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Synthesis and characterisation of zinc, cadmium and mercury complexes of benzilbisthiosemicarbazone. Structure of cadmium derivative

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Abstract

Complexes $[MLH_6(NO_3)_2]$ (M = Cd, Hg) (1 and 2), $[MLH_4]$ (M = Hg, Zn) (3 and 5) and $[ZnLH_5NO_3]$ (4) have been synthesised by reaction of benzilbisthiosemicarbazone LH₆ with cadmium, mercury and zinc nitrates in ethanol. The X-ray diffraction study of cadmium complex 1 shows that the azomethine nitrogen atoms, the sulfur atoms and the nitrate groups are bonded to the cadmium atom giving, the first time for this kind of ligands, a distorted octahedral geometry. Complexes have been characterised by elemental analyses and mass spectra as well as by IR, ¹H, ¹³C and ¹¹³Cd NMR and ¹³C and ¹¹³Cd CP/MAS NMR spectroscopies. In all complexes LH₆ acts as a tetradentate N₂S₂ ligand. The electrochemical behaviour of complexes, studied by cyclic voltammetry, shows metal centred and ligand reduction processes for all of them. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many studies on complexes of transition metal ions with macroligands have been reported due to their relationship with biological molecules, most of them contain tetradentate SNNS ligands [1–6]. However, complexes of metals of Group 12 constitute an especially attractive topic in view of the marked differences among these metals as regards both chemical behaviour and biological activity. Zn(II) is an essential ion because of its presence in certain metalloenzymes [7–9] while cadmium and mercury, present in the environment, are toxic but only recent studies have considered the reactivity of macroligands containing sulfur with zinc, cadmium and mercury [10–23].

In the last few years, a large number of works have tried to design compounds highly selective and sensitive to heavy metals, in order to detect and if it is possible, to remove them. Many different strategies have been proposed, such as the preparation of fluorescent or electrochemical sensors [24-26].

In previous works [27-31], we have been interested in the synthesis and characterisation of transition metal complexes with macroligands containing thiosemicarbazone moieties. Benzilbisthiosemicarbazone (LH₆) is a suitable ligand because it has donor atoms (nitrogen and sulfur) which bond to mercury, cadmium and zinc. LH₆ complexes are very stable because of its chelating character, yielding pseudomacrocyclic complexes. Furthermore, LH₆ copper complexes have been applied in potentiometric copper sensors [32]. Now, we have extended our interest in cadmium and mercury complexes because of their potential application as electrochemical sensors of these metals.

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The high sensitivity of the ¹¹³Cd chemical shift to the co-ordination environment (donor atom, co-ordination number and geometry) enables to apply ¹¹³Cd NMR spectroscopy as a probe of the metal in binding sites in biological system and co-ordination compounds. When cross polarisation magic angle spinning (CP/MAS) ¹¹³Cd NMR spectroscopy is combined with X-ray crystallography, an excellent opportunity is provided to study and correlate metal ion geometry with the chemical shifts. ¹¹³Cd NMR signals in solid or solution are able to describe the ligand and its geometry about the cadmium atom [17,33-35]. The aim of this work is to prepare new benzilbisthiosemicarbazone complexes with zinc, cadmium and mercury nitrates and to characterise them in solution and in solid state by infrared, nuclear magnetic resonance of proton, carbon and cadmium spectroscopies, conductivity measurements, mass spectrometry together with X-ray data for the cadmium nitrate derivative. We also explore the electrochemical behaviour of the new compounds, which is the first requirement to apply them as electrochemical sensors.

2. Experimental

2.1. Reagents

Cadmium, mercury and zinc nitrates were commercial products of highest chemical grade (Fluka). Solvents were purified according to standard procedures.

2.2. Synthesis

Benzilbisthiosemicarbazone, LH_6 was prepared following the procedure previously reported [36].

2.2.1. $[CdLH_6(NO_3)_2]$ (1)

A solution of cadmium nitrate hexahydrate (0.52 g, 1.70 mmol) in ethanol (25 cm³) was added to a suspension of LH₆ (0.60 g, 1.70 mmol) in the same solvent (25 cm³). The mixture, which immediately changed to yellow, was: stirred at room temperature for 6 h or refluxed with stirring for 6 h. In both procedures the yellow solid formed was filtered off and then treated with ethanol with stirring for 15 min. The residual solid was separated by filtration. The filtrate was concentrated until a pale-yellow solid was obtained. Yield 62%, m.p. 220 °C. *Anal.* Found: C, 32.48; H, 2.76; N, 18.78; S, 10.75. C₁₆H₁₆N₈S₂CdO₆ requires C, 32.41; H, 2.70; N, 18.91; S, 10.80%. *m/z* 569 (*M* – 2NO₃, 10%). $\Lambda_{\rm M} = 62 \, {\rm cm}^2 \, {\Omega}^{-1} \, {\rm mol}^{-1}$ in DMF, $\Lambda_{\rm M} = 13 \, {\rm cm}^2 \, {\Omega}^{\rm mol}^{-1}$ in CH₃CN.

