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Reactions of thiosemicarbazones derived from β-keto amides and β-keto esters with Zn(II) and Cd(II) acetates: influence of metal, substitution, reagent ratio and temperature on metal-induced cyclization †

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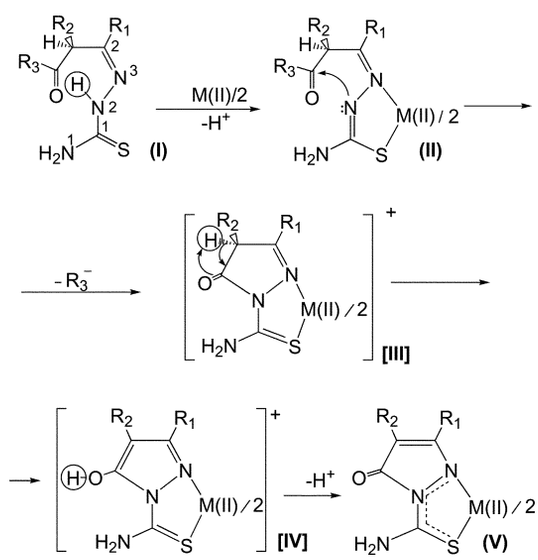
Zinc(II) and cadmium(II) acetates were reacted in methanol under various experimental conditions with thiosemicarbazones derived from β-keto amides or β-keto esters (HTSC). Some of these reactions afforded thiosemicarbazonate complexes $[M(TSC)_2]$ with IR and NMR spectra compatible with N,S-coordination, but most gave complexes $[ML_2]$, where HL is a substituted 2,5-dihydro-5-oxo-1*H*-pyrazole-1-carbothioamide resulting from cyclization of the HTSC. Some of these pyrazolonates and two of the HL ligands were studied by X-ray diffractometry, and their structures are discussed. Surprisingly, the reactions of zinc(II) acetate with HTSC in 1 : 1 mol ratio usually gave a third, previously unreported type of complex with a dideprotonated ligand, [Zn(L − H)], which was also formed when $[ZnL_2]$ and $Zn(OAc)_2$ interacted at room temperature in 1 : 1 mol ratio. These L − H complexes are highly insoluble in all common solvents, which hinders their characterization but suggests that they are polymeric in nature.

Introduction

Although examples of chain-ring tautomerization of thiosemicarbazones have long been known,[1] exploration of this phenomenon among monothiosemicarbazones derived from β-keto esters and β-keto amides (**I** in Scheme 1) is more recent.[2] Cyclization of **I** in the presence of a metallic salt or organometallic substrate such as $Zn(OAc)_2$, $Cd(OAc)_2$, $[ReX(CO)_5]$ or $[ReX(CO)_3(MeCN)_2]$ (X = Cl, Br) usually constitutes a mild route to the corresponding pyrazolone, the free pyrazolones easily being obtained from the resulting metal complex. Pyrazolones are an interesting synthetic target because of their potential as antiinflammatory drugs.

Previous studies[2] suggest that these cyclizations probably start with the complexation of **I** by the metal or organometallic substrate inducing its deprotonation, and that cyclization of the resulting thiosemicarbazonate complex **II** comes about through nucleophilic attack by the deprotonated N(2) atom on the $C(O)R_3$ group (Scheme 1). The rearrangement of the resulting ring to the final pyrazolonate is less well-elucidated, but experiments with Re compounds[2a] suggest that loss of R_3^- gives **III**, which evolves *via* the enol form **IV** to the final complex **V**, losing a proton in the process.

In our earlier work we found that cyclization is faster with $Cd(OAc)_2$ than with $Zn(OAc)_2$.[2b] In the work described here we investigated the influence of the substituents R_1, R_2 and R_3, of the metal : **I** mol ratio and of the temperature on the cyclization of thiosemicarbazones $HTSC^n$ (Scheme 2) during reaction with zinc(II) and cadmium(II) acetates. Our findings included the discovery of a hitherto unreported kind of zinc complex with a dideprotonated ligand, $[Zn(L^n - H)]$.



