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Mercury and methylmercury complexes with a triazine-3-thione ligand

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Abstract

Reactions of 5-methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]triazine-3-thione LH_2OCH_3 with $Hg(NO_3)_2 \cdot H_2O$ and HgMeCl afforded monomeric compounds in which the triazine loses the methoxy group and binds to the mercury through the sulphur atom, acting as monodentate. The coordination number found around the metal ion in both complexes is two, giving a linear disposition. This coordination mode is different from the ones that have been previously reported, where the ligand acts as bidentate NS or bidentate NS bridging via the sulphur atom, and unusual behaviour for a triazine ligand. Complexes have been characterised by mass spectrometry, IR, multinuclear (^{1}H , ^{13}C) NMR, and X-ray diffraction. The redox behaviour was explored by cyclic voltammetry and both complexes show Hg(II)/Hg(I) processes.

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1. Introduction

The increasing interest in thiosemicarbazones (TSCs) that has arisen in the last decades is related to their wide range of biological and pharmacological properties, which confers numerous applications, for example as antibacterial, antiviral and anticancer agents [1-4]. In addition, in our research group we have been interested in the preparation of potentiometric ion-selective electrodes (ISE), to detect and if possible to remove toxic metals, as mercury and copper. In particular, we have applied copper complexes with the open chain ligand benzilbis(thiosemicarbazone) in the development of potentiometric sensors for copper determination [5]. A macrocyclic thiohydrazone ligand (derived from benzil) has been successfully used as modified carbon paste electrode for voltamperometric determination and speciation of copper in water samples [6] and we have recently studied the application of a carbon paste electrode modified with benzilbis(thiosemicarbazone) to mercury speciation in water [7]. Mercury is a very toxic element, in particular its alkyl derivatives, due to its action as enzymatic blocking agent and affinity for thiol groups, so selective complexation and extraction of this cation at low concentrations levels are necessary [8,9].

Furthermore, triazine derivatives have traditionally found applications in analytical chemistry as complexation agents, in electrochemistry as multi-step redox systems and as pesticide or herbicide components in agriculture. In the last years, there has been a growing interest in these compounds that have been used, for example, as templates in multidimensional crystal engineering involving metal complexes for producing nanometre sized oligonuclear coordination compounds, as scaffold in combinatorial chemistry, as well as new building blocks in peptidomimetics and as anticancer agents [10,11]. Therefore, the synthesis of mercury compounds with triazines derived from thiosemicarbazones is an interesting topic to pursue.

Due to the electronic delocalisation, which is enhanced upon deprotonation, TSC ligands are very versatile. This fact, together with the presence of different types of donor atoms, allows several coordination modes possible [12,13]. So that, depending on the metal coordination preferences a

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Scheme 1. Drawing of LH₂OCH₃.

particular ligand can show different coordination behaviour, as we have established in previous works [14]. In fact, we have characterized complexes of the title ligand acting as bidentate NS giving monomeric complexes with some organotin (IV) derivatives [15], as well as with nickel and cobalt salts. With other metals, as cadmium, acts also as bidentate bridging via the sulphur atom, giving dinuclear structures [16].

The most usual type of coordination in compounds of Hg(II) is a distorted octahedron with two bonds much shorter than the other four. In extreme, this results in a linear-2 coordination in which case bonds are largely covalent. This situation usually takes place with S-donor ligands. The complexes $[Hg(5-CF_3-pyS_2)]$ and $[Hg(5-CF_3-MepyS_2)]$ are examples of this type of coordination, where the Hg(II) ion is bonded to two ligands via the sulphur atoms, giving a linear SS disposition [17,18].

The aim of this work is the synthesis and characterization of mercury complexes derived of 5-methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]triazine-3-thione LH_2OCH_3 (Scheme 1), in order to get new complexes and to explore their potential capability as modifiers of a carbon paste electrode for mercury determination and kinetic speciation in water samples. In this paper, we report the synthesis and structural characterisation of two mercury compounds with this cyclic ligand. In both complexes, and induced by the metal structural preferences, the triazine acts as monodentate through the sulphur atom, behaviour that has not been observed previously.

