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Oxidation Processes in a Phosphine-Thiocarbohydrazone Ligand †

Sandra Fernández-Fariña [1,*], Isabel Velo-Heleno [1], Lara Rouco [2], Miguel Martínez-Calvo [1] and Ana M. González-Noya [1]

[1] Departamento de Química Inorgánica, Facultade de Química, Campus Vida, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

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

* Correspondence: sandra.fernandez.farina@usc.es

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Abstract: In this work, we have isolated a pentadentate [P_2N_2S] phosphine-thiocarbohydrazone ligand H_2L with a bulky phosphine group in both linker domains that undergoes an oxidation process in solution. This ligand was synthesized by direct reaction between two equivalents of 2-diphenylphosphinebenzaldehyde and one equivalent of thiocarbohydrazide. Two types of crystals derived from this ligand were obtained and studied by X-ray diffraction spectroscopy. One structure corresponds to the monooxidized ligand $H_2L(O)$ while the other indicates a dioxidation of the compound, $H_2L(OO)$.

Keywords: thiocarbohidrazone; phospine; oxidation; X-ray diffraction

1. Introduction

Thiocarbohydrazones are compounds of great interest in health-related fields such as pharmacology, as several studies have shown that these compounds possess promising antifungal [1], antimicrobial [1] and even antitumoral properties [2]. Nevertheless, the coordination chemistry of this type of ligands has been less studied than that of its thiosemicarbazone analogues.

In general, the thiocarbohydrazones found in the literature act as [NS] or [ONS] donor ligands giving rise to structures of different nuclearity [3]. However, our group have recently reported the first examples of complexes derived from a phosphine-thiocarbohydrazone ligand H_2L [4] confirming that the presence of the bulky groups give rise to the formation of mesocate species. At this point, we decided to synthesize the phosphine-thiocarbohydrazone ligand H_2L with the aim of obtaining the first example of a [NSP] thiocarbohydrazone crystal structure.

2. Experimental Section

The [P_2N_2S] phosphine-thiocarbohydrazone ligand H_2L was obtained by means of a condensation reaction, as reported before [4]. Yellow X-ray-quality crystals of the monooxidized ligand, $H_2L(O)\cdot CH_3CH_2OH$, were collected by slow evaporation of the mother liquors after 24 h.

With the aim of obtaining the non-oxidized crystal structure of the ligand H_2L, recrystallization experiments of the solid obtained during the synthesis were carried out by using acetonitrile, acetone, methanol, or a mixture of dichloromethane/methanol solvents. Thus, X-ray-quality crystals of $H_2L(OO)\cdot 3CH_3CN$ were obtained by recrystallization of

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the solid in acetonitrile. It should be note that $H_2L(OO)\cdot 3CH_3CN$ crystals were obtained after 7 days.

Crystallographic Data

$[H_2L(O)]\cdot CH_3CH_2OH$: $C_{41}H_{38}N_4O_{1.30}P_2S$, *MW*: 701.55; crystal dimensions: 0.36 × 0.18 × 0.11; triclinic; $P\bar{1}$ $a = 9.9576(5)$; $b = 10.3691(5)$; $c = 18.9587(9)$ Å; $\alpha = 92.257(3)$; $\beta = 98.607(3)$; $\gamma = 107.014(3)$ ^{0}; V = 1843.58(16) Å^3; Z = 2; $\mu = 0.213$ mm^{-1}; measured reflexions= 53678; indpendent reflexions [Rint]= 8729 [0.0529]; R= 0.0603; wR= 0.1773.

$[H_2L(OO)]\cdot 3CH_3CN$: $[C_{45}H_{41}N_7O_{1.75}P_2S$, *MW*: 801.85; crystal dimensions: 0.25 × 0.21 × 0.20; triclinic; $P\bar{1}$ $a = 9.2907(4)$; $b = 12.1770(5)$; $c = 18.5702(8)$ Å; $\alpha = 88.132(2)$; $\beta = 83.987(2)$; $\gamma = 74.965(2)$ ^{0}; V = 2017.79(15) Å^3; Z = 2; $\mu = 0.207$ mm^{-1}; measured reflexions = 16387; independent reflexions [Rint] = 7271 [0.0573]; R = 0.0614; wR = 0.1674.

3. Results and Discussion

Slow evaporation of the mother liquors from the ligand synthesis and recrystallization of the ligand solid in acetonitrile allowed us to obtain yellow crystals suitable for X-ray diffraction studies. The structures revealed the monooxidized $H_2L(O)\cdot CH_3CH_2OH$ (Figure 1) and the dioxidized $H_2L(OO)\cdot 3CH_3CN$ (Figure 2) ligand structures, respectively. Both crystal structures are very similar and will therefore be discussed together below.

