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Design, Synthesis and Characterization of a Phosphino-Azine Ligand †

Uxía Barreiro-Sisto [1], Marcelino Maneiro [1] and Rosa Pedrido [2,*]

[1] Suprabioin Lab, Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela, Campus Terra, 27002 Lugo, Spain; uxibarsis@gmail.com (U.B.-S.); marcelino.maneiro@usc.es (M.M.)
[2] Suprabioin Lab, Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, Campus Vida, 15782 Santiago de Compostela, Spain
* Correspondence: rosa.pedrido@usc.es

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Abstract: Azine compounds has recently gained significant attention due to the interesting properties that they display which could be relevant in fields such as Pharmacology and Material Sciences. These types of ligands stand out in Coordination Chemistry because of the facilities that exhibit to easy coordinate to transition and *post*-transition metal ions. Besides to the azine skeleton (C=N-N=C), the addition of other donor atoms such as sulphur, oxygen or phosphorus in the ligand increases the coordination possibilities. In this sense, we are interested in azine ligands as precursors of novel metallosupramolecular architectures. The research herein reported is focused on the synthesis and characterization of a potentially tetradentate $[P_2O_2]$ organic phosphine-azine ligand (LP). The addition of the phosphine group to the azine skeleton allows the stabilization of soft metal ions and the assembly of functional structures. The azine ligand LP^8 has been prepared by a condensation reaction between two equivalents of (diphenylphosphino)benzaldehyde and one equivalent of azine monohydrate and was fully characterized by using several techniques such as elemental analysis, mass spectrometry, infrared spectroscopy, ^{1}H NMR spectroscopy and X-ray diffraction.

Keywords: azine; ligand; metallosupramolecular architectures

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1. Introduction

From the last years, azines has been attracted Schiff bases compounds due to their potential applications in fields such as Material Sciences [1,2] and Pharmacology [3–5]. Moreover, these compounds are being widely used in Coordination Chemistry because of their capacity to coordinate different transitional and *post*-transitional ions thus generating diverse metallosupramolecular architectures. The derived complexes are particularly interesting as a result of their magnetic [6], antimicrobial [7] and catalytic [8] properties.

Our research group has a broad experience using multiple Schiff bases functionalized with phosphine groups to obtain different metallosupramolecular architectures [9,10]. With the final aim of achieving helicate and mesocate architectures, here we report the design, synthesis and structural characterization of a new azine ligand named LP and functionalized with two triphenylphosphine groups (Figure 1).

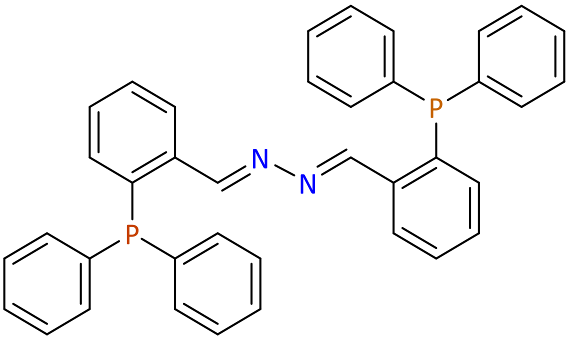


Figure 1. Phosphine-azine ligand LP.

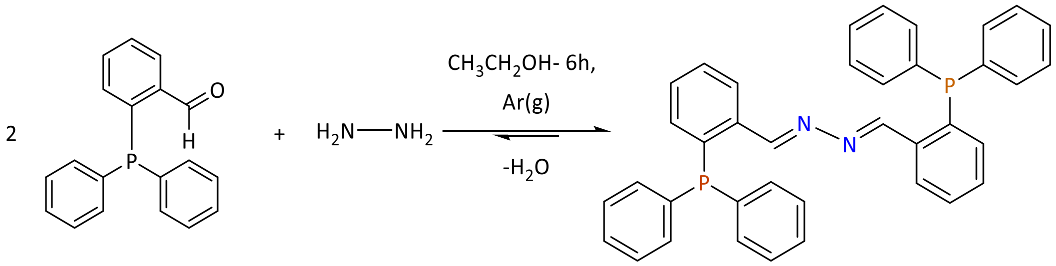
2. Experimental Section

2.1. Reactants and Solvents

All solvents, hydrazine monohydrate and 2-difenilphosphinebenzaldehyde are commercially available ant they were used without further purification.