2.2.2. $[HgLH_6(NO_3)_2]$ (2)

To a suspension of LH_6 (0.40 g, 1.11 mmol) in ethanol (30 cm³) was added a suspension of mercury

nitrate monohydrate (0.38 g, 1.11 mmol) in ethanol (40 cm³). The mixture was stirred for 12 h at room temperature (r.t.). The yellow solid formed was filtered off and then partially dissolved in ethanol (filtering again to remove the insoluble fraction) and concentrated in vacuo until a yellow solid was obtained. Yield 42%, m.p. 180 °C with decomposition. $\delta_{\rm H}$ (300 MHz, (CD₃)₂SO) 8.4 (2H, s, NH), 7.5 (4H, s, NH₂), 7.1–7.3 (10H, m, HPh). m/z 557 (M – 2NO₃, 8%) $\Lambda_{\rm M}$ = 66 cm² Ω^{-1} mol⁻¹ in DMF, $\Lambda_{\rm M}$ = 16 cm² Ω mol⁻¹ in CH₃CN.

2.2.3. $[HgLH_4]$ (3)

After complex **2** was maintained in ethanol during several days an orange solid was obtained, which was filtered off and dried in vacuo. M.p. 190 °C. $\delta_{\rm H}$ (300 MHz); solvent (CD₃)₂SO, 7.5 (4H, s, NH₂), 7.1–7.3 (10H, m, HPh), m/z 557 (M^+ + 1, 15%). $\Lambda_{\rm M}$ = 17 cm² Ω^{-1} mol⁻¹ in DMF.

2.2.4. $[ZnLH_5NO_3]$ (4)

To a suspension of LH₆ (0.50 g, 1.58 mmol) in ethanol (40 cm³) was added zinc nitrate hexahydrate (0.50 g, 1.88 mmol) in the same solvent (10 cm³). The mixture was stirred under reflux for 4 h. The yellow–orange solid was filtered off, washed with ethanol and dried in vacuo. Yield 50%, m.p. 260 °C. *Anal.* Found: C, 39.65; H, 3.15; N, 20.17; S, 13.18. C₁₆H₁₅N₇S₂ZnO₃ requires C, 39.80; H, 3.11; N, 20.31; S, 13.27%. *m/z* 419 ($M - NO_3$, 100%). $A_M = 51$ cm² Ω mol⁻¹ in DMF.

2.2.5. $[ZnLH_4]$ (5)

An orange solid was formed from the filtrate of the previous synthesis after cooling it during 2 months at -20 °C. The solid was filtered off and dried in vacuo. M.p. 260 °C. Found: C, 45.64; H, 3.34; N, 20.01, S, 14.76. C₁₆H₁₄N₆S₂Zn requires C, 45.78, 3.60; N, 19.78; S, 14.66%. m/z 419 (M^+ + 1, 10%).

2.3. Physical measurements

Microanalyses were carried out using a Perkin-Elmer 2400 II CHNS/O elemental analyser. IR spectra were recorded as KBr pellets on a Bomen-100 spectrophotometer in the range 4000-400 cm⁻¹ and between 550 and 200 cm⁻¹ on a Bruker IFS 66V. UV-Vis spectra in solution were registered on a Ati-Unicam UV2 spectrophotometer. Conductivity data were measured using freshly prepared DMF and CH₃CN solutions (ca. 10^{-3} M) at 25 °C with a Metrohm Herisau model E-518 instrument. ¹H, ¹³C and ¹¹³Cd NMR spectra in solution were recorded on a spectrophotometer Bruker AMX-300 using dimethylsulfoxide-d₆ or methanol-d₄ as solvents and TMS or 0.1M aqueous Cd(ClO₄)₂ as references. ¹¹³Cd CP/MAS NMR spectrum was obtained at 298 K in a Bruker MSL-400 spectrometer, using a standard cross-polarisation pulse sequence [37-39]. The external magnetic field was 9.4 T, and the sample was spun at 4-4.5 kHz around an axis inclined 54°44' with respect to this field. Spectrometer frequencies were set to 88.76 MHz. For recorded spectrum a contact time of 10 ms was used. The number of scans ranged 4000. ¹³C CP/MAS NMR spectra were obtained in the same spectrophotometer with the frequency set to 100.63 MHz and a contact time of 1ms. Chemical shifts values were referenced to the same solution. The analysis of ¹¹³Cd CP/MAS NMR spectrum was done with the WINFIT Program. In this program the principal values of the chemical shift anisotropy tensor were determined from the intensity of sidebands with Herzfeld and Berger's method [40]. 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.

2.4. Crystallography

Single crystals of CdLH₆(NO₃)₂ (1) were grown by vapour diffusion of Et₂O into a 2:1 methanol: acetonitrile solution. Crystal data: CdC₁₆H₁₆N₈O₆S₂, M =592.89, orthorhombic, a = 14.522(3), b = 11.161(2), c = 27.754(6) Å, U = 4498(2) Å³, T = 293(2) K, space group *Pbca*, Z = 8, μ (Mo K α) = 1.208 mm⁻¹, 7518 reflections measured, 3902 unique ($R_{int} = 0.0316$). The final indices were $R_1(I > 2\sigma(I)) = 0.034$, $wR_2 = 0.0728$ and S = 0.988 for 298 parameters.

