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New Neutral Metal Complexes from the 4-*N*-Phenylthiosemicarbazone-2-pyridinecarboxaldehyde Ligand – ^{113}Cd and ^{207}Pb NMR Studies

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Dedicated to Professor Alfonso Castiñeiras on the Occasion of his 65th Birthday

Abstract. The metal complexes studied in this report derive from the ligand 4-*N*-phenylthiosemicarbazone-2-pyridinecarboxaldehyde, abbreviated HL, and the transition and post-transition metals manganese, iron, cobalt, nickel, copper, silver, zinc, cadmium and lead.

The new complexes were obtained by an electrochemical procedure and were found to be of the form $ML_2 \cdot nH_2O$ (n = 1–4) for divalent metals and $ML \cdot nH_2O$ (n = 0, 4) for Cu and Ag metals. These complexes have been wholly characterized by elemental analysis, mass spectrometry, infrared spectroscopy, magnetic measurements and molar conductivities. NMR studies in solution (^{1}H, ^{113}Cd and ^{207}Pb NMR) were also performed. $[MnL_2] \cdot CHCl_3$ (**1**), $[ZnL_2] \cdot CH_3CN$ (**2**) and $[CdL_2] \cdot CH_3CN$ (**3**) could be crystallographically characterized and their crystal structures show the metal atoms in a distorted octahedral environment.

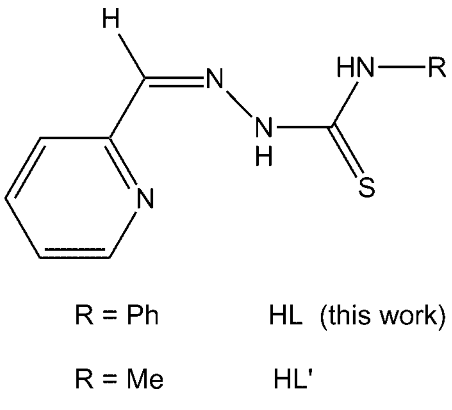
Keywords: Transition metals; Thiosemicarbazone ligands; Electrochemical synthesis; NMR (^{113}Cd and ^{207}Pb); Crystal structures

Introduction

Inorganic and bioinorganic chemists have shown a vast interest in devising small molecules, which can act as models for different metalloproteins or exhibit therapeutic activity. For this purpose the thiosemicarbazone ligands and their metal complexes have resulted very appropriate [1–3]. Specifically, neutral copper complexes with this type of ligands commenced recently to be used as radionuclide agents [4, 5].

Thiosemicarbazone ligands reveal other important applications, for instance as anions receptors [6], as ionophores [7] or for the HPLC separations and determinations of metal ions since their capability to form highly stable complexes [8].

During last years we have centred our efforts in the development of a convenient synthetic route to neutral metal complexes derived from a large variety of thiosemicarbazone ligands. As a result of these studies, we have been able to stabilize neutral complexes with transition and post-transition metal ions using an electrochemical synthesis [9–12]. Lately, we have reported new metal derivatives of the ligand 4-*N*-phenylthiosemicarbazone-2-pyridinecarboxaldehyde (HL′, Scheme 1) [13]. Pharmacologic studies have proved that the introduction of different groups in the 4-N position of the thiosemicarbazone ligand has an important influence in its biological activity [14, 15]. However, it has not been completely proved the clear relationship between biological activity and structure [16]. Accordingly, we have decided to modify the previously reported ligand, H_2L', incorporating a bulkier group in the 4-N position (H_2L, Scheme 1). The earlier work on this system is merely confined to some spectroscopies studies [17, 18]. The interaction of this ligand with transition and post-transition metals by means of an electrochemical procedure was carried out, and the results achieved are reported herein.



Scheme 1

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Results and Discussion

The electrochemical oxidation of a metal anode (Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd and Pb) in the presence of the ligand HL in an organic solvent [19] has been used as an efficient method to stabilize neutral metal complexes.

The reaction of HL with manganese, iron, cobalt, nickel, zinc, cadmium and lead yields complexes: $MnL_2 \cdot H_2O$, $FeL_2 \cdot 2H_2O$, $CoL_2 \cdot 4H_2O$, $NiL_2 \cdot H_2O$, $ZnL_2 \cdot 2H_2O$, $CdL_2 \cdot 2H_2O$, and $PbL_2 \cdot 3H_2O$. The electrochemical efficiency of the cell for these complexes was close to 0.5 mol F^{-1}, which is in accordance with the following mechanism for the reaction:

Cathode: $2HL + 2e^- \rightarrow 2L^- + H_2$
Anode: $2L^- + M \rightarrow ML_2 + 2e^-$

The syntheses of $CuL \cdot 4H_2O$ and AgL involve one electron and the electrochemical efficiency of the cell was around 1 mol F^{-1}. In these cases the proposed mechanism for the reaction can be described as follows:

Cathode: $HL + e^- \rightarrow L^- + {}^1/_2\, H_2$
Anode: $L^- + M \rightarrow ML + e^-$

The metal compounds are obtained in high yield and purity. They are solids apparently stable in the solid state and in solution, with melting points over 300 °C.

These complexes have been characterized by elemental analysis, mass spectrometry and magnetic measurements (Table 6), infrared spectroscopy and molar conductivities (Table 4) and ^1H NMR studies (Table 5). For cadmium(II) and lead(II) complexes we have also performed studies on ^{113}Cd and ^{207}Pb NMR.