2.2. Synthesis and Characterization of the Bisthiosemicarbazone Ligand LP

The phosphine-azine ligand LP has been prepared by a condensation reaction in inert atmosphere between one equivalent of hydrazine monohydrate and two equivalents of 2-diphenilphosphinebenzaldehyde (Scheme 1). First, 1.007 g (3.47 mmol) of 2-diphenilphosphinebenzaldehyde were solved in absolute ethanol (ca. 50 mL). Once the aldehyde is solved, 0.0868 g (1.73 mmol) of azine monohydrate were added. The solution was refluxed under magnetic stirring and argon atmosphere for 6 h. The yellow solid that precipitated was filtered off and then washed with diethyl ether. Yield: 0.8632 g, (86%). Elemental analyse, %theoretical ($C_{38}H_{30}N_2P_2$): C, 79.15; H, 5.24; N, 4.86; %experimental C, 78.26; H, 5.62; N, 4.86; IR spectrometry (KBr, cm^{-1}): ν(C=N) 1616 (f). Mass Spectrometry (ESI+, *m/z*): 609.2 [LPO$_2$+H]$^+$, 539.40 [LP+H]$^+$; ^{1}H NMR [DMSO-d$_6$]: 9.05 (s, 2H, H$_1$), 7.51–6.87 (m, 31H, Ar). ^{13}C NRM [CDCl$_3$]: 159.3 (C=N), 137.4-126.9 (C-Ar). ^{31}P NRM [CDCl$_3$-d$_6$]: −14,64.



Scheme 1. Synthesis of the phosphine-azine ligand LP.

2.3. Crystallographic Data of LPO$_2$·2CH$_3$OH

LPO$_2$·2CH$_3$OH: $C_{38}H_{30}N_2O_2P_2 \cdot 2(CH_4O)$; *MW:* 672.66 g·mol^{-1}; crystal dimensions 0.10 × 0.08 × 0.05 mm; monoclinic; P2$_{1/c}$; *a* = 15.822 (2), *b* = 12.4488 (12), *c* = 8.8980 (12) Å; β = 101.290 (5) ^{0}; V = 1718.7 (4) Å^3; Z = 2; μ = 0.17 mm^{-1}; measured reflections= 24408; independent reflections [R$_{int}$] = 4236 [0.089]; R = 0.048; wR = 0.121.

Table 1. Selected bond length and angles for ligand H$_2$L.

Main Bond Distances (Å)			
P1-O1	1.4946 (14)	P1-C8	1.806 (2)
P1-C14	1.795 (2)	N1-N1′	1.413 (3)
Angles (°)			

C7-N1-N1′	111.10 (2)	O1-P1-C14	112.62 (9)
O1-P1-C8	110.97 (8)	O1-P1-C14	113.31 (8)

3. Results and Discussion

The azine LP compound is a potentially dianionic and tetradentate $[N_2P_2]$ ligand (Figure 1).

The phosphino-azine ligand LP was successfully isolated and characterized. The ligand is a yellow powdery compound and the elemental analyse of C, H and N shows that the compound was obtained in a high purity grade. Infrared spectroscopy of the obtained solid presents a peak at 1616 which corresponds to the imine (C=N) vibration frequency and a peak at 756 that corresponds to the N-N bond. Furthermore, the infrared spectra stand out for the disappearance of a peak over 1700 of the precursor aldehyde and a wide peak at 3438 that confirm the presence of solvation molecules. Additionally, in the mass spectra there are two peaks: one at 609.2 which corresponds to the dioxidized ligand $[LPO_2+H]^+$ and one at 539.40 that correspond to the molecular ion $[LP+H]^+$. Recrystallization of LP azine ligand in methanol allowed us to obtain good-quality crystals for monocrystal X-ray studies. Nevertheless, the obtained structure shows that during the long crystallization process the phosphine groups of the azine ligand suffered oxidation.

The crystal structure of the oxidised ligand LPO_2 consists of discrete molecule, solvated by methanol that crystallize in the monoclinic $P2_{1/c}$ system (Figure 2).