The unit cell parameters were determined and the data collected on a Siemens STADI4 diffractometer. The data were corrected for Lorentz-polarisation effects and for absorption (empirical scan). The structure was solved by direct methods and refined (full-matrix least-squares on F^2) by using the SHELXTL/PC v5.0 package [41]. All non-hydrogen atoms were refined anisotropi-



Fig. 1. An ORTEP drawing of complex [CdLH₆(NO₃)₂] (1).

cally while hydrogen atoms were included in calculated positions and treated as riding atoms.

2.5. Electrochemical properties

Electrochemical measurements were performed with a BAS CV 27 voltammograph and a BAS A-4 XY register using a glassy carbon (ϕ 5 mm) as working electrode, a platinum wire as auxiliary, and a double junction, with porous ceramic wick, Ag/AgCl as reference electrode, standardised by the redox couple ferricinium/ferrocene ($E_{1/2} = +0.48$ V, $\Delta E_p = 60$ mV). Cyclic voltammetry studies of the ligand 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 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.

3. Results and discussion

Reactions of LH_6 with cadmium nitrate only give complex 1. From mercury nitrate two complexes 2 and 3 are isolated as well as from zinc nitrate, where complexes 4 and 5 are isolated.

Analytical data for complexes indicate a variable grade of deprotonation in the ligand depending on the metal ion. For complex 1, data are in agreement with the presence of two nitrate groups, with LH₆ acting as a neutral molecule. Complexes from zinc nitrate show variable grade of deprotonation: complex 4 contains a nitrate group and the ligand acts as a monoanion but in complex 5 benzilbisthiosemicarbazone is a dianionic ligand. Conductivity data in DMF of complexes indicate that all of them are non-electrolyte compounds, so the nitrates are bonded to the metal ion. Data for complexes 1 and 2 are close to the limit values for 1:1 electrolytes, probably due to a partial substitution of one of the nitrate groups by solvent molecules [42].

3.1. X-ray structure of complex 1

The crystal structure of **1** consists of discrete $[CdLH_6(NO_3)_2]$ molecules, held together in the crystal packing by hydrogen bonds. A perspective view of the complex with the atom labeling scheme is given in Fig. 1 whereas selected bond lengths and angles are in Table 1. Within the complex the cadmium(II) ion is hexa-coordinated in a distorted octahedral arrangement toward a symmetry pseudo- C_{2v} . In this octahedral description four of the co-ordination positions belong to the unde-

Table 1 Bond lengths (Å) and bond angles (°) for 1

Bond lengths			
Cd(1)–N(4)	2.437(3)	Cd(1)–S(9)	2.5492(12)
Cd(1)–N(7)	2.438(3)	Cd(1)–O(23)	2.436(3)
Cd(1)–S(2)	2.5348(13)	Cd(1)–O(32)	2.491(3)
N(1)-C(2)	1.314(5)	C(9)–N(10)	1.320(5)
C(2)–N(3)	1.365(5)	N(8)–C(9)	1.369(5)
C(2)-S(2)	1.685(4)	C(9)–S(9)	1.685(4)
N(3)–N(4)	1.353(4)	N(7)–N(8)	1.359(4)
N(4)–C(5)	1.291(5)	C(6)–N(7)	1.289(5)
Bond angles			
S(2)-Cd(1)-S(9)	146.50(4)	O(23)-Cd(1)-S(2)	95.74(9)
S(2)-Cd(1)-N(4)	74.30(8)	O(23)-Cd(1)-N(4)	87.62(11)
N(4)-Cd(1)-S(9)	139.18(8)	O(23)-Cd(1)-N(7)	75.03(11)
N(4)-Cd(1)-O(32)	84.27(11)	O(23)–Cd(1)–S(9)	88.57(9)
N(7)-Cd(1)-N(4)	65.27(11)	O(23)–Cd(1)–O(32)	159.44(10)
N(7)-Cd(1)-S(9)	74.49(8)	O(32)-Cd(1)-S(2)	100.18(8)
N(7)-Cd(1)-S(2)	138.68(8)	O(32)–Cd(1)–S(9)	85.32(8)
N(7)-Cd(1)-O(32)	84.42(10)	N(10)-C(9)-N(8)	114.4(4)
N(1)-C(2)-N(3)	114.9(4)	N(10)-C(9)-S(9)	120.7(3)
N(1)-C(2)-S(2)	120.9(3)	N(8)-C(9)-S(9)	124.8(3)
N(3)-C(2)-S(2)	124.2(3)	N(7)–N(8)–C(6)	120.2(3)
N(4)–N(3)–C(2)	120.2(3)	N(7)–N(8)–C(9)	119.9(3)
C(5)-N(4)-N(3)	119.4(3)	N(7)-C(6)-C(5)	115.7(3)
N(4)-C(5)-C(6)	115.8(3)		

