



Zinc and mercury complexes of benzil bis(4-methyl-3-thiosemicarbazone)



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ABSTRACT

The ligand benzil bis(4-methyl-3-thiosemicarbazone), LMe₂H₄, reacts with zinc and mercury nitrates, both in the presence or in the absence of lithium hydroxide. Complexes containing a neutral or a doubly deprotonated ligand, depending on the reaction conditions, have been prepared. In all the complexes, the bis(thiosemicarbazone) acts as a N₂S₂ tetradentate ligand and in complex **4** probably also as a bridge through the sulfur atom leading to a dinuclear structure, while complex **3** is a monomer with a water molecule coordinated to the zinc atom in a penta-coordinated environment. Complexes **1** and **2** contain monodentate nitrate ligands in a hexa-coordinated structure, which is confirmed by the crystal structure of complex **2**, [Hg(LMe₂H₄)(NO₃)₂]. The complexes have been thoroughly characterized by elemental analysis, mass spectrometry, FTIR and ¹H, ¹³C and ¹⁹⁹Hg NMR spectroscopy and in the case of complex **2**, also by single crystal X-ray diffraction.

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1. Introduction

Thiosemicarbazones, TSCs, are ligands of great interest, due to their versatility as donor systems, the variety of chemical species that form [1,2], the wide and important type of reactions that can lead and their biological, structural and optical properties [3–5], which are normally increased in bis(thiosemicarbazones), since they form very stable complexes with metal ions due to its capacity to form several five-member chelate rings. All of this makes that their pharmacological properties and coordinative behavior towards transition metal ions are widely studied. Moreover, copper(II) bis(thiosemicarbazone) complexes have been explored as radiopharmaceuticals for positron emission tomography (PET) over the last decade [6–8]. The selective detection of heavy and toxic metal ions in the background of biologically relevant metal ions is important with respect to human health and the environment. Therefore, development of chemical turn-on sensors for the selective and sensitive determination of toxic metals [9], such as copper [10] or mercury [11–13] in aqueous medium is of crucial importance. However, very few mercury(II) complexes with thiosemicarbazones are known, although they are potentially good candidates to give stable complexes with this soft and toxic ion.

Following our interest in the coordinating behavior of symmetric and dissymmetric bis(thiosemicarbazone) ligands with

different metals with potential biological applications such as nickel [14], copper [15], zinc [14,16] or tin [17] or with demonstrated toxicity as cadmium [14,18,19], lead [20] and mercury [21,22], in this paper we report an extension of our previous work with the symmetric ligand benzil bis(4-methyl-3-thiosemicarbazone), LMe₂H₄. This ligand has shown a versatile behavior with toxic metals such as PbPh₂²⁺ and cadmium(II) and, depending of the pH, it acts as neutral or doubly deprotonated ligand. In all the complexes behaves as a tetradentate quelate donor and in some complexes also as a bridge through a sulfur atom, leading to the formation of dimeric species [17,19,20].

In this paper, the synthesis and spectroscopic characterization of four new complexes of zinc(II) and mercury(II) nitrates, and the crystal structure of the mercury complex, [Hg(LMe₂H₄)(ONO₂)₂], **2**, are reported.

2. Experimental

2.1. Materials and general methods

All reagents were obtained from standard commercial sources and were used as received. **Caution!** Mercury is highly toxic cumulative poison, and their compounds should be handled carefully. Microanalyses were carried out using a LECO CHNS-932 Elemental Analyzer. FTIR spectra in the 4000–400 cm⁻¹ range were recorded as KBr pellets on a Jasco FT/IR-410 spectrophotometer. Fast atom bombardment mass spectra were recorded on a VG Auto Spec instrument using Cs as the fast atom and *m*-nitrobenzylalcohol

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(*m*-NBA) as the matrix. Electrospray mass spectrometry experiments were performed with an ion trap instrument LCQ Deca XP plus (Thermo Instruments). An ESI source was used in positive ionization mode. Conductivity was measured using a freshly prepared DMF solution (ca. 10^{-3} M) at 25 °C with a Crison EC-Meter BASIC 30+ instrument. ^1H , ^{13}C and ^{199}Hg NMR spectra were recorded on a spectrometer Bruker AMX-300 using DMSO- d_6 , CDCl_3 or DMF + CDCl_3 as solvents and TMS (^1H and ^{13}C) or HgMe_2 (^{199}Hg) as internal reference. ^{13}C CP/MAS NMR spectra were recorded at 298 K in a Bruker AV400WB spectrometer equipped with a 4 mm MAS NMR probe (magic-angle spinning) and obtained using a cross-polarization pulse sequence. The external magnetic field was 9.4 T, the sample was spun at 10–14 kHz and the spectrometer frequency was 100.61 MHz. For the recorded spectra a contact time of 4 ms and recycle delays of 4 s were used. Chemical shifts are reported relative to TMS, using the CH group of adamantane as a secondary reference (29.5 ppm).

