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Reactivity of benzil bis(4-methyl-3-thiosemicarbazone) with cadmium nitrate. Crystal structure of $[Cd(LMe_2H_4)(NO_3)_2][Cd(LMe_2H_4)(NO_3)(H_2O)]NO_3 \cdot H_2O$

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ABSTRACT

The reaction between cadmium nitrate dihydrate and benzil bis(4-methyl-3-thiosemicarbazone), LMe_2H_4, depends on the working conditions. In methanol the reaction gives the novel complex $[Cd(LMe_2H_4)(NO_3)_2][Cd(LMe_2H_4)(NO_3)(H_2O)]NO_3 \cdot H_2O$ (**1**). Its crystal structure shows the presence of two cadmium atoms with different coordination numbers, seven and eight, and the ligands acting as N_2S_2 neutral molecules. One cadmium has the coordination sphere completed by a bidentate nitrato group and a water molecule, whereas the other one is bonded to two bidentate nitrato groups. Both molecules are joined to one nitrate ion and to an additional water molecule by hydrogen bonds. In the presence of lithium hydroxide, the reaction leads to a binuclear complex with the ligand doubly deprotonated $[Cd(LMe_2H_2)]_2$ (**2**). The complexes were characterized by elemental analysis, mass spectrometry, ^{13}C and ^{113}Cd CP/MAS NMR and, in the case of complex **1**, by X-ray diffraction.

1. Introduction

In recent years, the heavy element cadmium has received increased attention due to its impact on plants and toxicity to humans, as well as for the luminescent properties of its complexes [1–6]. Cadmium is an extremely toxic element that is naturally present in the environment and also as a result of human activities. Its toxicity derives from the fact that it is rapidly localized intracellularly, mainly in the liver, and then is bound to metallothionein forming a complex that is slowly transferred to the bloodstream to be deposited in the kidneys. Therefore, it is an interesting area of research to get compounds which are able to form stable complexes with cadmium, because they could be employed as detoxificating agents. For this purpose thiosemicarbazone ligands could be very appropriate as both the ligands and their complexes have shown a wide range of pharmacological properties [7–9]. In particular, cadmium and mercury complexes of the related ligand benzil bis(thiosemicarbazone) have antimicrobial and antifungal activity [10], so it could be expected that these cadmium derivatives also possess some activity and studies are underway.

The coordination number of six for Cd(II) ions is well documented [11–13], but seven-coordinate complexes are scarce [14–17], and they are rarely found together in one compound [18]. An eight-coordinate structure is usually formed with species having larger ion radius, such as lanthanides and third row transition metals, and it is relatively unusual for the Cd(II) ion [19]. As far as we know, there are only two complexes containing simultaneously both seven- and eight-coordinate cadmium(II), a cluster and a complex with the ligand acting as bridge [20,21]. On the other hand, there are only two seven-coordinate cadmium(II) complexes of thiosemicarbazones that have been structurally characterized, one with a tridentate ligand and another containing 2,6-diacetylpyridine bis(^{2}*N*-methylthiosemicarbazone) [17,21]. Benzil bis(4-methyl-3-thiosemicarbazone) LMe_2H_4 (see Scheme 1) has four donor atoms that can lead to a tetradentate coordination mode, so there are at least two sites available on the Cd(II) ion for the NO_3^- coordination. This ligand has shown versatile behaviour with $PbPh_2Cl_2$, depending on the pH it acts as a monodeprotonated or dideprotonated ligand, it also acts as a bridge through a sulfur atom [22].