protonated bisthiosemicarbazone ligand which occupies the equatorial positions through the imine nitrogen atoms N(4) and N(7) and the thione groups S(2) and S(9), as could be expected for this kind of ligands. The two remaining positions in the octahedral geometry are the axial ones which are occupied by two nitrate anions. It should be noted that, to the best of our knowledge, the hexa-co-ordination is not frequent for Cd(II) complexes with thiosemicarbazone ligands [43]. Thus, major part of these complexes show a co-ordination number of five or seven [16,18,44–47], and only three could be considered as hexa-co-ordinated [45,48,49]. Nevertheless this complex represents the first example of a hexa-co-ordinated Cd(II) complex with a bisthiosemicarbazone ligand.

In accordance with the symmetry of the ligand bond distances and angles in both thiosemicarbazone moieties are very similar. Bond lengths agree well with an imine-thione form of the ligand, as does the NMR spectroscopy (see below), but with a considerable electronic delocalization through the thiosemicarbazone backbone. Thus, the thione bond distances of ca. 1.69 Å (Table 1) are intermediate between a theoretical C–S single and double bond (1.82 and 1.56 Å, respectively) [50] as occur with the N–N bonds (ca. 1.35 vs. 1.44 Å calculated for a single N–N) and the three C–N bonds of each thiosemicarbazone branch. Furthermore the bond angles in the bisthiosemicarbazone ligand of approximately $120 \pm 5^{\circ}$ are also compatible with the electronic delocalization. Remaining bond distances and

angles are similar to those found in similar Cd(II) complexes and do not deserve further comments. The presence of two distances for the Cd–O and Cd–S bonds agrees with the distorted octahedral geometry.

The pseudo-macrocyclic co-ordination mode of the ligand afford three five-membered chelate rings. The bisthiosemicarbazone core can be considered planar with a maximum deviation from the mean plane of 0.2059 Å for S(9), while the phenyl rings form, with respect to this plane, dihedral angles of 69.2 and 66.8° for C(51)-C(56) and C(61)-C(66), respectively. Thus, from the three limit conformations for the phenyl rings: both rings co-planar with equatorial co-ordination plane, one co-planar and the other perpendicular and both rings perpendicular, the system adopts the latter one which is the disposition less sterically hindered. On the other hand, in bisthiosemicarbazone ligands containing a single phenyl group [46] the ring, less sterically constrained, adopts a closer co-planar arrangement with a dihedral angle in the range of $20-30^\circ$, while in pyridinethiosemicarbazone the aromatic ring is, of course, co-planar with the basal co-ordination plane [17]. Thus, the dihedral angle between the mean basal co-ordination plane and the aromatic ring seems to be a balance of two opposite factors: the steric crowding and the electronic delocalization of the π -system of the thiosemicarbazone branch and the aromatic ring. Therefore, in bisthiosemicarbazone ligands containing a single phenyl ring the electronic factor might be predominant leading to a nearly co-planar conformation while in compounds having two neighboring phenyl rings, these tend to minimize the steric hindrance adopting a greater value of the dihedral angle, being, in addition, both rings parallel to each other.

Finally, the molecules are held together in the crystal packing through an extended network of intermolecular hydrogen bonds involving the amino groups, the protonated N(3) and N(8) atoms and the nitrate anions (see Table 2).

3.2. Spectroscopy

The NMR signal assignments for the free ligand were previously reported [28]. ¹H NMR spectra of mercury complexes 2 and 3, show different number of acidic hydrogen atoms. The spectrum of 2 indicates the presence of hydrogens from the primary and secondary amine groups, while the spectrum of complex 3 does not contain the signals corresponding to the hydrazinic protons. In both spectra the thioamidic proton signals are shifted to high field. These data indicate that LH₆ is in its neutral form in complex 2 but acts as a dianionic ligand, owing to the deprotonation, in complex 3. From the proton resonance data the formulae of mercury complexes 2 and 3 must be equivalent of complex 1 and complex 5, respectively.

Table 2 Relevant hydrogen bonds for 1

Hydrogen bond	N…O (Å)	NHO (°)		
N(1)-H(1A)····O(31) ⁱ	2.993	162.6		
$N(1)-H(1B)\cdots O(31)^{ii}$	3.019	159.3		
N(3)–H(3A)····O(31) ⁱ	3.232	145.3		
N(8)–H(8A)····O(21) ⁱⁱⁱ	3.191	155.8		
N(10)–H(10A)····O(23) ⁱⁱⁱ	2.945	142.0		
$N(10) - H(10A) - O(21)^{iv}$	2.959	153.7		

i = 1-x, y - 1/2, 1.5-z; ii = x - 1/2, y, 1.5-z; iii = 1-x, -y, 1-z; iv = x + 1/2, 1/2-y, 1-z.



Fig. 2. FAB mass spectrum of complex [ZnLH₅(NO₃)] (4).