2.2. Synthesis of the ligand, LMe_2H_4

This molecule was synthesised following the procedure previously reported [23]. Selected spectroscopic data: ^1H NMR (DMSO- d_6), δ/ppm : 9.85 (2H, s, NH), 8.89 (2H, q, CH_3NH , $^3J = 4.6$ Hz), 7.72 (4H, m, Ph), 7.38 (6H, m, Ph), 3.01 (6H, d, CH_3N , $^3J = 4.6$ Hz). ^{13}C NMR (DMSO- d_6), δ/ppm : 178.6 (CS), 140.4 (CN), 133.2, 130.3, 129.1, 126.8 (Ph), 31.5 (CH_3). ^{13}C CP/MAS NMR δ/ppm : 177.2 (CS), 139.8 (CN), 130.6, 128.1, 124.7 (Ph), 32.1 (CH_3). FTIR (KBr, cm^{-1}): 3383(sh), 3335(s) [$\nu(\text{NH})$], 1608(sh) [$\nu(\text{CN})$], 1546(s) [thioamide II] and 845(w) [$\nu(\text{CS})$].

2.3. Synthesis of the complexes

All the reactions were carried out using the same general procedure: a solution of 0.18 mmol of the corresponding metal nitrate in 2 mL of solvent was added to a suspension of 0.18 mmol of LMe_2H_4 in 20 mL of solvent with 1, 2 or any equivalent of $\text{LiOH}\cdot\text{H}_2\text{O}$.

The particular conditions of each reaction, together with the product obtained and yield, are described below.

2.3.1. $[\text{Zn}(\text{LMe}_2\text{H}_4)(\text{ONO}_2)_2][\text{Zn}(\text{LMe}_2\text{H}_4)(\text{OH}_2)(\text{ONO}_2)]\text{NO}_3\cdot\text{H}_2\text{O}$ **1**

The suspension was stirred in ethanol under reflux for 24 h. The yellow solid precipitated was filtered off, washed with ethanol and dried in *vacuo*. Yield: 79% (85 mg). *Anal. Calc.* for $\text{C}_{36}\text{H}_{44}\text{N}_{16}\text{O}_{14}\text{S}_4\text{Zn}_2$ (1183.91): C, 36.49; H, 3.75; N, 18.92; S, 10.81. Found: C, 36.29; H, 3.61; N, 18.80; S, 10.69%. MS (ESI $^+$): m/z 446.9 ($[\text{Zn}(\text{LMe}_2\text{H}_3)]^+$). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mL}^{-1}$): 120.8. ^1H NMR (DMSO- d_6), δ/ppm : 11.03, 9.50 (2H, s, NH), 8.65, 8.60 (2H, q, CH_3NH), 7.9–7.1 (10H, m, Ph), 3.05, 2.98 (6H, d, CH_3NH). ^{13}C NMR (DMSO- d_6), δ/ppm : 179.3, 179.0 (CS), 143.8, 143.6 (CN), 135.5, 131.4, 130.8, 129.9, 128.9, 128.4, 127.9, 127.1 (Ph), 31.8, 31.7 (CH_3) ppm. FTIR (KBr, cm^{-1}): 3435(m) [$\nu(\text{OH})$], 3223(m), 3141(m) [$\nu(\text{NH})$], 1633(w) [$\nu(\text{CN})$], 1589(s) [thioamide II] 1384(s) [$\nu(\text{NO})$] and 823(w) [$\nu(\text{CS})$].

If the reaction was carried out in methanol under reflux, the starting compounds were recovered.

2.3.2. $[\text{Hg}(\text{LMe}_2\text{H}_4)(\text{ONO}_2)_2]$ **2**

The resulting ethanolic suspension was stirred for 24 h at room temperature. The obtained yellow solid was filtered off, washed with ethanol and dried in *vacuo*. Yield: 57% (73 mg). MS (FAB $^+$): 585.1 ($[\text{Hg}(\text{LMe}_2\text{H}_3)]^+$, 80%). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mL}^{-1}$): 57.1. ^1H NMR (DMSO- d_6), δ/ppm : 9.55 (2H, br. s, NH), 8.19 (2H, br. s, CH_3NH), 7.82–7.25 (10H, m, Ph), 2.95 (6H, d, CH_3N). ^{13}C CP/MAS NMR δ/ppm : 174.7 (CS), 146.6 (CN), 130.1, 128.5 (Ph), 33.3 (CH_3). ^{199}Hg NMR (DMSO- d_6), δ/ppm : –917.8. ^{199}Hg NMR (DMF + CDCl_3) δ/ppm : –898.3. FTIR (KBr, cm^{-1}): 3237(m) [$\nu(\text{NH})$], 1634(w)

[$\nu(\text{CN})$], 1588(s) [thioamide II], 1384(s) [$\nu(\text{NO})$] and 826(w) [$\nu(\text{CS})$]. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution in methanol.