2. Experimental

2.1. Physical measurements

IR spectra in the 4000–400 cm⁻¹ range were recorded as KBr pellets on a Jasco FT/IR-410 spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a spectrophotometer Bruker AMX-300 using CDCl₃ and DMSO- d_6 as solvents and TMS as reference. Fast atom bombardment (FAB) mass spectra were recorded on a VG Auto Spec instrument using Cs as the fast atom and *m*-nitrobenzilalcohol (*m*NBA) as the matrix. Conductivity data were measured using freshly prepared DMF solutions (ca. 10⁻³ M) at 25 °C with a Metrohm Herisau model E-518 instrument. Electrochemical measurements were performed with a BAS CV 27 voltammograph and a BAS A-4 XY register using a glassy carbon (\emptyset 5 mm) as working electrode, a platinum wire as auxiliary, and a double junction, with porous ceramic wick, Ag/AgCl as reference electrode, standardized for the redox couple ferricinium/ ferrocene ($E_{1/2} = +0.400$ V, $\Delta E_p = 60$ mV). Cyclic voltammetry studies of LH2OCH3 and complexes were carried out on 0.01 M solutions in dimethylformamide containing 0.1 M [NBu₄][PF₆] as supporting electrolyte. The range of potential studied was between +1.0 and -2.2 V. All solutions were purged with nitrogen steam for 5 min before measurement and the working electrode was polished before each experiment with diamond paste. The procedure was performed at room temperature and nitrogen atmosphere was maintained over the solution during the measurements.

2.2. Crystallography

Crystals were mounted on a glass fibre and transferred to a Bruker SMART 6K CCD area-detector three-circle diffractometer with a MAC Science Co., Ltd. Rotating Anode (Cu K α radiation, $\lambda = 1.54178$ Å) generator equipped with Goebel mirrors at settings of 50 kV and 110 mA. X-ray data were collected with a combination of six runs at different φ and 2θ angles, 3600 frames. The data were collected using 0.3° wide ω scans and crystal-to-detector distance of 4.0 cm. Empirical absorption corrections (SADABS) [19] were applied using multiple measurements of symmetry-equivalent reflections (ratio of minimum to maximum apparent transmission: 0.373482 for complex 1 and 0.556564 for complex 2). The unit cell parameters were obtained by full-matrix least-squares refinements of 5528 and 7730 reflections for complexes 1 and 2, respectively. The raw intensity data frames were integrated with the SAINT [20] program, which also applied corrections for Lorentz and polarization effects. The software package SHELXTL [21] version 6.10 was used for space group determination, structure solution and refinement. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods (SHELXS-97) [22], completed with difference Fourier syntheses, and refined with full-matrix least squares using SHELXL-97 [23] minimizing $\omega (F_o^2 - F_c^2)^2$. Weighted R factors (R_w) and all goodness of fit (S) are based on F^2 ; conventional R factors (R) are based on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersions factors are contained in the SHELXTL [24] 6.10 program library. H atoms were found in a difference map, but were then positioned geometrically and included as riding, with C-H = 0.95and 0.99 Å, and $U_{iso}(H) = 1.2 U_{eq}(C)$. The coordinates were refined as riding on the parent atom and the occupancy and U_{ii} were fixed.

2.3. Syntheses

All reagents and other solvents were obtained from standard commercial sources and were used as received.

2.4. 5-Methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]triazine-3-thione, LH₂OCH₃

The characterisation of the ligand LH_2OCH_3 was previously published [24], although it was synthesised according to a modified procedure [25].

Selected spectroscopic data: IR (KBr, cm⁻¹): 3184s and 3131s (NH), 1608w (C=N), 1550s (NCS), 846w (CS). ¹H NMR (300 MHz, CDCl₃, 25 °C): 3.4 (s, 3H, OCH₃), 6.9 (d, 1H, NH), 7.1–7.3 (m, 6H, Ph), 7.4 (m, 2H, Ph), 7.6 (m, 2H, Ph), 9.5 (d, 1H, NH), ¹³C NMR (300 MHz, CDCl₃, 25 °C): 169.7 (CS), 142.4 (CN), 141.7, 133.7, 129.3, 126.5, (Ph), 83.2 (CR₄), 50.7 (CH₃O).

2.5. $[HgL_2](1)$

This complex was prepared as previously reported [26]. M.p. 218 °C (D). $\Lambda_{\rm M}$ (DMF, Ω^{-1} cm² ml⁻¹): 25. m/z (FAB⁺): 731 ([HgL₂ + 1]⁺, 30%). Selected spectroscopic data: IR (KBr, cm⁻¹): 1601w, 1581w (C=N), 1491s (NCS), 815w (CS). ¹H NMR (300 MHz, DMSO, 25 °C): 7.4–7.1 (m, Ph). ¹³C NMR (300 MHz, DMSO- d_6 , 25 °C): 174.7 (CS), 154.3, 153.2 (CN), 135.2, 134.4, 130.9, 129.5, 129.4, 129.0, 128.6, 128.1 (Ph). Single crystals of complex 1 suitable for X-ray analysis, were grown by slow evaporation of a solution of the complex in acetonitrile.