Mass spectra of all complexes show peaks for the cation $[C_{16}H_{15}N_6S_2M]^+$ revealing the loss of nitrate

Table 3 $^{13}\mathrm{C}$ NMR data in DMSO-d_6 for LH_6 and their complexes

groups in complexes 1, 2 and 4 and peaks corresponding to the molecular ion in complexes 3 and 5. In Fig. 2 the mass spectrum with the theoretical and the experimental isotopic pattern of complex 4 is showed.

¹³C NMR spectra of complexes in DMSO-d₆ solution (Table 3) reveal the thione form of the ligand and co-ordination by the azomethine nitrogens in all complexes [16]. The high field shift of the thione carbon atom (Table 3) in complexes 2 and 3 indicates the co-ordination of the sulfur atoms to the mercury [14,18]. However, the spectrum of complex 1 in methanol shows this signal slightly shifted to low field. The ¹³C CP/MAS NMR spectrum of 1 exhibits aromatic carbon atoms, and the same number of imine and thione carbon atoms (148.9 and 178.9 ppm) than in solution. The thione carbon is slightly shifted to high field indicating that LH_6 acts as a N_2S_2 ligand, as the X-ray structure has established. Because of the low solubility of zinc complexes for NMR studies in solution, the ¹³C CP/MAS NMR of complex 4 was recorded. The spectrum shows signals in the aromatic carbon region and two corresponding to imine carbon at 141.5 and 149.5 ppm and one signal attributable to the thione carbon at 181.0 ppm. These data agree with the asymmetric behaviour of the ligand in this complex, showing the peak at higher field due to the reduction of the double bond character after deprotonation of one NH group. For comparison with the spectral data of complex 1, the co-ordination sphere of the zinc atom must be formed by two azomethine nitrogen, two sulfur and one oxygen atoms, giving a pentaco-ordinated environment for the metal ion, although the tetrahedral geometry is the most common for this metal. This fact can be explained by the planar disposition of the SNNS ligand observed in the cadmium complex, being the fifth position occupied by the nitrate group [15,22].

¹¹³Cd NMR spectrum of complex 1 in methanol exhibits a peak at 177.8 ppm, which agrees with the cadmium co-ordination sphere formed by nitrogen, sulfur and oxygen atoms [17,33]. The sideband pattern of ¹¹³Cd CP/MAS NMR spectrum of complex 1 traces out the envelope of a shielding tensor with an orthorhombic symmetry according to the value $\eta = 0.50$. The anisotropy value (-270.37 ppm) correlate well with a distortion from regular polyhedron due to the presence of three different donor atoms bonded to the cadmium

	C=S	C=N	C ₁	C_2	C ₃	C_4	
LH ₆	179.1	140.5	133.1	130.1	128.9	126.8	
$1 \text{ a } LH_6Cd(NO_3)_2$	181.4	149.7	131.9	130.8	130.7	129.4	
2 $LH_6Hg(NO_3)_2$	173.7	147.7	132.4	129.5	129.0	128.0	
3 LH ₄ Hg	170.8	148.0	135.4	129.7	127.8	127.6	

^a Methanol-d₄ as solvent.

Table 4 Relevant IR spectral data and assignments of LH_6 complexes

	v(NH)	$v(\mathrm{NH}_2)$	v(C=N)	$\delta(\mathrm{NH}_2)$	Thioamide II	Thioamide IV	v(M–S)	v(M–N)	$v(M-O_3N)$
LH ₆	3415, 3342, 3236	3384, 3328, 3145	1610	1585	1465	848			
$1 H_6Cd(NO_3)_2$	3415, 3248	3288, 3150	1628	1575	1433	804	315	494	297
$2 LH_6Hg(NO_3)_2$	3460, 3250	3320, 3141	1613	1573	1489	802	321	459	292
3 LH₄Hg	3433, 3127	3267	1617, 1590	1607	1441	812	342	459	
4 LH ₅ ZnNO ₃	3440, 3268, 3111	3421, 3169	1629, 1576	1615	1439	816	341	447	341
5 LH ₄ Zn	3495, 3266	3327, 3152	1595	1567	1496	816	357	438	

ion (two N, two S and two O) as the crystal structure has shown. The isotropic chemical shift of $\sigma_{iso} = 285$ ppm is in the range expected for an octahedron. NMR parameters and crystallographic data of solid cadmium complex correlate well. The orthorhombic distortion observed at the metal centre of geometrical constraint is due to the crystal geometry. The different chemical shift values observed from cadmium resonance in solution and in solid state are not surprising, since the same fact was described from the carbon resonance studies. In solution, the cadmium co-ordination sphere change with respect to the solid state due to the displacement of the sulfur atoms by the methanol molecules.