Scheme 1

Experimental

Physical measurements

Elemental analyses were performed on a Fisons instruments EA1108CHNS-O microanalyser or, for some $[Zn(L^n - H)]$ complexes, by Galbraith Laboratories Inc. (Knoxville, TN, USA). Melting points (mp) were determined with a Büchi apparatus. The EI mass spectra of the ligands were recorded on a Hewlett-Packard model HT5988A spectrometer. The electrospray mass spectra of the complexes were measured on a

† Electronic supplementary information (ESI) available: SM1: Analytical and spectroscopic data for the ligands. ST1: Complexes obtained in the assayed experimental conditions. ST2: IR spectra of the new complexes. ST3: ^{1}H NMR spectra of the new $HTSC^n$ and HL^n complexes. ST4: ^{13}C and ^{113}Cd NMR spectra of some new complexes. ST5: Hydrogen bond lengths (Å) and angles (°) in ligands and complexes. SF1: Intermolecular interactions in $[CdL^5_2(DMSO)]\cdot DMSO$. SF2: (a) ^{1}H NMR spectrum of $[Cd(TSC^4)_2]$ at room temperature; (b) ^{1}H NMR spectrum of the same sample after 1 h heating at 90 °C. SF3: O 1s core level spectra for $[ZnL^4_2]\cdot H_2O$ and $[Zn(L^4 - H)]$. See http://www.rsc.org/suppdata/dt/b4/b401674b/

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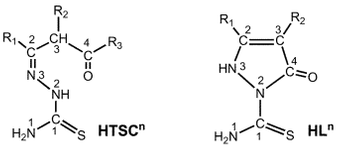
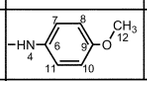
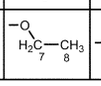


	HSTC[1] HL[1]	HSTC[2] HL[2]	HSTC[3] HL[3]	HSTC[4] HL[4]	HSTC[5] HL[5]
R_1	$-CH_3$	$-CH_3$	$-CH_2-CH_3$	$-CH_2-O-CH_3$	
R_2	H	$-CH_3$	H	H	H
R_3			$-OCH_3$	$-OCH_3$	

Scheme 2

Hewlett-Packard model LC-MSD 1100 instrument (positive ion mode, 98 : 2 MeOH–HCOOH as mobile phase, 30 to 100 V). The mass spectra of the [Zn(L^n − H)] complexes (see below) were also explored by LDI or MALDI experiments using a Voyager-DE PRO apparatus (Applied Biosystems) operating in linear mode {5 mg ml^{-1} of DHB or *trans*-2-[(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile in 50 : 50 of water–acetonitrile with 0.1% trifluoroacetic acid, 337 nm nitrogen laser, 25 keV}. The masses of the metallated peaks were calculated for ^{114}Cd or ^{64}Zn. IR spectra were recorded from KBr discs on a Bruker IFS66V FT-IR spectrometer and are reported in cm^{-1}. The ^1H, ^{13}C and ^{113}Cd NMR spectra of DMSO solutions were recorded on Bruker WM-250, AMX-300 or AMX-500 instruments; chemical shifts are expressed on the δ scale (downfield shifts positive) relative to tetramethylsilane (^1H and ^{13}C NMR spectra) or 0.1 M $Cd(ClO_4)_2$ (^{119}Cd NMR). X-Ray photoelectron spectra were recorded at the University of Malaga using a Physical Electronics PHI 5700 spectrometer, non–monochromatic Mg–Kα radiation (300 W, 15 kV, 1253.6 eV) and a multichannel detector for determination of the photoelectronic signals of C 1s, N 1s, O 1s, S 2p and Zn 2p. The Zn LMN Auger line was also observed to calculate the Auger parameter. Spectra of powdered samples were recorded with constant pass energy values at 29.35 eV using a 720 μm diameter analysis area. In processing the XPS spectra, binding energy values were referred to the C 1s peak (248.8 eV) of the adventitious contamination layer. The PHI ACCESS ESCA–V6.0 F software package was used for data acquisition and analysis. A Shirley–type background was subtracted from the signals. All recorded XPS spectra were fitted with Gauss–Lorentz curves for more accurate determination of the binding energies of the various element core levels. The error in BE was estimated to be *ca*. 0.1 eV. All physical measurements except the elemental analyses (performed by Galbraith), the XPS spectra (performed at the University of Malaga) and the LDI and MALDI MS spectra (see Acknowledgements) were carried out in the RIAIDT services of the University of Santiago de Compostela.