2.3.3. $[\text{Zn}(\text{LMe}_2\text{H}_2)(\text{OH}_2)]\cdot 2\text{H}_2\text{O}$ **3**

The reaction was carried out in methanol in the presence of two equivalents of $\text{LiOH}\cdot\text{H}_2\text{O}$. The suspension was stirred at room temperature for 24 h. The yellow precipitate formed was filtered off, washed with methanol and dried in *vacuo*. Yield: 87% (79 mg). *Anal. Calc.* for $\text{C}_{18}\text{H}_{24}\text{N}_6\text{O}_3\text{S}_2\text{Zn}$ (501.96): C, 43.07; H, 4.82; N, 16.74; S, 12.78. Found: C, 43.09; H, 4.88; N, 16.66; S, 12.50%. MS (FAB $^+$): m/z 446.9 ($[\text{Zn}(\text{LMe}_2\text{H}_3)]^+$, 20%). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mL}^{-1}$): 4.3. ^{13}C CP/MAS NMR δ/ppm : 172.1 (CS), 160.8 (CN), 129.0 (Ph), 30.6 (CH_3). FTIR (KBr, cm^{-1}): 3431(m) [$\nu(\text{OH})$], 3386(m) [$\nu(\text{NH})$], 1620 (w), [$\nu(\text{CN})$], 1544(m) [thioamide II] and 843(w) [$\nu(\text{CS})$].

This complex was also isolated in the presence of one equivalent of $\text{LiOH}\cdot\text{H}_2\text{O}$, but with a lower yield (42%) than in the presence of two equivalents.

2.3.4. $[\text{Hg}(\text{LMe}_2\text{H}_2)]_2$ **4**

The reaction was performed in methanol in the presence of two equivalents of $\text{LiOH}\cdot\text{H}_2\text{O}$ and the suspension was stirred for 24 h at room temperature. The yellow solid formed was filtered off, washed with methanol and dried in *vacuo*. Yield: 95% (100 mg). MS (ESI $^+$): m/z 585.1 ($[\text{Hg}(\text{LMe}_2\text{H}_3)]^+$), 969.2 ($[\text{Hg}(\text{LMe}_2\text{H}_3)_2\text{H}]^+$), 1166.2 ($[\text{Hg}_2(\text{LMe}_2\text{H}_2)_2\text{H}]^+$). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mL}^{-1}$): 2.4. ^1H NMR (DMSO- d_6), δ/ppm : 8.65 (2H, q, CH_3NH), 7.62 (4H, m, Ph), 7.29 (6H, m, Ph), 3.18 (6H, d, CH_3NH). ^{13}C CP/MAS NMR δ/ppm : 178.3, 174.8 (CS), 148.0 (CN), 129.3 (Ph), 31.0 (CH_3). ^{199}Hg NMR (DMSO- d_6), δ/ppm : –714.3. ^{199}Hg NMR (CDCl_3) δ/ppm : –1241.1. FTIR (KBr, cm^{-1}): 3375(m) [$\nu(\text{NH})$], 1615(w) [$\nu(\text{CN})$], 1550(s) [thioamide II] and 841(w) [$\nu(\text{CS})$].

If the reaction was carried out in the presence of one equivalent of $\text{LiOH}\cdot\text{H}_2\text{O}$, a mixture of **2** and **4** (major product) was obtained.

2.4. Crystallography

Data for complex **2** was acquired using a Bruker AXS Kappa Apex-II diffractometer equipped with an Apex-II CCD area detector using a graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å). The substantial redundancy in data allows empirical absorption corrections (SADABS) [24] to be applied using multiple measurements of symmetry-equivalent reflections. The raw intensity data frames were integrated with the SAINT program, which also applied corrections for Lorentz and polarization effects [25]. The software package SHELXTL version 6.10 was used for space group determination, structure solution and refinement. The structure was solved by direct methods (SHELXS-97) [26], completed with difference Fourier syntheses, and refined with full-matrix least squares using SHELXL-97 minimizing $\omega(F_0^2 - F_c^2)$. Weighted R factors (R_w) and all goodness of fit S are based on F^2 ; conventional R factors (R) are based on F [27]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The NH atoms were located in a difference Fourier map and their coordinates and isotropic thermal parameters subsequently refined. CH hydrogen atoms were positioned geometrically after each cycle of refinement.

3. Results and discussion

3.1. Synthesis

The synthesis conditions as well as the proposed structures of the complexes are summarized in Scheme 1. The reactions were carried out mixing the corresponding metal nitrate dissolved in

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