The most significant IR bands of LH₆ and their complexes are listed in Table 4. The absence of any bands in the 2600 cm⁻¹ region suggest the absence of any thiol tautomer in the solid state [51]. Spectra of complexes 1 and 2 show several bands in the 3460-3050 cm⁻¹ region, corresponding to NH stretching vibrations, thus indicates that the ligand is in its neutral form. The nitrate ion co-ordinates to a metal as a unidentate, symmetric and asymmetric chelating bidentate, and bridging ligand. It is rather difficult to differentiate these structures by vibrational spectroscopy since the symmetry of the nitrate ion differs very little among them $(C_{2v} \text{ or } C_s)$. In general the separation of the two highest-frequency bands is larger for bidentate than for unidentate co-ordination if the complexes are similar. Both spectra show bands corresponding to the nitrate ion co-ordinated to the metal ion, but due to the presence of multiple bands in this region it is difficult to differentiate the co-ordination mode [52,53]. The three bands observed in the spectra of complexes 3 and 5 between 3500 and 3150 cm⁻¹, together with the absence of bands from the nitrate group, indicate the total deprotonation of the ligand. The spectrum of 4 shows an intermediate situation, with the presence of a nitrate group and a partial loss of the hydrazinic protons in the ligand. The band at 1585 cm⁻¹ assigned in the free ligand to v(C=N) is shifted in all complexes to lower wave number. The new bands observed between 500 and 200 cm⁻¹ assigned to v(MN) confirm the co-ordination through the azomethine nitrogen in all complexes and the oxygen atom from the nitrate in complexes 1, 2 and 4. The co-ordination by the sulphur atoms is observed by a decrease in the frequency of the v(CS) in the spectra of all the complexes. These new bonds are confirmed by the appearance of new bands assignables to v(MS) [46].

The UV–Vis spectrum of LH₆ has a band at 28.985 cm⁻¹ ($\varepsilon = 4.3 \times 10^4$ dm³ mol⁻¹ cm⁻¹) associated with the insaturations present in the molecule. The electronic spectra of complexes **1**, **2** and **3** show a $\pi \rightarrow \pi^*$ centred band at 30.959 cm⁻¹ ($\varepsilon = 1.9 \times 10^4$ dm³ mol⁻¹ cm⁻¹), 32.051 cm⁻¹ ($\varepsilon = 1.3 \times 10^4$ dm³ mol⁻¹ cm⁻¹) and 31.446 cm⁻¹ ($\varepsilon = 1.3 \times 10^4$ dm³mol⁻¹ cm⁻¹), respectively, and an additional band in the visible region at 21.929 cm⁻¹ ($\varepsilon = 1.5 \times 10^3$ dm³ mol⁻¹ cm⁻¹) and 22.522 cm⁻¹ ($\varepsilon = 3.8 \times 10^3$ dm³ mol⁻¹ cm⁻¹), respectively, that are assignable to charge transfer transitions.

3.3. Cyclic voltammetry

The cyclic voltammogram of the ligand in DMF only shows two irreversible cathodic waves in the negative margin (-1.440 and -1.746 V), which can be attributed to the reduction of the imine and thioamide groups present in the ligand [54].

The cyclic voltammograms of all complexes show metal centred reduction processes and waves corresponding to the ligand.

The voltammetric response of complex 1 (Fig. 3) shows an irreversible wave at -1.125 V which can be attributed to a cadmium reduction process, since $Cd(NO_3)_2$ ·4H₂O shows a peak at -0.667 V. Moreover other two peaks corresponding to the ligand shifted to more negative potential values can be observed. Because of the position of the first peak it can be deduced the bigger difficulty to reduce the Cd(II) ion in the complex.

The cyclic voltammogram of complex 2 (Fig. 4) exhibits in the cathodic scan peaks at -0.460, -1.469 and -1.950 V. In the reverse scan, a peak at +0.320 V associated with the one at -0.460 V is observed. The more negative waves correspond to ligand reduc-

tion processes. The redox couple is associated to the process involving the mercury due to the fact that $Hg(NO_3)_2 \cdot H_2O$ in DMF solution shows peaks at -0.162 and +0.570 V.

Voltammetric response of complex 3 shows a similar pattern to that of complex 2, but the reduction process of the metal ion is shifted to positive values, +0.111 V. Potential values for both complexes indicate that is easier the reduction process of the mercury ion for this complex than for complex 2.

The cyclic voltammogram pattern of complex 4 (Fig. 5) depends on the potential range studied. In the range between +1 and -2.2 V two irreversible waves in the negative margin at -1.444 and -1.950 V correspond-



Fig. 3. Cyclic voltammogram for complex $[CdLH_6(NO_3)_2]$ (1), $v = 100 \text{ mV s}^{-1}$.



Fig. 4. Cyclic voltammogram for complex $[HgLH_6(NO_3)_2]$ (2), $v = 100 \text{ mV s}^{-1}$.



Fig. 5. Cyclic voltammogram for complex $[\text{ZnLH}_5(\text{NO}_3)]$ (4), $v = 100 \text{ mV s}^{-1}$.

ing to ligand reductions are observed. However, in the range from 0 to -2.2 V additional peaks are observed.