Recrystallisation of the orange powder of $MnL_2 \cdot H_2O$ in chloroform lets us to isolate orange crystals of $[MnL_2] \cdot CHCl_3$ (**1**). Slow evaporation of the mother-liquors from the electrochemical reaction of the zinc and cadmium complexes allow isolation of yellow crystals of $[ZnL_2] \cdot CH_3CN$ (**2**) and $[CdL_2] \cdot CH_3CN$ (**3**), respectively.

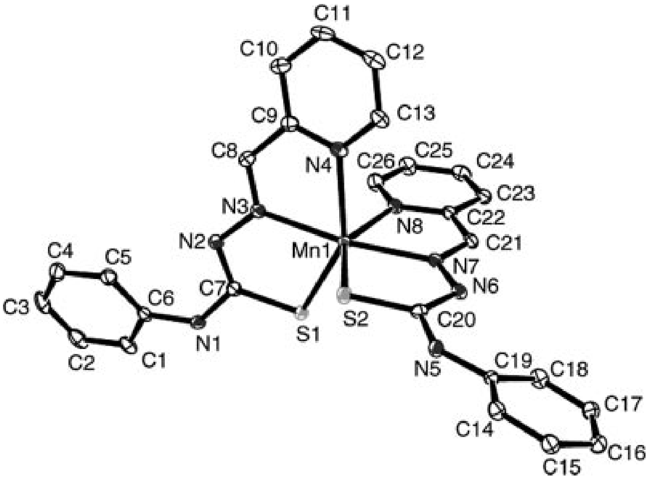

Fig. 1 ORTEP view of complex **1** showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50 % probability level. Lattice $CHCl_3$ is not depicted. Hydrogen atoms are omitted for clarity.

X-ray studies

***Crystal structures of* $[MnL_2] \cdot CHCl_3$ (1), $[ZnL_2] \cdot CH_3CN$ (2) and $[CdL_2] \cdot CH_3CN$ (3):** These analyses show that **1**, **2**, and **3** have similar structures that consist of discrete molecules ML_2. These molecules contain two monodeprotonated ligand units and one metal centre. Additionally, zinc and cadmium complexes contain one acetonitrile molecule as solvate, whilst manganese complex is solvated by one molecule of chloroform.

ORTEP view of **1**, **2** and **3** are shown in Figures 1, 2 and 3, respectively. Selected crystallographic data for the complexes are summarised in Table 1. Bond lengths and angles are listed in Table 2.

All of them crystallize in the monoclinic system, space group P21/c for **1** and C2/c for **2** and **3**. The structures of **2**

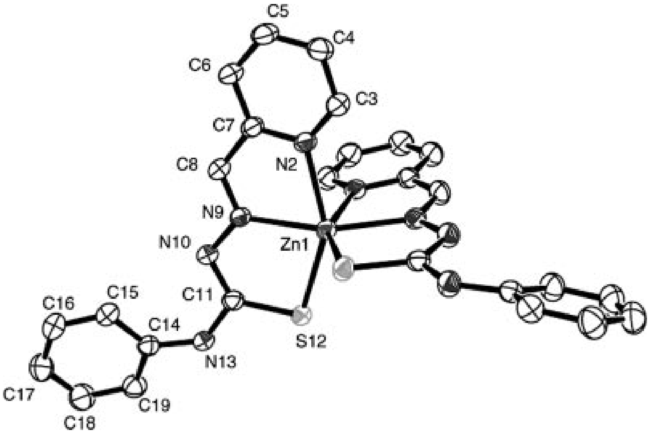

Fig. 2 ORTEP plot of complex **2**. Atoms showing the atomic numbering scheme are represented by their 30 % probability ellipsoids. Lattice CH_3CN is not depicted. Hydrogen atoms are omitted for clarity.

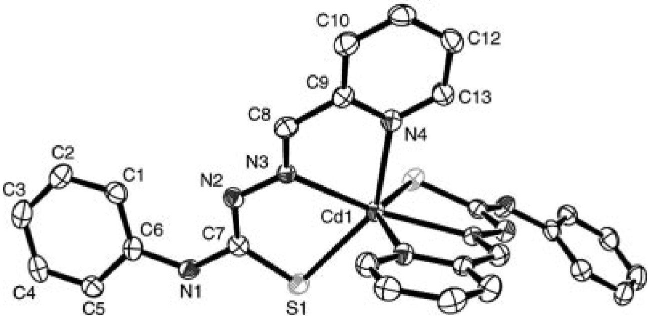

Fig. 3 ORTEP view of complex **3**. Atoms showing the atomic numbering scheme are represented by their 50 % probability level. Lattice CH_3CN is not depicted. Hydrogen atoms are omitted for clarity.

Table 1 Crystal data and details of refinement of **1**, **2** and **3** [a].