2.6. [HgMeL] (2)

Over a solution of LH₂OCH₃ (0.32 g, 1.1 mmol) and $LiOH \cdot H_2O$ (0.05 g, 1.1 mmol) in 50 ml of methanol was drop wise added a solution of HgMeCl (0.27 g, 1.1 mmol) in the same solvent. The solution was stirred at room temperature for 6 h. Then it was evaporated until a yellow solid appeared, which was filtered off and vacuum dried. Yield 73%. m.p 140 °C. Λ_{M} (DMF, $\Omega^{-1} \text{ cm}^{2} \text{ ml}^{-1}$): 9. m/z (FAB+): 482.0 ([HgMeL + 1]⁺, 100%). 696.0 $([Hg_2MeL + 1]^+, 30\%), 945 ([Hg_2Me_2L_2]^+, 4\%), 961.1$ $([Hg_2Me_2L_2]^+, 2\%)$. IR (KBr, cm⁻¹): 1598w, 1578w (C=N), 1483s (NCS), 816w (CS). ¹H NMR (300 MHz, DMSO- d_6 , 25 °C): 7.3–7.5 (m, 10H, Ph), 0.89 (s, 3H, CH₃, $J^2(^{199}\text{Hg}^{-1}\text{H}) = 186 \text{ Hz}$). ¹³C NMR (300 MHz, DMSO- d_6 , 25 °C): 176.5 (CS), 154.6, 153.1 (CN), 135.6, 135.4, 130.7, 129.6, 129.2, 129.1, 128.6, 128.5 (Ph), 9.4 (CH₃). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the complex in DMF.

3. Results and discussion

In the synthesis of both complexes takes place the loss of the methoxy group as a methanol molecule, probably due to acid–base reaction with the relatively high acidic N–H bond, yielding LH, according to a mechanism previously published. Reaction with mercury nitrate does not need the presence of lithium hydroxide, which is necessary in the reactions studied with other metal salts [15,16].

Conductivity measurements in DMF indicate the presence of non-ionic species in this solvent [27]. The mass spectrometry indicates the different mercury/ligand ratio. Mass spectrum of complex 1 shows a peak corresponding to $[HgL_2 + 1]^+$, which indicates the presence of a specie containing one mercury ion and two deprotonated ligands. However, mass spectrum of complex 2 shows a peak at 482.0 amu, which is attributed to $[HgMeL + 1]^+$ and corresponds to the molecular ion. The other peaks observed are probably due to molecular associations produced during the experiment.

The X-ray analysis shows that the crystal structure of complex 1 is made up of discrete centrosymmetric molecules of $[HgL_2]$ (Fig. 1), which agrees with the spectroscopic data, but rules out the structure previously proposed for this complex [26]. The mercury atom is bonded to two sulphur atoms of two thiosemicarbazone ligands in a linear disposition (S-Hg-S = 180.0°). Complex 2 consists of [HgMeL] entities (Fig. 2), where the mercury is also in a linear disposition, bonded to the sulphur atom of a triazine ligand and the methyl group (S-Hg-C = 175.7°). Crystallographic data and selected bond distances and angles are given in Tables 1–3.

In both complexes, the triazine rings can be considered planar with a maximum deviation of 0.0498 Å for C(3) in complex 1 and 0.0571 Å for C(1) in complex 2. The sulphur atom is 0.260 Å above this plane in complex 1 and 0.3385 Å under in complex 2. The mercury atom is 0.5938 Å above this plane and 0.2791 Å under in complexes 1 and 2, respectively. The aromatic rings form with respect to this plane dihedral angles of 44.9° for C(10)–C(15) and 36.95° for C(4)–C(9) in complex 1 and 47.22° and 31.92°, respectively, in complex 2. An important change is observed with respect to LH₂OCH₃, where the dihedral angles are 95.07° and 36.94°, respectively, [24]. This change in one of the phenyl rings could be explained by the loss of the methoxy group, although it also could be attributed to crystal packing. Owing to deprotonation, there is a considerable electronic delocalisation through the thiosemicarbazone backbone, which is slightly larger in complex 2. As a consequence all the C-N bonds have almost the same length, which does not occur in LH2OCH3 (1.28-1.459 Å). In the complexes, the thione bonds distances (1.755 and 1.763 Å for complexes 1 and 2) are longer than in the precursor ligand (1.628 Å) and they are closer to the value expected for a single bond (1.82 Å) [28]. In addition the N(3)-C(2)-C(3) angles are close to 120°, as would be expected for sp^2 hybridisation, while in LH₂OCH₃ is 108° , corresponding to sp³ hybridisation.