4. Conclusions

Although the reactions have been carried out following the same procedure for all metal ions, the complexes obtained present different stoichiometry and geometries in accordance with the preferences of each metal ion. The distorted octahedral geometry for the cadmium complex, deduced from the IR spectrum and resonance studies, shows a good correlation with that from the crystallographic data. In the absence of crystal structure data for mercury and zinc complexes, we have proposed those that agree with the spectroscopical data.

Structural characteristics and reactivity of a ligand are valuable information for its potential use as base of a sensor for metals. In this respect, the simplicity to get complexes, their stability and structural characteristics are the most important features for a co-ordination compound to be applied as a sensor. For electrochemical sensors is necessary that the complexes show metal centred redox activity. In previous work, copper complexes of LH₆ have been used as base for potentiometric sensors. From our results, cadmium and mercury complexes have also the requirements to be used as a base of potential modified electrodes for determination and speciation of these metals. In fact the redox properties of LH_6 and of the complex **2** have allowed us to incorporate this ligand to a carbon paste electrode as an amperometric sensor for mercury in natural waters [55]. On the other hand, the N_2S_2 co-ordination sphere for the zinc atom could make it suitable as a metalloen-zyme mimic complex.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 171085. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033; e-mail: deposit@ aadc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

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References

- [1] M.J.M. Campell, Coord. Chem. Rev. 15 (1975) 279.
- [2] D.X. West, S.B. Padhye, B.P. Sonawane, Struct. Bonding 76 (1991) 1.
- [3] S. Padhye, G.B. Kauffman, Coord. Chem. Rev. 63 (1985) 127.
- [4] D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, B.P. Sonawane, A.S. Kumbhar, R.G. Yerande, Coord. Chem. Rev. 123 (1993) 49.
- [5] C.M. Liu, G. Xiong, X. You, Y. Liu, Polyhedron 15 (1996) 4565.
- [6] Z. Duracková, J. Labuda, J. Inorg. Biochem. 58 (1995) 297.
- [7] D.E. Fenton, Biocoordination Chemistry, Oxford University Press, Oxford, 1995.
- [8] W.N. Lipscomb, N. Sträter, Chem. Rev. 96 (1996) 2376.
- [9] H. Holm, P. Kenepohl, E.I. Solomon, Chem. Rev. 96 (1996) 2239.
- [10] J.J. Vittal, P.A.W. Dean, Polyhedron 17 (1998) 1937.
- [11] F. Huesco-Ureña, A.L. Peñas-Chamorro, M.N. Moreno-Carretero, M. Quirós-Olozábal, J.M. Salas-Peregrín, Polyhedron 18 (1998) 351.
- [12] P. Ghost, M. Wood, J. Bonnano, T. Hascall, G. Parkin, Polyhedron 18 (1998) 1107.
- [13] J. Costa, R. Delgado, M.G.B. Drew, V. Félix, J. Chem. Soc., Dalton Trans. (1999) 4331.
- [14] Z. Popovic, D. Matkovic-Calogovic, Z. Soldin, G. Pavlovic, N. Davidovic, D. Vikic-Topic, Inorg. Chim. Acta 294 (1999) 35.
- [15] C. Hennig, K.-H. Hallmeier, G. Zahn, F. Tschwatschal, H. Hennig, Inorg. Chem. 38 (1999) 38.
- [16] E. Bermejo, A. Castiñeiras, R. Domínguez, R. Carballo, C. Maichle-Mössmer, J. Strähle, D.X. West, Z. Anorg. Allg. Chem 625 (1999) 961.
- [17] S. Sen, M.K. Saha, P. Kundu, S. Mitra, C. Kryger, J. Bruckmann, Inorg. Chim. Acta 288 (1999) 118.
- [18] E. Bermejo, R. Carballo, A. Castiñeiras, R. Domínguez, A.E.

Liberta, C. Maichle-Mössmer, M.M. Salberg, D.X. West, Eur. J. Inorg. Chem. (1999) 965.