	1	**2**	**3**
Formula	$C_{26}H_{22}MnN_8S_2$	$C_{26}H_{22}ZnN_8S_2$	$C_{26}H_{22}CdN_8S_2$
M. W.	565.58	614.04	623.04
a/Å	13.8267(2)	14.0266(13)	13.9556(3)
b/Å	18.9985(3)	19.3208(12)	19.8907(4)
c/Å	11.2970(2)	11.1553(10)	10.7766(2)
β/°	99.0070(10)	105.523(8)	108.0640(10)
V/Å^3	2930.98(8)	2912.9(4)	2843.99(10)
Z	4	4	4
Dc/g cm^{-3}	1.282	1.400	1.455
Space group	$P2_1/c$	C2/c	C2/c
Crystal system	monoclinic	monoclinic	monoclinic
Crystal size/mm	0.16 × 0.10 × 0.06	0.20 × 0.12 × 0.12	0.11 × 0.07 × 0.04
θ range/°	1.49 to 28.32	3.99 to 74.92	1.85 to 26.41
Reflections collected	51648	3079	25402
No. Unique reflections	7298 [R(int) = 0.0688]	2960 [R(int) = 0.0341]	3020 [R(int) = 0.0509]
No. Variables	280	187	136
μ /mm^{-1}	0.621	2.790	0.944
F(000)	1164	1260	1256
Largest Peak and hole/e Å^{-3}	1.528 and −1.593	0.356 and −0.342	3.355 and −1.810
Final R indices [I>2sigma(I)]	R1 = 0.0560, wR2 = 0.1047	R1 = 0.0356, wR2 = 0.0966	R1 = 0.0539, wR2 = 0.1322
R indices (all data)	R1 = 0.0842, wR2 = 0.1143	R1 = 0.0750, wR2 = 0.1110	R1 = 0.0642, wR2 = 0.1375

[a] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC−645786 (**1**), 645787 (**2**), 645785 (**3**). Copies of the data can be obtained free on application to The Director. CCDC. 12. Union Road. Cambridge CB2 1EZ. UK (Fax: int. code + (1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

Table 2 Selected bond lengths/Å and angles/° for **1**, **2** and **3**.

Mn(1)-N(7)	2.2448(17)	Zn(1)-N(2)	2.252(2)	Cd(1) N(3)	2.358(2)
Mn(1)-N(3)	2.2465(17)	Zn(1)-N(2)#1	2.252(2)	Cd(1)-N(3)#1	2.358(2)
Mn(1)-N(8)	2.2870(18)	Zn(1)-N(9)	2.158(2)	Cd(1)-N(4)	2.408(2)
Mn(1)-N(4)	2.2985(18)	Zn(1)-N(9)#1	2.158(2)	Cd(1)-N(4)#1	2.408(2)
Mn(1)-S(2)	2.5318(6)	Zn(1)-S(12)	2.4633(8)	Cd(1)-S(1)	2.5720(12)
Mn(1)-S(1)	2.5383(6)	Zn(1)-S(12)#1	2.4633(8)	Cd(1)-S(1)#1	2.5720(12)
N(7)-Mn(1)-N(3)	171.74(7)	N(2)−Zn(1)−N(2)#1	85.87(11)	N(3)-Cd(1)-N(3)#1	158.11(11)
N(7)-Mn(1)-N(8)	72.36(6)	N(9)−Zn(1)−S(12)#1	113.71(6)	N(3)-Cd(1)-N(4)#1	93.77(8)
N(3)-Mn(1)-N(8)	103.48(6)	N(9)#1−Zn(1)−S(12)#1	77.55(6)	N(3)#1-Cd(1)-N(4)#1	69.34(8)
N(7)-Mn(1)-N(4)	99.95(6)	N(2)−Zn(1)−S(12)	151.34(6)	N(4)-Cd(1)-N(4)#1	82.22(11)
N(3)-Mn(1)-N(4)	72.34(6)	N(2)−Zn(1)−S(12)#1	94.35(6)	N(3)#1-Cd(1)-S(1)	120.87(6)
N(8)-Mn(1)-N(4)	84.99(6)	N(9)−Zn(1)−N(9)	163.53(11)	N(3)-Cd(1)-S(1)	73.76(6)
N(7)-Mn(1)-S(2)	74.81(5)	N(9)−Zn(1)−N(2)#1	93.92(8)	N(4)-Cd(1)-S(1)	142.96(6)
N(3)-Mn(1)-S(2)	108.87(5)	N(9)#1−Zn(1)−N(2)#1	73.85(8)	N(4)-Cd(1)-S(1)#1	97.19(6)
N(8)-Mn(1)-S(2)	147.12(5)	S(12)−Zn(1)−S(12)	98.75(4)	S(1)-Cd(1)-S(1)#1	104.42(4)
N(4)-Mn(1)-S(2)	99.15(5)				
N(7)-Mn(1)-S(1)	112.71(5)				
N(3)-Mn(1)-S(1)	74.21(5)				
N(8)-Mn(1)-S(1)	92.55(5)				
N(4)-Mn(1)-S(1)	144.84(5)				
S(2)-Mn(1)-S(1)	101.58(2)				

and **3** contain a crystallographic twofold axis bisecting the molecules. The environment around the metal atoms can be described as distorted octahedral, where both ligand molecules act as tridentate and monoanionic. In any case the disposition of these ligands drives to the formation of *mer* type isomers.

It must be noted that complexes **2** and **3** are isotypical. The disposition of the two ligands around the metal centre determines the arrangement of these complex molecules in the crystal cell. Therefore, the high symmetry exhibit by complexes **2** and **3** leads to the formation of an ordered network (see Figure 4), in which the solvent molecules (acetonitrile) are accommodated inside.

