Supramolecular self-assembly of a symmetric imine ligand functionalized with a dansyl fluorophore moiety

María J. Romero,[1] Luis M. González-Barcia,[1] Manuel R. Bermejo,[1] M. Isabel Fernández,[2] Esther Gómez-Fórneas[2]

[1]Departamento de Química Inorgánica, Facultade de Química, Campus Vida, Universidade de Santiago de Compostela, Santiago de Compostela, 15782, Spain. E-mail: mariajose.romero@usc.es

[2]Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela, Lugo, 27002, Spain.

ABSTRACT

We report the synthesis and characterization of a symmetric [N_4] tetradentate imine-type ligand H_2L that incorporates a dansyl fluorophore group in both ligand arms. Two binding domains separated by a short arene spacer and two bulky arms with an *anti* conformation make this organic molecule suitable as precursor of metallosupramolecular species such as helicates. The molecular structure of H_2L has been analyzed by X-ray diffraction. This technique has revealed the formation of intermolecular hydrogen bond interactions that lead to the supramolecular self-assembly of ligand molecules in the solid state and the generation of oval-shaped channels in the 3D crystal packing.

KEYWORDS

Imine-type ligand, dansyl fluorophore, supramolecular assembly

INTRODUCTION

The coordination chemistry of fluorescent polydentate ligands has received an increased attention in the last decades because of their potential applications in areas of research such as medical diagnosis, environmental chemistry, cellular biology and molecular machines.[1] These ligands can exhibit a high sensitivity and selectivity towards the detection of metal ions,[2] anions[3] and bioactive organic molecules.[4]

Our research group has employed imine-type ligands as suitable kernels to assemble metallosupramolecular complexes.[5] As part of our ongoing research work, we have designed and synthesized a new tetradentate imine-type ligand H_2L (Figure 1) bearing a fluorophore dansyl group and two [NN] bidentate binding domains separated by an arene spacer. The aim of this work is to evaluate whether the symmetric ligand H_2L is a suitable precursor for the assembly of metallosupramolecular species (e.g. helicates).

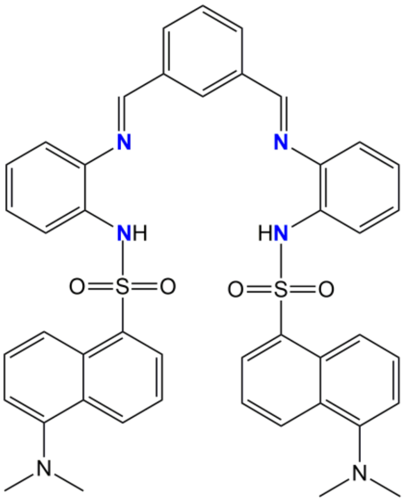

Figure 1: Imine-type tetradentate ligand H_2L.

EXPERIMENTAL

The $[N_4]$ tetradentate imine ligand H_2L was synthesized by condensation of isophthalaldehyde (0.26 g, 1.9 mmol) and *N*-(2-aminophenyl)-5-(dimethylamino)-1-naphthalenesulfonamide (1.31 g, 3.8 mmol) in a 1:2 molar ratio. The synthesis of the precursor *N*-(2-aminophenyl)-5-(dimethylamino)-1-naphthalenesulfonamide was previously reported by us.[5b] The reaction was carried out in ethanol for 7 h under reflux conditions. The yellow solid was filtered off, washed with diethyl ether and characterized with the usual techniques. Recrystallization of H_2L in acetonitrile afforded single crystals suitable for X-ray diffraction studies.

H_2L: M.p. 140 ºC. Yield 1.29 g (84%). Elemental analysis, Calc. for $C_{44}H_{40}N_6O_4S_2$: C, 67.6; H, 5.2; N, 10.8; S, 8.2. Found: C, 66.3; H, 5.2; N, 10.7; S, 8.0 %. FAB (m/z): 781.2 (H_2L); IR (KBr, cm^{-1}): v(N-H) 3270, v(C=N+C-N) 1626, $v(SO_2)_{AS}$ 1335, $v(SO_2)_S$ 1165. ^1H NMR (DMSO-d_6, ppm), δ (m, nH): 9.58 (s, 2H), 8.31 (t, 4H, J= 8.3 Hz), 8.14 (s, 2H), 8.05 (d, 2H, J = 7.6 Hz), 7.94 (s, 1H), 7.86 (d, 2H, J = 7.7 Hz,), 7.54-7.38 (m, 5H), 7.31 (t, 2H, J= 8.1 Hz), 7.26-7.14 (m, 4H), 7.08 (d, 2H, J= 7.6 Hz), 6.97 (d, 2H, J= 7.5 Hz), 2.67 (s, 6H).

RESULTS AND DISCUSSION

The molecular structure of the ligand H_2L and selected bond distances and angles are shown in Figure 2. The X-ray structure of H_2L consists of discrete molecules with an *E* conformation around the imine bonds. Moreover the dansyl groups are arranged in an *anti* conformation in order to minimize steric repulsions. The binding of two metal ions to H_2L would be possible due to the existence of two bidentate binding domains separated by a short arene spacer and the possibility of rotation around the imine bonds in this ligand.

