

Double imidazolidine condensation in a polynucleating Schiff base

Matilde Fondo^a, Ana M. García-Deibe,^a Noelia Ocampo^a, Jesús Sanmartín^b

^a Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela, E-27002 Lugo, Spain. E-mail: matilde.fondo@usc.es

^b Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain

Abstract

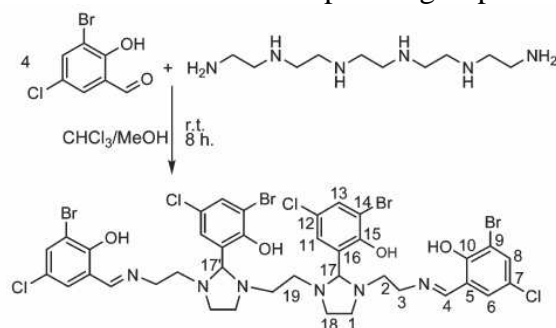
Condensation of pentaethylenehexamine and 3-bromo-5-chlorosalicylaldehyde yielded the bisimidazolidine Schiff base ligand 5,6'-(1*E*,1'*E*)-(2,2'-(3,3'-(ethane-1,2-diyl)bis(2-(3-bromo-5-chloro-2-hydroxyphenyl)imidazolidine-3,1-diyl))bis(ethane-2,1-diyl))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2-bromo-4-chlorophenol), H₄L. This diimine could be suitably characterised both in the solid state and in solution.

Introduction

The formation of imidazolidine rings when condensing salicylaldehyde derivatives and linear polyamines is a well known process, and already described in the 50's [1]. In last years, we have been working with three-branched compartmental ligands, whose imidazolidine *NCN* bridges mediate a ferromagnetic interaction, as DFT calculations demonstrated [2]. In view of this interesting ability, now we intend to increase the number of this type of bridging interactions, so we present here a novel Schiff base containing two of these saturated heterocycles. This chiral potentially decadentate ligand can act as trinucleating [3], and now we report a suitable characterisation, including its crystal structure.

Results and discussion

Despite the simplicity of the method employed (Scheme 1), the yield is acceptable and the product obtained shows a high purity. This latter was mostly based on analytical, MS, FT-IR and NMR data. But now we have determined its crystal structure, so we could establish some important aspects of its spatial arrangement. In this sense, both imine groups display an *E* configuration, as occurs for most of the Schiff bases. Likewise, classic intramolecular H bonds can be observed between the azomethine groups and both terminal phenol groups of the salicylaldehyde residues. The other two OH groups display bi- or trifurcated H bonds, which involve neighbouring imidazolidine and/or the middle phenol groups.



Scheme 1. Synthetic route to H₄L, with a numbering scheme for NMR characterisation

Despite the clear symmetry of the molecule, both methine groups are stereogenic. The racemic crystals only consist of crystallographically independent neutral molecules of the ligand, where both asymmetric *C* atoms show the same

configuration. At the same time, the four *N* atoms of the imidazolidine rings also display similar configurations (Fig. 1).

Regarding to conformation, both imidazolidine rings appear inverted, and showing envelope conformations, where the methine groups protrude from the plane formed by the *N* and ethylene *C* atoms. Both five-membered cycles are connected through the central ethylene group, which is *gauche* conformed, as one of the terminal ethylene spacers, while the other one (C107 and C108) shows an *anti* disposition.

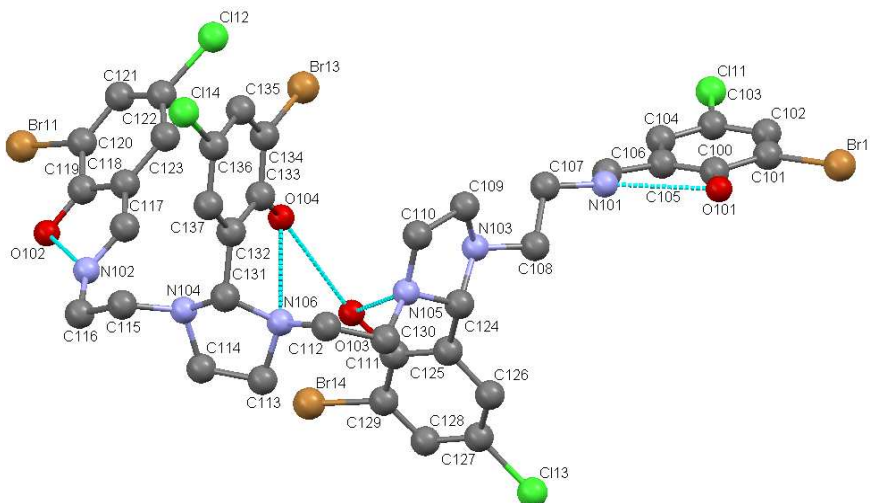


Fig. 1. Molecular structure of the (*R,R,R,R,R,R*) isomer of H₄L .

Experimental procedure

3-Br-5-Cl-Salicylaldehyde (0.595 g, 2.53 mmol) and 15 mL of methanol were added to a chloroform solution (5 mL) of pentaethylenehexamine (0.147 g, 0.63 mmol) at room temperature. The mixture was stirred in air for 8 h, precipitating a yellow solid. The solid was filtered off, washed with diethyl ether, and dried in air (0.38 g, 55%). Mp: 190-192 °C. Calcd for C₃₈H₃₆Br₄Cl₄N₆O₄ (1102.0): C, 41.38; H, 3.27; N, 7.62. Found: C, 41.34; H, 3.33; N, 7.52. MS (FAB): *m/z* 1102.8 [H₄L]⁺. IR (KBr, v/cm⁻¹): 1636 (C=N), 3437 (OH). ¹H NMR (500 MHz, DMSO-*d*₆): δ 2.27-2.39, 2.40-2.49, 2.54-2.76, 2.76-2.89, 2.90-3.07, 3.57-3.64 (all m, 20H, 4H1 + 4H2 + 4H3 + 4H18 + 4H19), 3.80, 3.94 (both s, 1H each, H17 + H17'), 7.15, 7.38, 7.49, 7.67 (all s, 2H each, 2H6 + 2H8 + 2H11 + 2H13), 8.36 (s, 2H, 2H4), 12.02 (broad, 2H, OH), 14.30 (broad, 2H, OH). Crystal data for H₄L: (at 100(2) K): monoclinic, *C*2/*c* (No. 15), C₃₈H₃₆Br₄Cl₄N₃O₃S, *MW* = 1102.14, *a* = 26.362(7), *b* = 12.458(3), *c* = 26.554(6) Å, β = 106.879(5), *V* = 8345(4) Å³, *Z* = 8; ρ_{calc} = 1.755 g·cm⁻³; *R*₁ = 0.0596 and *wR*₂ = 0.1076 (*I* > 2σ*I*), residual electron density 0.634 e⁻ Å³.

References

- [1] (a) A. K. Mukherjee, *Science and Culture*, **1953**, *19*, 107; (b) R. J. Ferm, J. L. Riebsomer, *Chem. Rev.*, **1954**, *54*, 593.
- [2] M. Fondo, A. M. García-Deibe, M. Corbella, E. Ruiz, J. Tercero, J. Sanmartín and M. R. Bermejo, *Inorg. Chem.*, **2005**, *44*, 5011
- [3] M. Fondo, N. Ocampo, A. M. García-Deibe, E. Ruiz, J. Tercero and J. Sanmartín, *Inorg. Chem.*, **2009**, *48*, 9861.