Each ligand molecule exists in its deprotonated form L$^-$, coordinating to the metal centre through the donor set N_2S, formed by the pyridine nitrogen atom (N4 and N8 for **1**, N2 and N2#1 for **2** and N4 and N4#1 for **3**), the imine nitrogen atom (N3 and N7 for **1**, N9 and N9#1 for **2** and N3 and N3#1 for **3**) and the thioamide sulfur atom (S1 and S2 for manganese complex, S12 and S12#1 for zinc complex and S1 and S1#1 for cadmium derivative). This octahedral geometry is the most found in these metal complexes

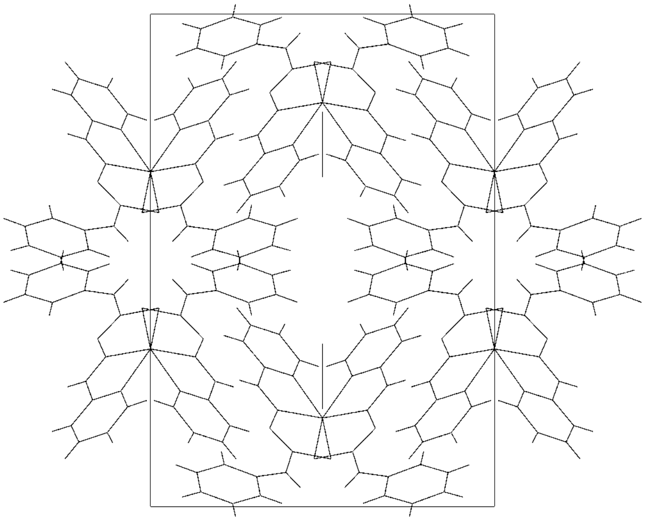

Fig. 4 Illustration of the packing of molecules in complex **2** along axis *c*.

[20−23], however other examples with coordination four or five were also reported with related ligands [24, 25].

This coordination gives rise two five-membered chelate rings with each ligand molecule. Two of the four angles subtended at metal atom by adjacent equatorial atoms are bigger than the value of 90° for an ideal octahedral arrangement [99.97°, 112.68° for **1**; 93.92°, 113.71° for **2**, and 93.77°, 120.87° for **3**], while the other two are smaller [72.31°, 74.27° for **1**; 73.85°, 77.55° for **2**, and 69.34°, 73.76° for **3**]. The axial angle is also smaller than the ideal value of 180° [147.18° for **1**, 151.34° for **2** and 142.96° for **3**].

The bond lengths M−N(imine) are shorter than the M−N(pyridine) ones. And, as expected, the distances M−S are the most longer. These imine C=N and thiolate C−S bond distances of the thiosemicarbazone threads are consistent with strong coordination by the imine nitrogen and the thiolate sulphur atoms [20−23].

In order to check the effect of different groups in the tail of this kind of ligands, we have compared the bond distances and the angles of the manganese complex **1** reported herein, with the previously prepared complex $[MnL'_2]\cdot H_2O$ [13] (Table 3). The $Mn-N_{imine}$ and $Mn-N_{pyridine}$ in **1**, phenyl substituted in the 4-N position, are longer that those found for $[MnL'_2]\cdot H_2O$, methyl substituted in that position. The Mn−S distances show the same tendency. The values of the angles are also more divergent from the ideal value of 90° and 180° for the equatorial and axial positions, respectively, in **1** than in $[MnL'_2]\cdot H_2O$, indicating a higher deviation of the octahedral coordination in **1**. This compared study confirms the steric effect exerted by a bulkier substituent on the 4-N position of the thiosemicarbazone in the resulting structure of the metal complexes.

Table 3 Compared study on selected bond lengths/Å for manganese complexes.

	Reference	$Mn-N_{imine}$	$Mn-N_{py}$	Mn-S
$[MnL_2]\cdot CHCl_3$ (**1**)	This work	2.2448(18) 2.2465(17)	2.2870(18) 2.2985(18)	2.5318(6) 2.5383(6)
$[MnL'_2]\cdot H_2O$	Ref. [13]	2.0205(19) 2.0265(19)	2.114(2) 2.1183(19)	2.4225(8) 2.4378(7)

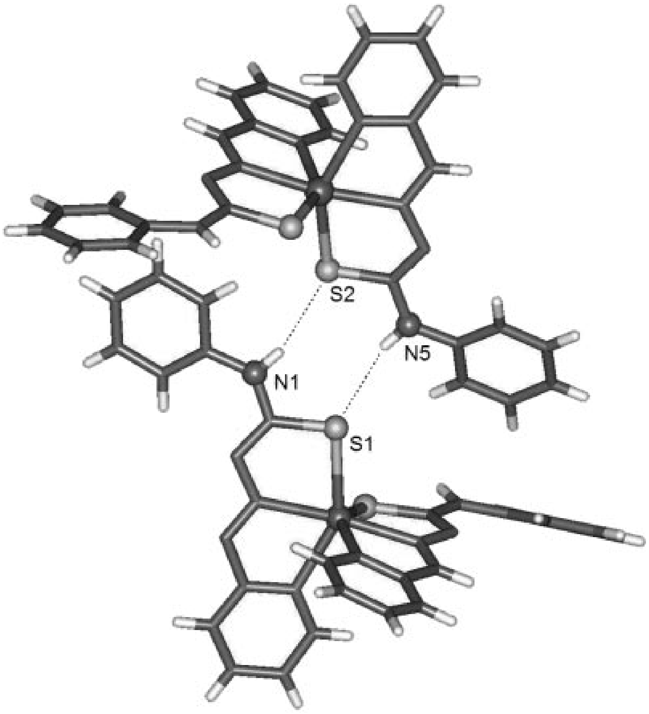

Fig. 5 Partial scheme of the network formed by hydrogen bonds in **1**.