Following our systematic study on the coordination chemistry of thiosemicarbazone ligands with toxic metals [22], here we report the synthesis and structural characterization of two new cadmium coordination compounds derived from benzil bis(4-methyl-3-thiosemicarbazone). Complex **1** is obtained in methanol and it contains two different types of Cd(II) ions. The Cd(1) atom is seven-coordinate by two nitrogen and two sulfur atoms from the ligand and three oxygen from a bidentate nitrato ligand and one water molecule, but in the Cd(2) coordination sphere the water molecule is replaced by an additional bidentate nitrato group. Both units are linked to a nitrate ion and a water molecule by hydrogen bonds. Complex **2** is synthesised in the presence of lithium hydroxide, so the ligand is doubly deprotonated and the cadmium(II) atom could be penta-coordinate in a binuclear structure. To the best of our knowledge, here we report the first thiosemicarbazone

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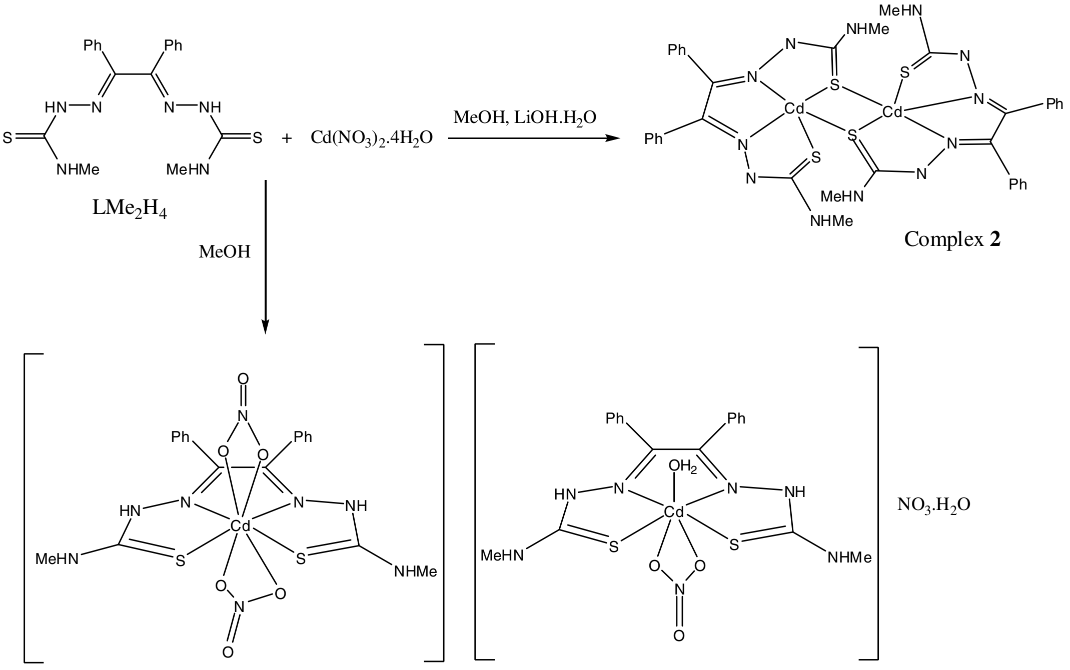

Complex **1**

Scheme 1. A drawing showing the working conditions and the complexes obtained.

complex with eight-coordinate Cd(II). Moreover, it also is the first compound in which two cadmium ions are present with seven and eight coordination spheres in two independent units.

2. Experimental

2.1. Materials and methods

4-Methyl-3-thiosemicarbazide, 1,2-diphenylethanedione and cadmium nitrate tetrahydrate were used as received. Microanalyses were carried out using a Perkin–Elmer 2400 II CHNS/O Elemental Analyser. IR 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 (*m*NBA) as the matrix. ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer using methanol-d_4 and DMSO-d_6 as solvents and TMS as an internal reference. ^{113}Cd NMR spectra were recorded in the same spectrometer using methanol-d_4 or DMSO-d_6 as solvents and using absolutes as references, the chemical shifts are reported relative to Cd(ClO$_4$)$_2$ 0.1 M. ^{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. For the recorded spectra a contact time of 4 ms was used and recycle delays of 4 s were used. Chemical shifts are reported relative to TMS, using the CH group of adamantano as a secondary reference (29.5 ppm). ^{113}Cd CP/MAS NMR spectra were also recorded in the same spectrometer and the chemical shifts are reported relative to Cd(ClO$_4$)$_2$ 0.1 M, using Cd(NO$_3$)$_2 \cdot$ 4H$_2$O as secondary reference (−100 ppm).