- [19] H. Adams, R. Bastida, D.E. Fenton, A. Macías, S.E. Spey, L. Valencia, J. Chem. Soc., Dalton Trans. (1999) 4131.
- [20] E. Bermejo, R. Carballo, A. Castiñeiras, R. Domínguez, C. Maichle-Mössmer, J. Strähle, D.X. West, Polyhedron 18 (1999) 3695.
- [21] S. Gourbatsis, S.P. Perlepes, Y.S. Butler, N. Hadjiliadis, Polyhedron 18 (1999) 2369.
- [22] M.L. Durán, A. Sousa, J. Romero, A. Castiñeiras, E. Bermejo, D.X. West, Inorg. Chim. Acta 294 (1999) 79.
- [23] Z. Li, Z.-H. Loh, S.-W. Audi Fong, Y.-K. Yan, W. Henderson, K.F. Mok, T.S.A. Hor, J. Chem. Soc., Dalton Trans. (2000) 1027.
- [24] C.W. Rogers, M.O. Wolf, Chem. Commun. (1999) 2297.
- [25] P.D. Beer, P.A. Gale, G.Z. Chen, J. Chem. Soc., Dalton Trans. (1999) 1897.
- [26] I.A. Shihadeh, A. Benito, J.M. Lloris, R. Martínez-Máñez, T. Pardo, J. Soto, M.D. Marcos, J. Chem. Soc., Dalton Trans. (2000) 1199.
- [27] A. Arquero, M.A. Mendiola, P. Souza, M.T. Sevilla, Polyhedron 15 (1996) 165.
- [28] A. Arquero, M. Cañadas, M. Martínez-Ripoll, M.A. Mendiola, A. Ruíz-Valero, Tetrahedron 54 (1998) 11271.
- [29] E. Franco, E. López-Torres, M.A. Mendiola, M.T. Sevilla, Polyhedron 19 (2000) 441.
- [30] M. Cañadas, E. López-Torres, A. Martínez-Arias, M.A. Mendiola, M.T. Sevilla, Polyhedron 19 (2000) 2059.
- [31] Z. Duracková, M.A. Mendiola, M.T. Sevilla, A. Valent, Bioelectrochem. Bioenerg. 48 (1999) 109.
- [32] M.J. Gismera, M.A. Mendiola, J. Rodríguez Procopio, M.T. Sevilla, Anal. Chim. Acta 385 (1999) 143.
- [33] K.H. Chung, E. Hong, Y. Do, C.H. Moon, J. Chem. Soc., Dalton Trans. (1996) 3363.
- [34] J. Sola, P. González-Duarte, J. Sanz, I. Casals, T. Alsina, I. Sobrados, A. Alvarez-Lorena, J.-F. Piniella, X. Solans, J. Am. Chem. Soc. 115 (1993) 10018.
- [35] N.G. Charles, E.A.H. Griffith, P.F. Rodesiler, E.L. Amma, Inorg. Chem. 22 (1983) 2717 and references therein.
- [36] P. Souza, M.A. Mendiola, A. Arquero, V. Fernández, E. Gutiérrez-Puebla, C. Ruíz-Valero, Z. Naturforsch., Teil b 49 (1994) 263.
- [37] S.R. Hartman, E.L. Hahn, Phys. Rev. 128 (1962) 2042.
- [38] A. Pines, M.G. Gibby, J.S. Waugh, J. Chem. Phys. 59 (1973) 569.
- [39] P.D. Murphy, W.C. Stevens, T.T.P. Cheung, S. Lacelle, B.C. Gerstein, D.M. Kurtz Jr, J. Am. Chem. Soc. 103 (1981) 4400.
- [40] J. Herzfeld, A.E. Berger, J. Chem. Phys 73 (1980) 1021.
- [41] G.M. Sheldrick, SHELXTL/PC v5.0, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1994.
- [42] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
- [43] F.H. Allen, O. Kennard, Chem. Des. Automation News 8 (1) (1993) 1.
- [44] E. Bermejo, R. Carballo, A. Castiñeiras, R. Domínguez, A.E. Liberta, C. Maichle-Mossmer, D.X. West, Z. Naturforsch., Teil b 54 (1999) 777.
- [45] J.S. Casas, M.V. Castaño, M.S. García-Tasende, I. Martínez-Santamarta, J. Sordo, E.E. Castellano, J. Zukerman-Schpector, J. Chem. Res. 324 (1992) 2626.
- [46] A. Castiñeiras, E. Bermejo, D.X. West, L.J. Ackerman, J. Valdés-Martínez, S. Hernández-Ortega, Polyhedron 18 (1999) 1463.
- [47] J.S. Casas, E.E. Castellano, M.S. García-Tasende, A. Sanchez, J. Sordo, J. Zukerman-Schpector, Z. Anorg. Allg. Chem. 623 (1997) 825.

- [48] I.F. Burstein, N.V. Herbellei, V.I. Losan, A. Yu. Kon, O.A. Bologa, T.I. Malinovskii, Zh. Strukt. Khim. 33 (1992) 197.
- [49] X.-G. Cui, Q.-P. Hu, Chin. Chem. Lett. 5 (1994) 893.
- [50] L.E. Sutton, Tables of Interatomic Distances and Configuration in Molecules and Ions (Supplement), The Chemical Society, London, 1965.
- [51] D.E. Fenton, D.H. Cook, J. Chem. Soc., Chem. Commun. (1977) 714.
- [52] J. Valdés-Martínez, R.A. Toscano, A. Zentella-Dehesa, M.M. Salberg, G.A. Bain, D.X. West, Polyhedron 15 (1996) 427.
- [53] K. Nakamoto, Infrared and Raman Spectra of Inorganic Coordination Compounds, 5th ed., Wiley, New York, 1997.
- [54] E. Eisner, E. Karowa-Eisner, in: A.J. Bard, H. Lund (Eds.), Encyclopedia of Electrochemistry of the Elements, vol. 13, Marcell-Dekker, New York, 1979, p. 1.
- [55] M. Colilla, Tesis de Licenciatura, U.A.M., 2000.