Significant intermolecular interactions *via* hydrogen bonds (see Figure 5) can also be observed between the sulphur atom of one molecule and the hydrazine nitrogen atom of a neighbouring molecule [$N1\cdots S2=3.3758(18)$ Å; $S2\cdots H1-N1 = 147.77°$ and $N5\cdots S1=3.3959(18)$ Å; $S2\cdots H5-N1 = 146.35°$ for **1**; $N13\cdots S12=3.400(2)$ Å; $S12\cdots H13-N13 = 146°$ for **2** and $N1\cdots S1=3.460(3)$ Å; $S1\cdots H1A-N1 = 130.24°$].

Magnetic characterization and conductivity measurements

The magnetic moments at room temperature for the paramagnetic compounds are close to those expected for magnetically diluted M^{II} ions in an octahedral environment. Cu^{I}, Ag^{I}, Zn^{II}, Cd^{II} and Pb^{II} complexes are diamagnetic. These values confirm the oxidation state +II (Mn, Fe, Co, Ni, Zn, Cd, Pb) and +I (Cu, Ag) for the central atom and, therefore, the monodeprotonation of the Schiff base ligand.

Molar conductivity measurements in 10^{-3} M DMF solutions are in the range $4-23\ \Omega^{-1}\ cm^2\ mol^{-1}$, which points towards the non-electrolyte nature of these complexes [26], as expected.

Table 4 IR spectroscopy and conductivity measurements for the ligand and complexes.

Compound	IR spectra /cm^{-1} a)				Λ_M b)
	ν(OH)	ν(NH)	ν(C=N)+ ν(C-N)	ν(C=S)	
HL	–	3308 m, 3125 w	1596 m, 1499 m	1110 w, 755 m	–
$MnL_2 \cdot H_2O$	3415 br	3287 w	1599 w, 1494 w	1120 m, 749 w	4.4
$FeL_2 \cdot 2H_2O$	3402 br	3234 w	1597 w, 1495 m	1117 m, 752 w	5.2
$CoL_2 \cdot 4H_2O$	3414 br	3242 w	1599 m, 1492 s	1132 s, 758 w	15.7
$NiL_2 \cdot H_2O$	3414 br	3302 w	1600 w, 1496 m	1127 m, 750 w	4.6
$CuL \cdot 4H_2O$	3420 br	3300 w	1599 m, 1494 s	1136 m, 766 w	4.6
AgL	–	3305 m	1598 m, 1494 s	1151 w, 746 m	4.1
$ZnL_2 \cdot 2H_2O$	3411 br	3297 w	1594 w, 1495 w	1126 s, 749 w	6.3
$CdL_2 \cdot 2H_2O$	3383 br	3302 w	1593 m, 1494 m	1121 f, 750 w	5.1
$PbL_2 \cdot 3H_2O$	3437 br	3278 w	1599 w, 1487 s	1122 m, 749 w	22.5

a) s = strong, m = medium, w = weak, sh = shoulder, br = broad; b) in $\Omega \cdot^{-1}$ cm^2 mol^{-1}

IR spectroscopy and mass spectrometry

The most significant infrared bands for these complexes are collected in Table 4. The partial deprotonation of the ligand is observed by the disappearance of one of the bands assigned to ν(N-H) in the free ligand [27]. Bands corresponding to ν(C=N) and ν(C-N) modes appear slightly shifted and overlapped to ν(C=C) absorptions in all complexes, indicating metal coordination to the pyridine and imine nitrogen atoms. The coordination to the thioamide sulphur atom is corroborated by the displacements of the bands ν(C=S). Besides, other bands due to the SH group between 2600 and 2500 cm^{-1} are not present, in agreement with the *thione* form of the ligand and with the presence of bands around 750 cm^{-1} for ν(C=S) [13, 28].

Finally, all spectra, except the silver one, show a broad band about 3400 cm^{-1}, according with the presence of coordinated and/or lattice water.

The electrospray mass spectra exhibit peaks assigned to $[ML_2]^+$ fragments for most complexes, indicating the coordination of two ligand units to the metal centres. Since in the spectra of iron, cobalt, nickel and lead the pattern of fragmentation is similar to that described for manganese **1**, zinc **2** and cadmium **3** complexes, crystallographically solved, the same structure for these complexes could be deduced. In the case of copper and silver compounds, only peaks due to $[ML]^+$ fragments are present.

NMR spectroscopy

The ^1H NMR spectra of the ligand HL and its zinc, cadmium and lead complexes were recorded in dmso-d_6 at room temperature, and the relevant data are collected in Table 5. The attempts of recording the spectrum for the silver complex were unsuccessful, due to the low solubility of this compound. In the case of the copper complex the spectrum could be recorded, indicating the presence of copper(I) species in solution; however its interpretation was not possible due to the poor quality of this spectrum.

The superposition of the ^1H NMR spectrum of the free ligand with those of the complexes is illustrated in Figure 6. The compared study of these spectra allows us to draw the following conclusions:

(a) In all cases, it is observed the disappearance of the NH hydrazine protons (H_1) present in the free ligand, in agreement with the monodeprotonation of the ligand [29].

(b) The signal due to the NH-Ph group (H_2) remains in the spectra of these complexes, and it's shifted to higher field. This effect is more pronounced for the lead complex.