2.2. Synthesis of benzil bis(4-methyl-3-thiosemicarbazone), LMe$_2$H$_4$

This molecule was synthesised as reported earlier [23]. Selected spectroscopic data: ^{13}C NMR (DMSO-d_6, 300 MHz, 25 °C): 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 (300 MHz, 25 °C): δ/ppm 177.2 (CS), 139.8 (CN), 130.6, 128.1, 124.7 (Ph), 32.1 (CH$_3$). FTIR (KBr, cm^{-1}): 3420, 3386, 3342, 3330, 3210, 3151 (s) [ν(NH)], 1608 (w) [ν(CN)], 1581 (s) [δ(NH$_2$)] and 848 (w) [ν(CS)].

2.3. Synthesis of [Cd(LMe$_2$H$_4$)(NO$_3$)$_2$][Cd(LMe$_2$H$_4$)(NO$_3$)(H$_2$O)]NO$_3 \cdot$ H$_2$O (**1**)

Cadmium nitrate tetrahydrate (0.12 g, 0.39 mmol) dissolved in methanol (15 mL) was added to a LMe$_2$H$_4$ (0.15, 0.39 mmol) solution in methanol (15 mL). The mixture was stirred under reflux for 6 h. The solution was concentrated whereby a solid precipitated, which was filtered off, washed with methanol and dried in vacuo. M.p.: 187 °C. The compound was isolated as a yellow solid (0.16 g, 64%). Suitable crystals for X-ray analysis were obtained by slow evaporation of the mother liquor. M.p.: 187 °C. *Anal.* Calc. for C$_{36}$H$_{42}$N$_{16}$O$_{14}$S$_4$Cd$_2$ (1275.9): C, 33.88; H, 3.32; N, 17.57; S, 10.03. Found: C, 33.75; H, 3.44; N, 17.16; S, 10.19%. ^{13}C NMR (300 MHz, methanol-d_4): δ/ppm 181.0 (CS), 148.8 (CN), 131.9, 130.9, 130.7, 130.3, 130.1, 129.8, 129.5, 129.2, 128.1, 128.0 (Ph), 32.1 (CH$_3$). ^{113}Cd NMR (300 MHz, methanol-d_4): δ/ppm 167.3 ^{13}C CP/MAS NMR (300 MHz): δ/ppm 180.2 (CS), 148.1, 147.0 (CN), 134.1, 131.9, 130.8, 129.0, 128.1, 127.1 125.8 (Ph), 35.3, 31.4 (CH$_3$). ^{113}Cd CP/MAS NMR (300 MHz): δ/ppm 186.3, 144.3. MS (FAB$^+$): *m/z* 496.8 ([Cd(LMe$_2$H$_3$)]$^+$, 100%). FTIR (KBr, cm^{-1}) 3446, 3344, 3222 (m) [ν(NH)], 1617 (w) [ν(CN)], 1574 (s) [δ(NCS)], 1384 (s) [ν(NO)], 819 (w) [ν(CS)].

2.4. Synthesis of [Cd(LMe$_2$H$_4$)]$_2$ (**2**)

The reaction was carried out as described previously, but in the presence of LiOH $\cdot$ H$_2$O (0.04 g, 0.79 mmol). Complex **2** was isolated as an orange solid (0.17 g, 88%), washed with methanol and dried in vacuo. M.p.: 247 °C. *Anal.* Calc. for C$_{36}$H$_{36}$N$_{12}$S$_4$Cd$_2$ (988.8): C, 43.68; H, 3.67; N, 16.98; S, 12.96. Found: C, 43.52; H, 3.65; N, 16.84; S, 12.87%. ^{113}Cd NMR (300 MHz, DCM + CDCl$_3$): δ/ppm 410.4. ^{13}C CP/MAS NMR (300 MHz): δ/ppm 178.7, 162.5, 158.7