Although there is no covalent bond between the mercury atom and N(1) in complex 1 and N(3) in complex 2, there is some interaction, because N–Hg distances are



Fig. 1. Molecular structure of complex [HgL₂] 1. Thermal ellipsoids are shown at 50% probability.



Fig. 2. Molecular structure of complex [HgMeL] 2. Thermal ellipsoids are shown at 50% probability.

2.806 and 3.146 Å, respectively, which are larger than the sum of the covalent radii (2.25 Å), but shorter than the sum of the Van der Waals radii (3.23 Å). Some authors assume that if the Hg–N distance is lower than the sum of the Van der Waals radii there is covalent bond [29]. The non-existence of a Hg–N bond in both complexes is supported by the S–Hg–S angle, which is perfectly linear. If the mercury ion would have to accommodate an additional bond with the nitrogen atom, there must be a change in the sp hybridisation, which will be reflected in a deviation of the angle [13].

There are π - π interactions between the phenyl rings, with a distance of 3.817 Å in complex 1 and 3.846 Å in complex 2.

The crystal structure of complex 1 belongs to the monoclinic system. In the crystal packing the mercury atoms are placed in the eight corners and in the middle of a cube, giving a body-centred cubic packing.

The absence of any band in the 2600-cm^{-1} region in the IR spectra of both complexes suggests the absence of any thiol tautomer [30]. In the spectra, there are no bands in the $3000-3300\text{-cm}^{-1}$ region, which indicates the absence of N–H bonds. Moreover bands attributable to the nitrate group in complex 1 are not observed [31]. The absence of these bands confirms that the ligand acts as a monoanion L in this complex. The band corresponding to the CS moiety is shifted to lower frequencies, indicating coordination of the sulphur to the metal ion. The presence of two bands

Table 1		
Crystal data an	d structure refinement for	complexes 1 and 2

	1	2
Formula	$C_{30}H_{20}N_6S_2Hg$	C ₁₆ H ₁₃ N ₃ SHg
M	729.23	479.94
Crystal system	monoclinic	orthorhombic
Space group	P2(1)/n	<i>P</i> 2(1)2(1)2(1)
a (Å)	10.3574(2)	5.9923(10)
b (Å)	11.5451(2)	14.0288(3)
c (Å)	11.5016(3)	18.5810(3)
α (°)	90	90
β (°)	98.9730(10)	90
γ (°)	90	90
$U(\text{\AA}^3)$	1358.50(5)	1562.01(5)
Ζ	2	4
$D_{\rm calc} ({\rm Mgm^{-3}})$	1.783	2041
Absorption coefficient (mm ⁻¹)	11.850	18.882
<i>F</i> (000)	708	904
Goodness-of-fit on F^2	1.002	1.064
Reflections collected	8487	9395
Independent reflections $[R_{int}]$	2469 [0.0443]	2872 [0.0539]
Completeness to $\theta = 70.53^{\circ}$ (%)	95.1	96.9
Absorption correction	sadabs v. 2.03	sadabs v. 2.03
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Final R_1 and $wR_2 [I > 2\sigma(I)]$	$R_1 = 0.0286, wR_2 = 0.0719$	$R_1 = 0.0316, wR_2 = 0.0783$
R indices (all data)	$R_1 = 0.0346, \ wR_2 = 0.0756$	$R_1 = 0.0335, wR_2 = 0.0800$

Table 2

Selected bond distances (Å) for complexes $[HgL_2] 1$ and [HgMeL] 2

	[HgL ₂] 1	[HgMeL] 2
Hg(1)–S(1)	2.3362(10)	2.3703(16)
Hg(1)-C(16)		2.086(8)
N(1)–N(2)	1.334(4)	1.335(8)
N(1)–C(1)	1.336(4)	1.312(9)
N(2)-C(3)	1.338(4)	1.343(7)
N(3)–C(1)	1.326(4)	1.341(7)
N(3)–C(2)	1.334(4)	1.326(8)
S(1)–C(1)	1.755(3)	1.763(7)
C(2)–C(3)	1.413(4)	1.430(8)