(c) The imine hydrogen atom (H_5) shows a shift to lower field for all the complexes, indicating a withdrawal of charge from the imine group upon coordination. This

Table 5 Some relevant ^1H NMR data (in ppm) for the ligand and the diamagnetic compounds.

Compound	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}
HL	12.01 (s, 1H)	10.24 (s, 1H)	8.57 (d, 1H)	8.41 (d, 1H)	8.19 (s, 1H)	7.85 (at b), 1H)	7.54 (d, 2H)	7.37 (m, 1H)	7.37 (m, 2H)	7.21 (t, 1H)
$ZnL_2 \cdot 2H_2O$	no a)	9.46 (s, 1H)	7.95 (d, 1H)	7.66 (d, 1H)	8.74 (s, 1H)	7.90 (at, 1H)	7.83 (d, 2H)	7.35 (at, 1H)	7.25 (at, 2H)	6.95 (t, 1H)
$CdL_2 \cdot 2H_2O$	no	9.48 (s, 1H)	8.06 (d, 1H)	7.66 (d, 1H)	8.67 (s, 1H)	7.93 (at, 1H)	7.84 (d, 2H)	7.41 (at, 1H)	7.26 (at, 2H)	6.96 (t, 1H)
$PbL_2 \cdot 3H_2O$	no	9.00 (s, 1H)	8.76 (d, 1H)	7.75 (d, 1H)	8.71 (s, 1H)	7.97 (at, 1H)	7.71 (d, 2H)	7.44 (at, 1H)	7.19 (at, 2H)	6.87 (t, 1H)

a) non observable; b) apparent triplet

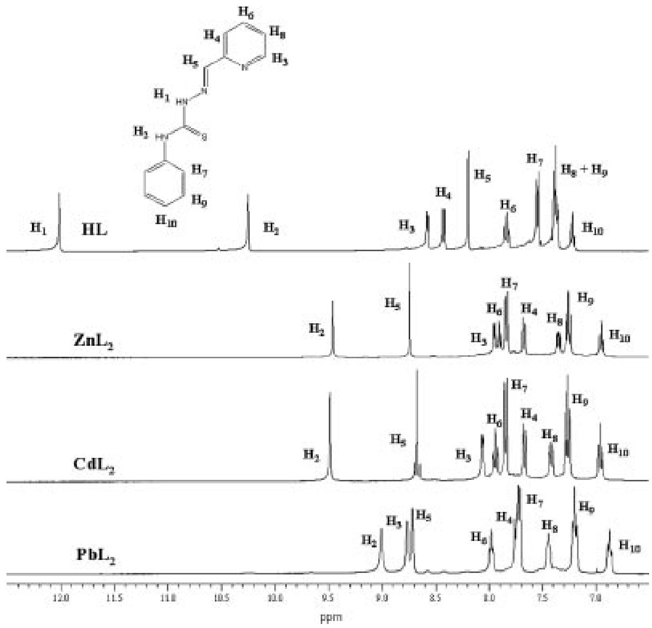

Fig. 6 ^1H NMR spectra in dmso-d_6 at room temperature for HL, $ZnL_2 \cdot 2H_2O$, $CdL_2 \cdot 2H_2O$ and $PbL_2 \cdot 3H_2O$.

signal is flanked by satellites arising from spin-spin coupling to $^{111/113}Cd$ in the cadmium complex spectrum indicating that this complex is kinetically inert on the NMR timescale.

(d) The pyridine aromatic protons (H_3, H_4, H_6 and H_8) are also affected on coordination, mainly the protons in *ortho* position respect to the nitrogen atom (H_3 and H_4). This could be attributed to the coordination of the metals to the pyridine nitrogen atom [9].

(e) The aromatic signals of the phenyl group (H_7, H_9 and H_{10}) experiment a slight change to higher field, with the exception of H_7 which shifts to lower field.

It must be noted that zinc and cadmium complexes exhibit very similar NMR spectra. Nevertheless, the spectrum of the lead complex is apparently quite different, showing changed displacements of the signals. This fact could be related with the structure presented for these species in solid state. Zinc and cadmium complexes reveal a distorted octahedral coordination around the metal centre, whilst the coordination polyhedron for the lead compound may be altered by the presence of the metal lone pair, as it was previously found for the related PbL'_2 [13].

On the other hand, the lead spectrum does not show signals attributed to the free ligand. It seems to indicate that this complex is stable in solution, contrary to the behaviour observed for the lead complex with a similar ligand 4-*N*-methylthiosemicarbazone-2-pyridinecarboxaldehide [13]. Besides, the quality of these ^1H NMR spectra is better than that showed by the related complexes with the latter ligand. This fact points to the 4-N substitution is involved with the capability of the thiosemicarbazones to stabilize metal ions in solution.