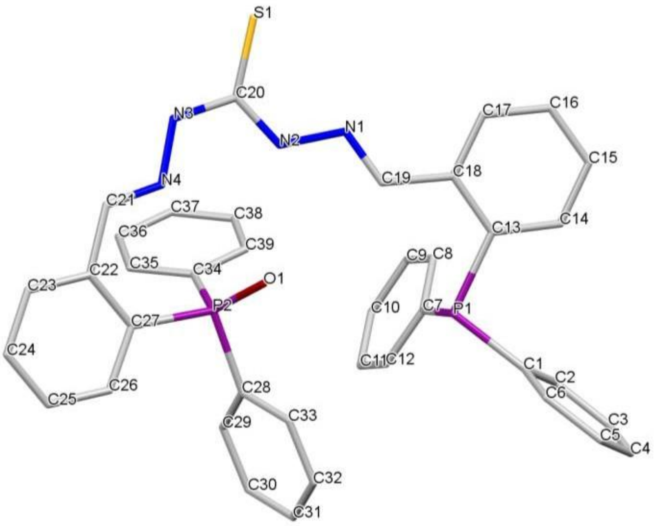

Figure 1. Crystal structure of the monooxidized phosphine-thiocarbohydrazone ligand $H_2L(O)\cdot CH_3CH_2OH$.

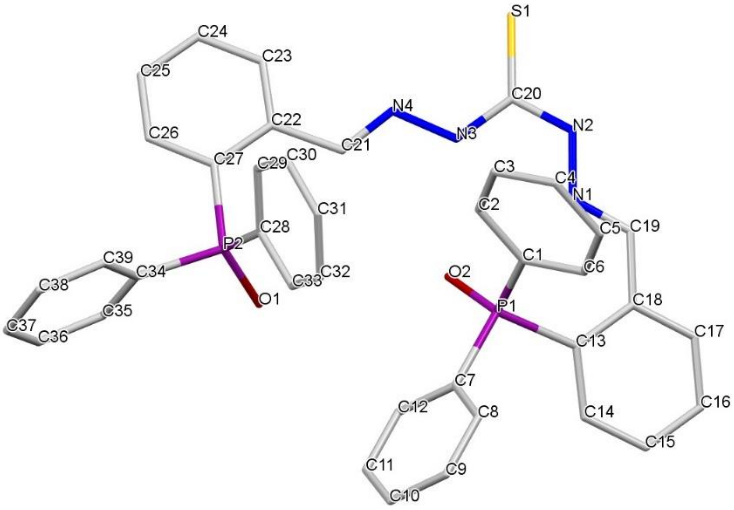

Figure 2. Crystal structure of the dioxidized phosphine-thiocarbohydrazone ligand $H_2L(OO)\cdot 3CH_3CN$.

Compounds $H_2L(O)\cdot CH_3CH_2OH$ (Figure 1) and $H_2L(OO)\cdot 3CH_3CN$ (Figure 2) crystallise solvated by one molecule of ethanol and three molecules of acetonitrile, respectively. In both ligands, the two imino-phosphine branches adopt an *E* configuration relative to the imino bonds and a *syn*-type conformation, with the two phosphine branches oriented towards the same side. The different arrangement of the thioamidic NH gives rise to a *syn* conformation in C=S bond with respect to the N3-H3 bond and an *anti* conformation with respect to the N2-H2 bond.

The conformation adopted by the ligands is mainly conditioned by the existence of moderate intramolecular hydrogen bonds between one of the thioamide nitrogens and the oxygen atom. In addition, weak intermolecular hydrogen bonds exist in both ligands. In the case of the monooxidized ligand, $H_2L(O)\cdot CH_3CH_2OH$, these interactions occur between the sulphur atom of one ligand molecule and one of the thioamide nitrogens of another ligand unit (Figure 3). In the case of the dioxidized ligand, $H_2L(OO)\cdot 3CH_3CN$, a hydrogen bond is observed between one of the thioamide nitrogens and the nitrogen of one of the solvating acetonitrile molecules (Figure 4).