Table 3

Selected angles (°) for complexes [HgL₂] **1** and [HgMeL] **2**

0 ()	1 1021 10	-
	[HgL ₂] 1	[HgMeL] 2
N(2)–N(1)–C(1)	118.1(3)	117.5(5)
N(1)-N(2)-C(3)	119.6(3)	120.5(5)
C(1)-N(3)-C(2)	116.5(3)	117.1(5)
N(3)-C(1)-N(1)	125.6(3)	125.9(6)
N(3)-C(1)-S(1)	116.6(2)	119.9(5)
N(1)-C(1)-S(1)	117.8(2)	114.2(4)
N(3)-C(2)-C(3)	119.6(3)	118.6(5)
N(3)-C(2)-C(4)	115.8(3)	117.6(5)
C(3)-C(2)-C(4)	124.6(3)	123.8(5)
N(2)-C(3)-C(2)	119.8(3)	119.1(6)
N(2)-C(3)-C(10)	115.2(3)	115.9(5)
C(2)-C(3)-C(10)	125.1(3)	125.0(5)
C(1)–S(1)–Hg(1)	94.01(11)	102.0(2)
S(1)#1-Hg(1)-S(1)	180.00(2)	
C(16)-Hg(1)-S(1)		175.7(3)

attributable to C=N bonds could indicate the formation of a new imine group, due to the loss of the methoxy group of the ligand LH_2OCH_3 , although the great electronic delocalisation in the ring probably leads to there being only one C=N band and the new band could be due to the hydrazinic CN. These imine nitrogen atoms are non-coordinate to the metal ion.

The ¹H NMR spectra of both complexes show a multiplet in the aromatic region, corresponding to the phenyl rings of the ligand. In complex 2 a signal at 0.89 ppm, corresponding to the CH₃ group, can also be observed. The absence of any signal corresponding to amine protons supports the ligand deprotonation. The absence of the singlet attributable to the methoxy group at 3.4 ppm confirms the loss of the inserted methoxy group. In the spectrum of complex 2, the singlet corresponding to the methyl group shows the satellites corresponding to the coupling with the mercury ion with $J^2 = 186$ Hz.

In the ¹³C NMR spectra the signals corresponding to the methoxy group (50.7 ppm) and the tetrasubstituted carbon atom (83.2 ppm) of LH₂OCH₃ have disappeared and a new signal corresponding to an imine group is observed. The imine groups are not bonded to the metal ion, as the X-ray diffraction has established for complexes 1 and 2. In addition the signal corresponding to the thione group is deshielded, suggesting the presence of metal–sulphur bonds. In complex 2, the signal of the methyl group bonded to the mercury atom appears at 9.4 ppm.

Cyclic voltammetry of the ligand LH₂OCH₃ and complex 1 have been previously published [26]. Complex 1 shows a reversible redox couple at $E_{1/2} = -0.492$ V. On scanning from +1.0 to -2.2 V cyclic voltammogram of complex 2 shows a redox couple at $E_{1/2} = -0.275$ V, corresponding to a Hg(II)/Hg(I) process (Fig. 3) and two irreversible cathodic peaks corresponding to ligand reduction processes at -1.325 and -1.825 V. Analysis of the redox couple in the interval 25–800 mV s⁻¹ shows a lineal variation of i_{pc} versus



Fig. 3. Cyclic voltammogram of complex [HgMeL] 2 in DMF; v = 100 mV/s. Inset the redox couple.

 $v^{1/2}$. Small dependence of the potential peak with the scan rate is observed, and the i_{pa}/i_{pc} ratio is close to the unity. These results suggest a diffusion controlled quasirreversible process [32]. The reduction process Hg(II)/Hg(I) is more difficult in complex 1, where the mercury atom is bonded to two sulphur atoms due to the fact that electronic density over the metal ion is bigger than when the environment is formed by one sulphur and one carbon atom, as occurs in complex 2.

4. Conclusions

Reactions of the ligand LH_2OCH_3 with two mercury salts lead to the formation of the corresponding coordination compounds, where the ligand has lost the methoxy group and acts as a monoanion. The methylmercury derivative is only obtained in the presence of basic medium.

In both complexes the ligand acts as monodentate and binds to the mercury ion through the sulphur atom, giving a linear disposition around the metal. This coordination mode is usually observed in mercury complexes, although coordination only via the sulphur atom is not frequent in triazines and it is observed for the first time in this particular ligand.

The results obtained confer good prospects for compound 2 to be used to prepare new sensors for the highly toxic HgMe⁺ ion. Development of these sensors is very important due to alkyl mercury derivatives are great environmental pollutants and could affect food and soils (some compounds are used as pesticides in the treatment of seeds and can be introduced in natural waters).

5. Supplementary material

CCDC 256950 for complex **1** and 269350 for complex **2** contain the supplementary crystallographic data for this

paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk.

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