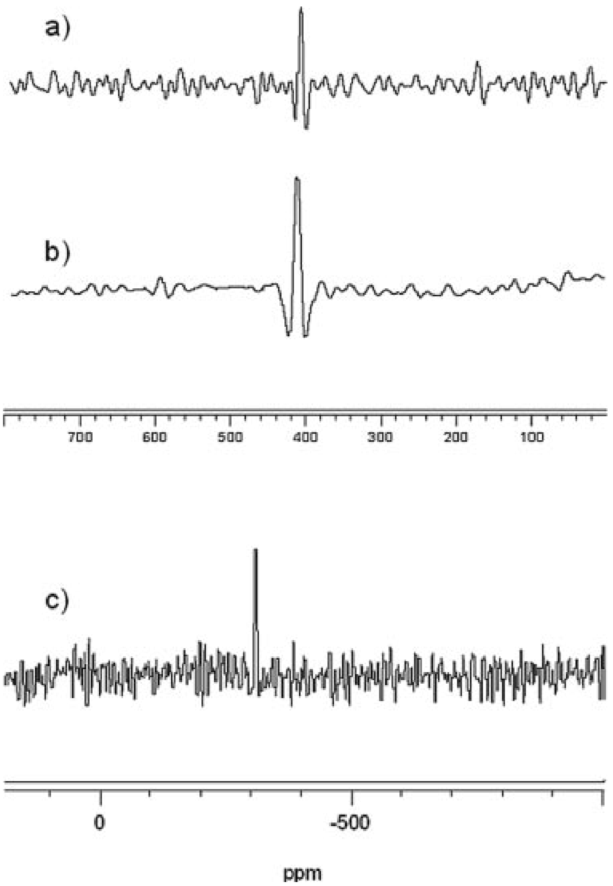

Fig. 7 Multinuclear NMR spectra: a) ^{113}Cd NMR for **3**; ^{113}Cd NMR for $CdL'_2 \cdot H_2O$ [13]; ^{207}Pb NMR for $PbL_2 \cdot 3H_2O$.

We were keen to further investigate the solution behaviour of the cadmium and lead complexes. For this purpose we have recorded their ^{113}Cd and ^{207}Pb NMR spectra.

The ^{113}Cd spectrum of complex **3**, in a dmso-d_6 solution, shows a unique signal at 405.8 ppm (Figure 7a). This value is rather similar to that observed for other six-coordination complexes with a kernel [N_4S_2] [30]. Therefore, it seems that this cadmium complex retains in solution the structure showed in solid state. The change of the phenyl group by the methyl one in the 4-N position of these ligands affects somewhat the displacement of the signal, from 405.8 to 410.2 ppm (Figure 7b). It is well known that the shielding of ^{113}Cd NMR signal increases when the donor atoms change and/or the coordination number is increased [31]. This effect can be exemplified by the comparison between the ^{113}Cd chemical shift values showed by a complex with a [N_3S_2] kernel (305 ppm), described by us in literature [32], and the herein presented (405.8 ppm) containing a [N_4S_2] core.

Relatively few ^{207}Pb NMR spectroscopy studies have been reported on soluble Pb(II) coordination compounds. In spite of this, it is known some information that correlates chemical shifts with coordination numbers and nature of the donor set for this kind of complexes. The lead(II) complex prepared by us shows a single signal at −309.7 ppm

(Figure 7c), in dmso-d_6 solution, which is similar to the value observed for a previous reported complex with the metal centre in a $[N_3S_2]$ environment (−304 ppm) [32], and close to that corresponding to a coordination number six. Having these data in mind, a coordination number six could be tentatively proposed for this complex in solution. Unfortunately, all attempts to obtain single crystals suitable for X-ray diffraction for this lead complex were vain, and for that reason it has not been possible to correlate the potential structure showed in solution with that presented in solid state.

Conclusions

The electrochemical method has been shown to be a simple and effective approach to prepare neutral transition and post-transition metal complexes with this type of thiosemicarbazones with high purity and good yield. We have demonstrated that the presence of the phenyl group in the 4-N position of the ligand, a bulkier substituent than the methyl one, favours the capability of this thiosemicarbone to stabilize metal ions. This effect is also stated in the structure of these metal complexes in solid state, as well, in their behaviour in the NMR studies in solution.

Experimental Part

General: All solvents, 2-pyridinecarboxaldehyde and 4-*N*-phenylthiosemicarbazide are commercially available and were used without further purification. Iron, cobalt, nickel, copper, silver, zinc, cadmium and lead were purchased from Aldrich and used as sheets 0.5 mm thick. Manganese (Stream Chemical) was used as platelets. Metals were cleaned of oxide in dilute hydrochloric acid prior to electrolysis. Elemental analyses of C, H, N and S were performed on a Carlo Erba EA 1108 analyser. ^1H and multinuclear NMR (^{113}Cd and ^{207}Pb) spectra were recorded on a Varian INOVA 400 and a Bruker AMX-500 spectrometers respectively, using dmso-d_6 as solvent. Chemical shifts are expressed relative to tetramethylsilane (^1H NMR), 0.1 M $Cd(ClO_4)_2$ (^{113}Cd NMR) and neat tetramethyllead using a saturated solution of $PbPh_4$ in $CDCl_3$ (−178 ppm) as external reference (^{207}Pb NMR). IR spectra were recorded as KBr pellets on a Mattson Cygnus 100 spectrophotometer in the range 4000−500 cm^{-1}. Mass spectrometry (Electronic Impact) was performed on a Hewlett Packard 5988A mass spectrometer, whilst Electrospray was performed on a Hewlett-Packard LC−MSD 1100 instrument (positive ion mode, 98:2 MeOH−HCOOH as mobile phase, 75 to 200 V). Room temperature magnetic susceptibility was measured using a Digital Measurement system MSB-MKI, calibrated using mercury tetrakis(isothiocyanato)cobaltate(II). Conductivity measurements were obtained at 25 °C from 10^{-3} M solutions in DMF on a CRISON Basic 30 instrument.