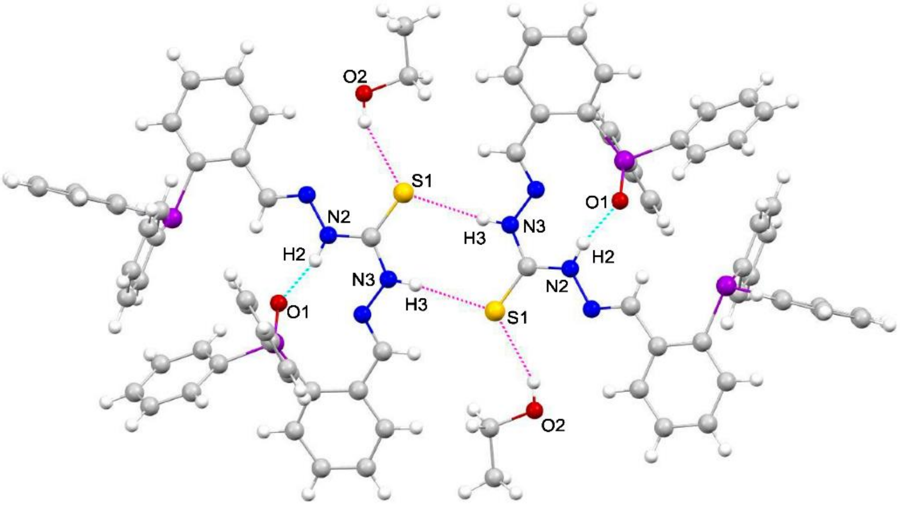

Figure 3. Intramolecular hydrogen bonds (blue) *[N_2–H_2···O1 2.86 (7) Å]* and intermolecular hydrogen bonds (pink) *[N_3–H_3···S1 3.332 (2) Å; O_2–H_2···S1 3.23 (4)]* in $H_2L(O)\cdot CH_3CH_2OH$.

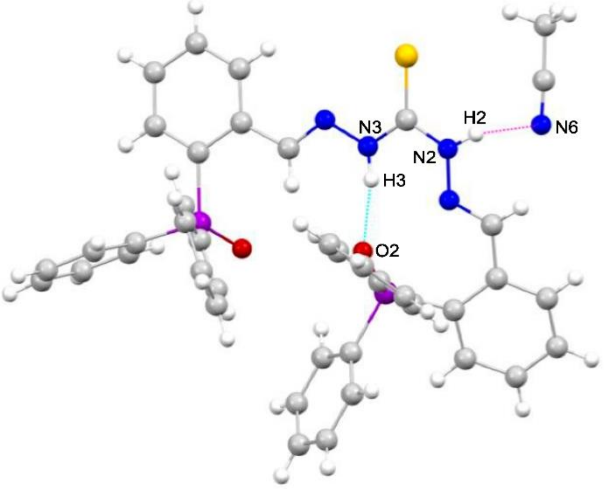

Figure 4. Intramolecular hydrogen bonds (blue) [N_3–H_3···O_2 2.78 (4) Å] and intermolecular hydrogen bonds (pink) [N_2–H_2···N_6 3.09 (4) Å] in $H_2L(OO)\cdot 3CH_3CN$.

Main bond lengths C=N, N-N and C-S given in Table 1 and Table 2 are in the expected range for thiocarbohydrazone ligands and do not need further discussion [5].

Table 1. Selected bond lengths (Å) for $H_2L(O)\cdot CH_3CH_2OH$.

Main Bond Distances (Å)			
C1—N1	1.456 (4)	N2—N3	1.387 (3)
N1—C2	1.338 (4)	N3—C4	1.288 (4)
C2—N2	1.365 (4)	C8—O1	1.399 (3)
N6—C20	1.451 (4)	C39—S4	1.695 (3)

Table 2. Selected bond lengths (Å) for $H_2L(OO)\cdot 3CH_3CN$.

Main Bond Distances (Å)			
C19—N1	1.280 (4)	C20—S1	1.674 (4)
C20—N2	1.352 (4)	C21—N4	1.278 (4)
C20—N3	1.348 (4)	N1—N2	1.368 (4)
P2—O1	1.578 (5)	N3—N4	1.378 (4)
P1—O2	1.478 (3)		

4. Conclusions

The obtainment of two different crystal structures derived from the phosphine-thiocarbohydrazone ligand, H_2L, lead us to know that the compound undergoes an oxidation process in solution. It is clear from the crystal structures obtained that both, solvent and time, have an effect on the final crystal structure of the ligand and therefore on the oxidation process, thus obtaining the monooxidized structure in ethanol after 24 h, $H_2L(O)\cdot CH_3CH_2OH$, and the dioxidized structure in acetonitrile after one week, $H_2L(OO)\cdot 3CH_3CN$.

Author Contributions: All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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