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# New bifunctional *N*-thiophosphorylated thiourea and 2,5-dithiobiurea derivatives. Crystal structures of $R[C(S)NHP(S)(OiPr)_2]_2$ ( $R = -N(Ph)CH_2CH_2N(Ph)-$ and $-NHNH-$ )

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## ABSTRACT

A new bifunctional *N*-thiophosphorylated thiourea and 2,5-dithiobiurea of the common formula  $R[C(S)NHP(S)(OiPr)_2]_2$  [ $R = -N(Ph)CH_2CH_2N(Ph)-$  ( $H_2L^a$ );  $-NHNH-$  ( $H_2L^b$ )] have been synthesized and characterized by IR, <sup>1</sup>H, <sup>31</sup>P spectroscopy and the single crystal X-ray diffraction method. The structure of the latter compound in CDCl<sub>3</sub> and acetone-*d*<sub>6</sub> solutions has been discussed in comparison with the monofunctional thiosemicarbazide PhNHHC(S)NHP(S)(OiPr)<sub>2</sub> ( $HL^c$ ).

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## 1. Introduction

Metal–organic architectures formed by d-metal cations and polyfunctional chelators, e.g. bis-β-diketonates and bis-*N*-acylthioureas, are of great interest due to their magnetic, gas storage and catalytic properties [1–6]. The propensity of ligands containing the fragment  $[R'_2NC(S)NHC(O)]_2Z$  to form *cis*-square-planar complexes with Ni(II), Pd(II) and Pt(II) has been used for the synthesis of metal-containing macrocycles [1–6]. Depending on the nature of the spacer, the formation of dimer  $M_2L_2$  ( $Z = m-C_6H_4$ ) or trimer  $M_3L_3$  ( $Z = o-C_6H_4$ ) coordination compounds [ $M(II) = Ni(II), Pd(II), Pt(II)$ ] have been observed.

The phosphorus containing analogues of these compounds have more flexible chelate units that provide interesting perspectives of new metal-containing macrocycle creations. A number of polyfunctional thiourea ligands,  $H_2L$ , containing several  $[R'_2P(S)NHC(S)NH]_2Z$  groups [7–10] and their complexes with d-metal cations have been synthesized in our scientific group (Scheme 1).

Herein, we report the structure and complexing properties of a bis-thiourea based on the *N,N'*-diphenyl-1,2-diaminoethane moiety ( $H_2L^a$ ) and the new 1,6-bis-thiophosphorylated 2,5-dithiobiurea ( $H_2L^b$ ) (Scheme 2). The structure of the latter compound in CDCl<sub>3</sub> and acetone-*d*<sub>6</sub> solutions have been discussed in comparison with the monofunctional thiosemicarbazide ( $HL^c$ ) (Scheme 2).

## 2. Experimental

## 2.1. Synthesis

A solution of *N,N'*-diphenyl-1,2-diaminoethylene, hydrazine hydrate or phenylhydrazine (5 mmol; 1.06, 0.25 or 0.54 g, respectively) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was treated under vigorous stirring with a solution of (*i*PrO)<sub>2</sub>P(S)NCS (11 mmol, 2.63 g; for 5.5 mmol, 1.31) in the same solvent. The mixture was stirred for 2 h. The solvent was removed in a vacuum, and the product was purified by recrystallization from a 1:5 (v/v) mixture of methylene chloride and *n*-hexane.

**$H_2L^a$ :** Yield: 3.24 g (94%). M.p. 88 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.22 (d, <sup>3</sup>J<sub>H,H</sub> = 6.2 Hz, 12H, CH<sub>3</sub>), 1.27 (d, <sup>3</sup>J<sub>H,H</sub> = 6.2 Hz, 12H, CH<sub>3</sub>), 4.49 (s, 4H, CH<sub>2</sub>), 4.83 (d, sept, <sup>3</sup>J<sub>POCH</sub> = 10.6 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.2 Hz, 4H, OCH), 6.24 (br. d, <sup>2</sup>J<sub>PNH</sub> = 10.0 Hz, 2H, NH), 7.14–7.17 (m, 4H, *o*-Ph), 7.37–7.51 (m, 6H, *m*-Ph + *p*-Ph) ppm. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = 58.8 (q, <sup>3</sup>J<sub>POCH</sub> ≈ <sup>2</sup>J<sub>PNH</sub> ≈ 10 Hz) ppm. IR: ν = 627 (P=S), 983, 1004 (POC), 1537 (S=C–N), 3354 (NH) cm<sup>−1</sup>. Calc. for C<sub>28</sub>H<sub>44</sub>N<sub>4</sub>O<sub>4</sub>P<sub>2</sub>S<sub>4</sub> (690.88): C, 48.68; H, 6.42; N, 8.11. Found: C, 48.79; H, 6.38; N, 8.15%.

**$H_2L^b$ :** Yield: 1.81 g (71%). M.p. 118 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.32–1.41 (m, CH<sub>3</sub>), 4.77 (d, sept overlapped with the main signal at 4.82 ppm, <sup>3</sup>J<sub>POCH</sub> = 9.9 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.2 Hz, OCH, minor form), 4.82 (d, sept, <sup>3</sup>J<sub>POCH</sub> = 10.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.0 Hz, OCH, major form), 5.09, 5.18 (NH, minor form), 7.02 (d, <sup>2</sup>J<sub>PNH</sub> = 13.0 Hz, PNH, major form), 11.05 (s, PNH, major form) ppm. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ = 1.33–1.39 (m, CH<sub>3</sub>), 4.80–4.95 (m, OCH), 8.60 (d, <sup>2</sup>J<sub>PNH</sub> = 14.2 Hz,

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