Syntheses

Preparation of 4-N-phenylthiosemicarbazone-2-pyridinecarboxaldehyde, HL. To a solution of 2-pyridinecarboxaldehyde (0.37 mL, 3.9 mmol) in ethanol (250 cm^3) was added 4-*N*-phenylthiosemicarbazide (0.652 g, 3.9 mmol). The solution was heated under reflux over a 6 h period, concentrated with a Dean Stark trap to *ca.* 30 cm^3. The white precipitate formed was collected by filtration. The resulting solid was finally washed with diethylether (3 × 10 cm^3) and dried *in vacuo.* M.p. 198 °C. This ligand was characterized by elemental analysis and mass spectrometry (Table 6), infrared (Table 5) and ^1H NMR spectroscopies (Table 6). In order to assign correctly the aromatic protons a COSY experiment was also performed. The ^{13}C NMR spectrum shows 9 signals between 120.7 and 153.4 ppm, assigned to the aromatic protons. Other two signals due to C=N and C=S groups are also present.

Synthesis of the Metal Complexes. The compounds were obtained using an electrochemical procedure [33] improved by us [34]. An acetonitrile solution of the ligand was electrolyzed using a platinum wire as the cathode and a metal plate or platelet (in the case of manganese) as the anode. The cell can be summarised as: Pt(−)|HL + MeCN|M(+), where M = Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd and Pb. The synthesis is typified by the preparation of $CdL_2 \cdot 2H_2O$. A solution (0.1 g, 0.39 mmol) of the ligand in acetonitrile (80 cm^3), containing 10 mg of tetraethylammonium perchlorate as supporting electrolyte, was electrolyzed for 1.2 h. using a current of 10 mA. The resulting pale yellow solid was filtered off, washed with diethyl ether and dried *in vacuo.* (CAUTIONS: although no problem has been encountered in this work, all perchlorate compounds are potentially explosive, and should be handled in small quantities and with great care. In addition, lead is a highly toxic cumulative poison, and lead complexes should be handled carefully). Slow evaporation from the mother liquors produces yellow crystals of $[CdL_2] \cdot CH_3CN$ (**3**), useful for X-ray studies.

The other complexes were obtained by the same method, using the appropriate metal anode. In the case of the copper derivative, a

Table 6 Elemental analysis and some selected data for the complexes

Compound	Yield	Colour	Found (Calcd.) (%)				MS (amu)[a]	μ (BM)
			% N	% C	% H	% S		
HL	90	White	21.5 (21.9)	60.3 (60.9)	4.5 (4.7)	11.8 (12.5)	256 (60)[b]	–
$MnL_2 \cdot H_2O$	77	Orange-red	19.2 (19.2)	52.1 (53.5)	3.7 (4.1)	10.1 (11.0)	565 (66)	6.1
$FeL_2 \cdot 2H_2O$	68	Green	18.5 (18.6)	52.0 (51.8)	3.7 (4.3)	10.6 (10.6)	566 (100)	5.5
$CoL_2 \cdot 4H_2O$	75	Brown	17.0 (17.5)	48.1 (48.7)	3.8 (4.7)	10.6 (10.0)	569 (100)	5.2
$NiL_2 \cdot H_2O$	75	Brown	19.4 (19.1)	53.2 (53.2)	3.9 (4.1)	9.9 (10.9)	568 (66)	3.5
$CuL \cdot 4H_2O$	96	Brown	15.5 (15.8)	43.4 (44.0)	3.1 (4.2)	8.1 (9.0)	318 (100)	d[c]
AgL	70	Yellow	15.5 (15.4)	42.6 (43.0)	3.0 (3.0)	8.4 (8.8)	406 (25)	d
$ZnL_2 \cdot 2H_2O$	74	Yellow	18.4 (18.3)	50.8 (51.0)	3.6 (4.3)	10.5 (10.5)	569 (60)	d
$CdL_2 \cdot 2H_2O$	78	Yellow	16.9 (17.0)	46.7 (47.4)	3.3 (4.0)	9.4 (9.7)	623 (98)	d
$PbL_2 \cdot 3H_2O$	68	Yellow	12.8 (14.5)	39.8 (40.5)	3.7 (3.7)	6.4 (8.3)	719 (66)	d

[a] Electrospray for complexes and Electronic Impact for ligand; [b] relative abundance in %; [c] diamagnetic

vigorous nitrogen stream was flowing through the reaction mixture, in order to avoid the oxidation of the copper(I) ion to the copper(II). Recrystallisation of the powder of $MnL_2 \cdot H_2O$ in chloroform lets us to isolate red crystals of $[MnL_2] \cdot CHCl_3$ (**1**). Slow evaporation from the mother liquors of the reaction of $ZnL_2 \cdot 2H_2O$ yields yellow crystals of $[ZnL_2] \cdot CH_3CN$ (**2**).

X-Ray Crystallographic Studies. Crystals of **1**, **2** and **3** suitable for X-ray diffraction studies were obtained as described above. Data for complex **1** and **3** were collected on an Bruker X8 Kappa APEXII, using a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), at T = 100.0(1) K. Data for complex **2** were collected on an Enraf Nonius TurboCAD4 using a graphite-monochromated Cu-Kα radiation (λ = 1.54180 Å), at T = 293(2) K. Detailed data collection and refinement of the compounds are summarized in Table 1. The structures were solved by direct methods, and then were refined by full-matrix, least-squares bases on F^2 [35−37]. The figures were drawn using the program ORTEP3 [38].

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