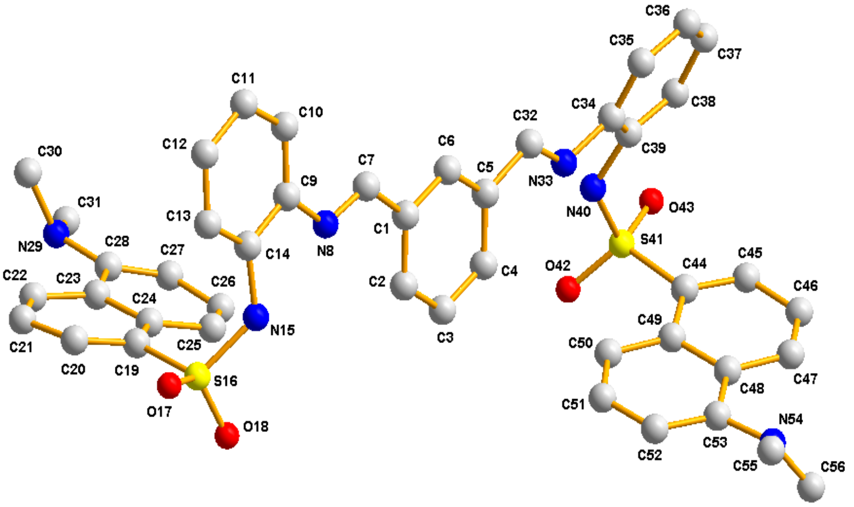

Figure 2: X-ray crystal structure of H_2L. Selected bond distances and angles: N8-C7 1.268(11) Å, C32-N33 1.285(12) Å, N33-C34 1.418(13) Å, N8-C9 1.416(12) Å; C7-N8-C9 122.3(8)°, C32-N33-C34 122.2(9)°.

An intermolecular hydrogen bond interaction between a sulfonamide NH group and a sulfonamide oxygen atom from a neighbour ligand molecule is observed. These intermolecular interactions lead to the supramolecular self-assembly of the ligand H_2L in the solid state and consequently oval-shaped channels with cavity dimensions of ca. 15 x 6 Å^2 are formed in its 3D crystal packing (Figure 3).

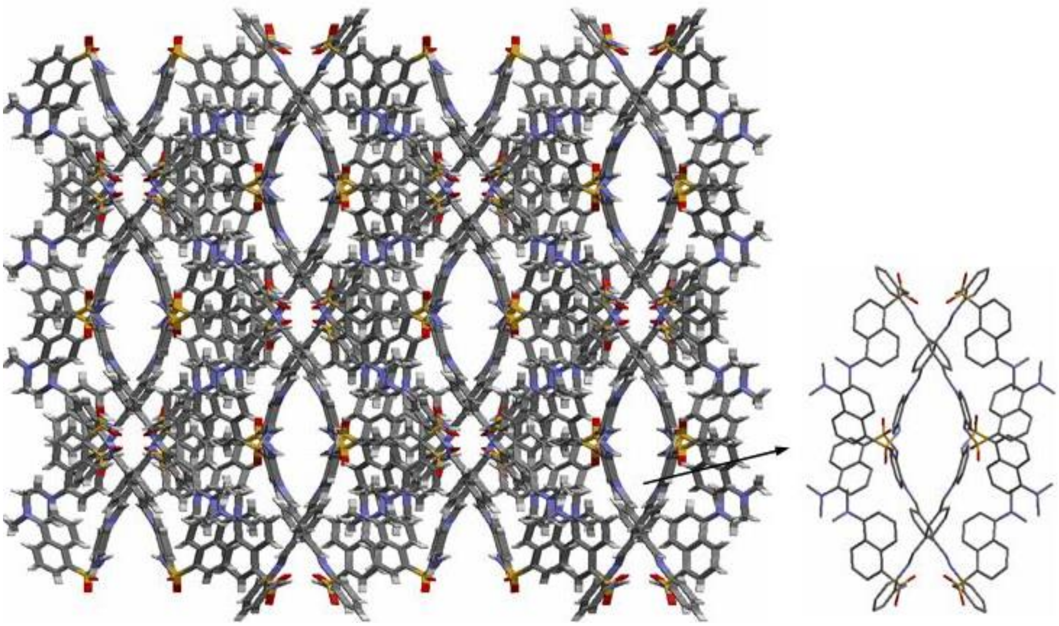

Figure 3: Supramolecular self-assembly of H_2L.

Each oval-shaped cavity is defined by four overlapped molecules crossing at the arene spacer and sulfonamide groups. Interestingly the hydrogen bond interactions established between the sulfonamide atoms are observed in smaller cavities.

CONCLUSIONS

The novel dansyl-functionalized ligand H_2L has been isolated with high purity and yield. The crystal structure of H_2L shows that the bulky dansyl groups are oriented in opposite directions. Both the spatial conformation observed in the solid state and the existence of two bidentate binding domains suggest that this ligand might be a suitable precursor of metallosupramolecular complexes with stoichiometry $[M_2L_2]$. Moreover this molecule is capable to form supramolecular self-assembled structures, hence it might also provide interesting 3D assemblies through the interaction with different metal ions.

ACKNOWLEDGEMENTS

We thank Xunta de Galicia (EM2014/018, GRC2014/025, R2014/004) and the Spanish MINECO networks CTQ2015-70371-REDT MetDrugs and CTQ2015-71211-REDT MetalBIO for financial support.

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