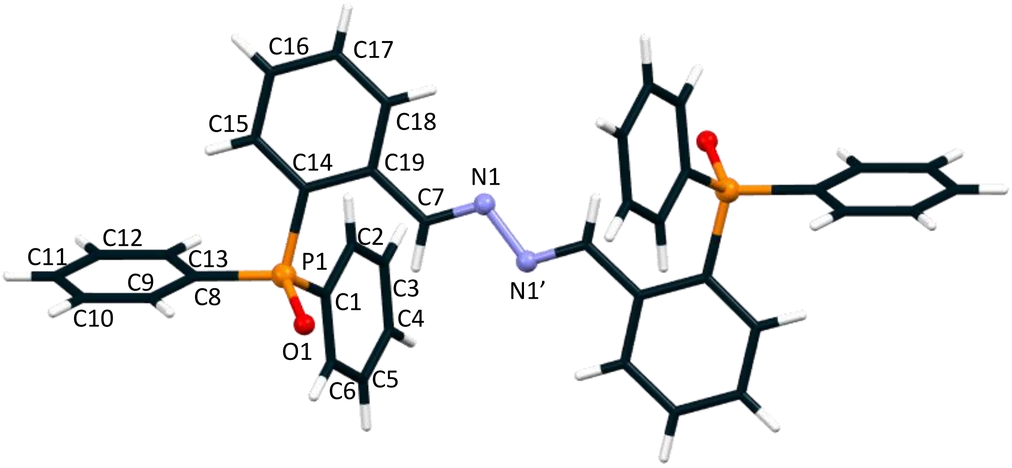


Figure 2. Crystal structure of $LPO_2·2CH_3OH$.

Each phosphine branch adopts an *E* conformation in relation to the imine bond and *anti*-configuration with both branches directed to opposite sides. This conformation minimized steric interactions and favors the stablishing of weak intermolecular hydrogen bonds interactions between the oxygen of the oxidized phosphorous and the hydroxyl groups of the methanol solvent molecules (O2-H20··· O1: 1.787 Å) (Figure 3).

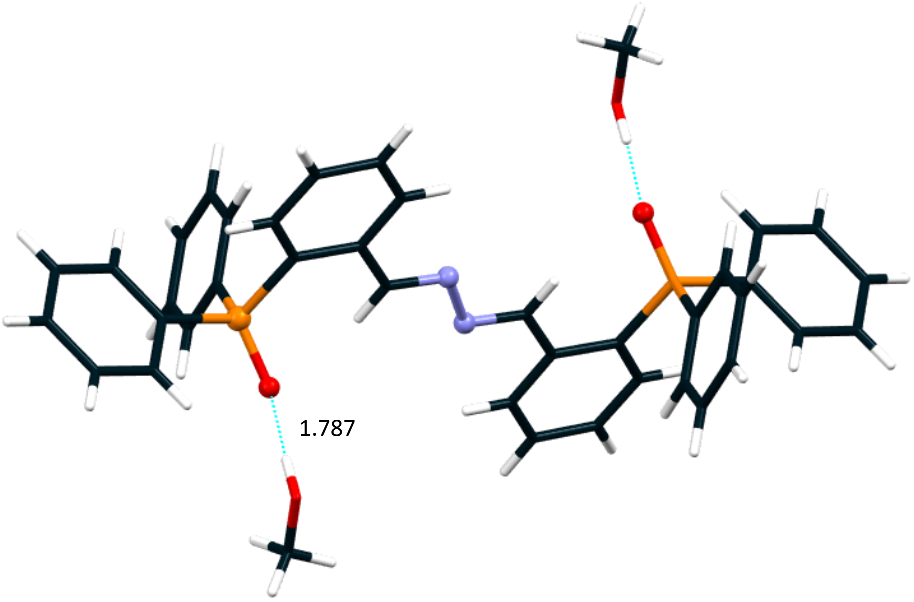


Figure 3. Intermolecular H-bonds in LPO_2. $2CH_3OH$ with methanol molecules.

We must point out that the solid ligand LP or its freshly prepared solutions remain without oxidation which will allow that this ligand could act as tetradentate precursor of metal complexes.

4. Conclusions

The azine ligand LP has been successfully synthesized with high purity and yield. The crystal structure shows that after a long crystallization time the phosphine ligand experiences an oxidation process leading to the di-oxidized form of the ligand.

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