

## Platinum (II) complexes with a diacetylmonooxime ethylthiosemicarbazonate ligand: from mononuclear to polynuclear complexes

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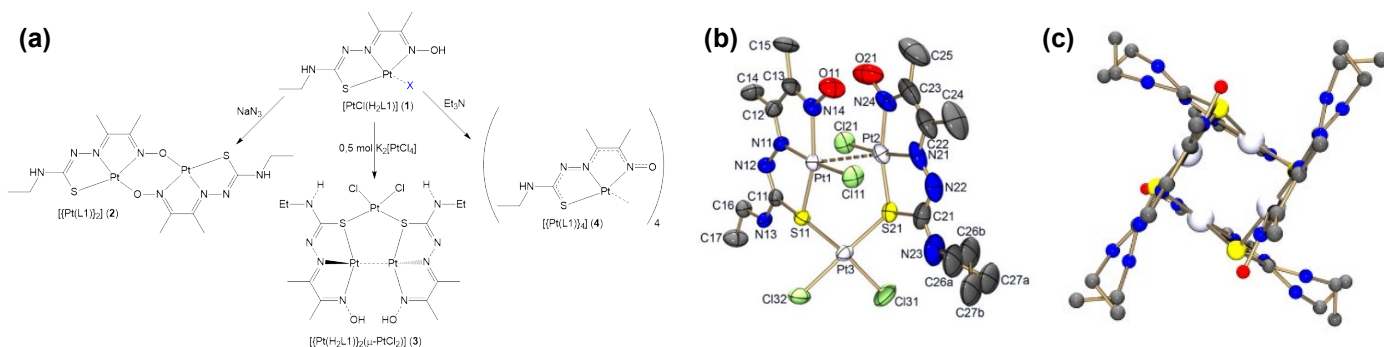
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### Highlights

The chemistry of thiosemicarbazones with platinum (II) is explored. Different synthetic routes have been used in order to enable the formation of different oligomers.

### Abstract

Thiosemicarbazones are bioactive ligands with a versatile coordination chemistry.<sup>1</sup> The additional pair of electrons from the sulfur atom is frequently explored in order to form bridges with more than one metal center.<sup>2</sup> This work presents the synthesis and characterization of three new di, tri and tetranuclear Pt<sup>II</sup> complexes derived from the monomeric complex [PtCl(L1)] (1), where L1<sup>2-</sup> = diacetylmonooxime-ethyl-thiosemicarbazonate. The dinuclear (2), trinuclear (3) and tetranuclear (4) complexes were obtained from reactions of the precursor [PtCl(L1)] (1) with NaN<sub>3</sub>, K<sub>2</sub>[PtCl<sub>4</sub>] and Et<sub>3</sub>N, respectively (Figure 1a). It is important to highlight that the formation of the dinuclear complex occurs after decomposition of the azide in solution, which should probably occur after the formation of the complex with N<sub>3</sub><sup>-</sup>. The formation of the trinuclear complex is explained by the order of addition of the reagents, while the tetranuclear complex is formed upon deprotonation of the OH group consequent formation of Pt-S bonds.



**Figure 1:** (a) Synthesis reactions of the dinuclear (2), trinuclear (3) and tetranuclear complexes (4). (b) Crystalline and molecular structure of the complex 3. (c) View of tetramer [Pt(L1)]<sub>4</sub> along the c axis.

The compounds were analyzed by IR, <sup>1</sup>H-NMR, CHNS and molar conductivity. These analyses indicated the formation of neutral complexes according to the proposed compositions. The confirmation of the formation of the dinuclear complex [Pt(L1)]<sub>2</sub> (2) was based on the high resolution ESI(+) mass spectrum, which showed a peak related to the [M+H]<sup>+</sup> ion at *m/z* 791,0806 (calculated = 791.0837). Suitable crystals for X-ray diffraction analysis were obtained for the complexes 3 and 4. The complex 3 crystallizes in the monoclinic space group *P2<sub>1</sub>/c*, while 4 presents the tetragonal space group *P4<sub>2</sub>/n*. DFT studies are now underway in order to explain the formation of these oligomers and also de Pt...Pt interactions.

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