2\).6H\(_2\)O with DPDS ligand and KCNS in water/methanol affords yellow prisms for compound (1). The structure is triclinic (P\(_\text{i}\)) (Table S1\(^{\dagger}\)) and consists of discrete units (Fig. 1) packed through intermolecular C-H...S and C-H...N bonds (Table S2\(^{\dagger}\)). The Mn (II) ions are coordinated by four equatorial nitrogen atoms belonging to terminal DPS ligands and two axial nitrogen atoms of almost linear [N1-C1-S1 = 179.6(4)\(^{\circ}\)] terminal thiocyanate groups. The resulting environment of Mn(II) ions conforms a compressed octahedron.

The structure of compound 2 (monoclinic, C\(_2/c\)) (Table S3\(^{\dagger}\)) shows infinite chains where the Fe(II) ions are connected by pairs of DPS ligands. The Fe (II) environment is similar to that of compound 1 (Fig. 1a and Table S9\(^{\dagger}\)). Water molecules are located in channels along the b-axis and are essential for the packaging of the chains in the plane ab through S...H-O-H...S bonds (Table S4\(^{\dagger}\) and Fig. 2).

![Fig. 3 Environment of Zn(II) (top left) and zig-zag chains (right) in compound 3. Projection of the structure showing the packing of the chains (bottom). Depth is marked by the degree of transparency. 1, 2 and 3 indicate three different chains that are connected by C-H...N bonds.](image)

Compound 3 (orthorhombic, Pca\(_2\)) (Table S5\(^{\dagger}\)) consists of infinite zig-zag chains extending along the [010] direction (Fig. 3) where the Zn(II) ions are connected by single DPS bridges. Two terminal N-cyanate groups also bond the ion to give a tetrahedral coordination polyhedron (see Fig. 3 top and Table S9\(^{\dagger}\)). The generated chains pack via intermolecular H-bonds (Table S6\(^{\dagger}\)) of which the most significant involves the oxygen atoms of the cyanate groups (O1) and the hydrogen of the carbon (C11) of the pyridinic rings in the DPS ligand.

The tetragonal (P\(_4\)2\(_1\)2\(_2\)) crystal structure of 4 (Fig. 4 top) consists of discrete units where Zn(II) ions are coordinated by four nitrogen atoms of four terminal DPS ligands occupying the equatorial positions. Two oxygen atoms corresponding to aqua molecules in axial sites complete a slightly distorted octahedral coordination polyhedron (Table S9\(^{\dagger}\)) similar to the one shown in Fig. 1a, after substituting NCS by water. Two perchlorate anions are located in channels along the e-axis (see Fig. 4 top) giving neutrality to the complex. In addition there is a crystallization water molecule that establishes H-Bonds with the terminal non-coordinated nitrogen atoms of two cis DPS ligands. Aqua molecules also establish H-Bonds with both water oxygen and those DPS nitrogen atoms not linked to crystallization water (see Table S8\(^{\dagger}\) and Fig. 4 bottom) conforming a global three-dimensional network in the complex.

![Fig. 2 Projection of the structure of compound 2 along the e-axis (top) and along the b-axis (bottom). In both cases the most prominent H bonds (dotted lines) involving guest water molecules are shown (Table S4\(^{\dagger}\)).](image)
Fig. 4 Projection along the c-axis (top) of the structure of compound 4 showing the channels where de ClO$_4^-$ ions are located. Scheme of the most relevant H-Bonds (bottom) represented with dotted lines (Table S8†). Crystallization water molecules are represented in red.

Owing to the high adaptability of DPS induced by the flexibility of the C-S-C angle and the easiness of C-S torsions, DPS compounds show an elevated lability as they can accommodate a rich variety of structures with different symmetry and supra-molecular design, some of them showing voids or infinite channels with different cross-sections. Therefore in situ cleavage of DPDS and its further reorganization into DPS under soft conditions could promote new trends towards controlled synthesis directed not only to new compounds but also to new properties. However, this can only be achieved if the cleavage reaction is understood. In the present study, provided the method of synthesis, such mechanism has to be based on the reaction medium and the reactivity of reagents. In the case of compounds (1)-(3) the reaction medium is protic (H$_2$O/CH$_3$OH) and exposed to room conditions. In these circumstances DPDS undergoes electron transfer (ET) reduction to afford the unstable radical anion that decomposes into pyridinethiol radical and pyridinethiol anion (Step 1 of Scheme 1). The pyridinethiol radical is in turn reduced in the presence of the DPDS radical and generates pyridinethiol in neutral conditions (Step 2) that, given the protic medium, is in tautomeric equilibrium with its corresponding thione (Step 3). Both react through 1,2-nucleophilic addition to yield the DPS ligand and SH$_2$ as a sub-product (Step 4). All the syntheses revealed a little amount of a yellow solid residue that can be associated to sulphur by a redox reaction (Step 5), in good agreement with the proposed mechanism. This synthesis route, unlike a radical reaction, exhibits a much slower kinetics when compared with that of DPDS ligands. Compounds with DPS as bridging ligand show a very low yield and appear sometimes like sub-products in syntheses where their DPDS homologous develop.

This work supports and explains a 1,2-nucleophilic addition mechanism where an in situ synthetic transformation from DPDS to DPS under soft conditions is produced. The versatility of DPS makes this method of synthesis useful for the design of porous or channelled metal-organic materials with potential applications derived from their absorption/desorption properties.
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Notes and references
1 Dpto. de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain.
2 Fax: +34 9 4601 3500; Tel: +34 9 4601 5487; E-mail: gotzon.madariaga@ehu.eus
3 Dpto. de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain. Fax: +34 9 4601 3500; Tel: +34 9 4601 5150; E-mail: roberto.cortes@ehu.eus
4 Facultad de Farmacia, Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain. Fax: +34 9 4601 3500; Tel: +34 9 4601 5487; E-mail: j.m.ezpeleta@ehu.eus
5 Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain. Fax: +34 9 4601 3500; Tel: +34 9 4601 5487; E-mail: gotzon.madariaga@ehu.eus
6 Dpto. de Química Inorgánica, Facultad de Farmacia, Universidad del País Vasco, Apdo. 450, 01080 Vitoria-Gasteiz, Spain. Tel: +34 9 4501 3039; E-mail: jm.pezleta@ehu.eus
7 Dpto. de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, Avda. Fuentenueva s/n, 18071 Granada, Spain. Tel: +34 9 5824 8525; E-mail: jsalas@ugr.es
8 E-mail: jsalas@ugr.es