Materials

Thiosemicarbazide (Merck), *p*-acetoacetanisidide (Aldrich), methyl propionylacetate (Aldrich), ethyl benzoylacetate (Aldrich), methyl 4-methoxyacetoacetate (Aldrich), ethyl 2-methylacetoacetate (Aldrich), zinc acetate (Aldrich) and cadmium acetate (Probus) were used as received.

Synthesis of ligands

The thiosemicarbazone ligands were prepared by a published method.[3] Physical and analytical properties of HTSC,[2] HL^1 and HL^2 have been reported elsewhere.[2b] HL^3 and HL^4 were obtained by adding a 0.1 M aqueous solution of NaOH to a solution of $HTSC^3$ or $HTSC^4$ (0.68 mmol) in MeOH (25 ml) until a pH of *ca*. 8 was reached, and then stirring for 6 h; the white solid formed was filtered out and dried under reduced pressure. HL^5 was obtained by bringing a solution of $HTSC^5$ in MeOH to pH 8 by addition of 0.1 M NaOH, and then adding trifluoroacetic acid to an aqueous solution of the resulting sodium salt (NaL^5). Recrystallization of HL^3 and HL^5 from MeOH solution gave crystals suitable for X-ray analysis. Analytical data and spectroscopic properties of all the ligands are included as ESI (SM1). †

Synthesis of complexes

The experimental conditions used for preparing the cyclized and uncyclized complexes are described below. Analytical data, physical properties and the main peaks in the mass spectra are listed in Table 1.

$M(OAc)_2$/$HTSC^1$ reaction. (a) M = Zn. *1 : 2 mol ratio, reflux.* A suspension of $HTSC^1$ (0.15 g, 0.54 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (0.06 g, 0.25 mmol) in methanol (25 ml) was refluxed for 6 h. The white solid formed, [$Zn(TSC^1)_2$], was filtered out and dried under reduced pressure. *1 : 1 mol ratio, reflux.* Similar treatment of a suspension of 0.25 mmol of $HTSC^1$ and 0.25 mmol of $Zn(OAc)_2\cdot 2H_2O$ in 25 ml of methanol afforded a mixture of unidentified products. At *room temperature*, reactions in 1 : 1 and 1 : 2 mol ratios both gave [$Zn(TSC^1)_2$]. (b) M = Cd. *1 : 2 mol ratio, reflux.* A suspension of $HTSC^1$ (0.15 g, 0.54 mmol) and $Cd(OAc)_2\cdot 2H_2O$ (0.07 g, 0.27 mmol) in methanol (25 ml) was refluxed for 6 h. Concentrating the solution to half its initial volume and keeping it for 12 h at low temperature allowed isolation of the complex $[CdL^1_2]\cdot 3H_2O$, which was dried under reduced pressure. The same compound was obtained using *1 : 1 mol ratio* and also at *room temperature* (in both 1 : 2 and 1 : 1 mol ratio). $[CdL^1_2]\cdot 3H_2O$ has previously been prepared by reacting cadmium acetate with methylacetoacetate thiosemicarbazone.[2c]

$M(OAc)_2$/$HTSC^2$ reaction. (a) M = Zn. The *1 : 2 mol ratio* reaction, at *room temperature* or *reflux*, afforded, as previously,[2b] $[ZnL^2_2(H_2O)]$. *1 : 1 mol ratio, reflux.* A solution of $HTSC^2$ (0.15 g, 0.69 mmol) in methanol (25 ml) was added to a solution of $Zn(OAc)_2\cdot 2H_2O$ (0.152 g, 0.69 mmol) in the same solvent (10 ml). The mixture was refluxed for 2 h and the solid formed, [$Zn(L^2$ − H)], was filtered out and dried under reduced pressure. The same compound was also obtained when this *1 : 1* mixture was stirred for one day at *room temperature*. (b) M = Cd. *1 : 2 mol ratio, room temperature*. A solution of $Cd(OAc)_2\cdot 2H_2O$ (0.09 g, 0.34 mmol) in methanol (3 ml) was added dropwise, with stirring, to a solution of $HTSC^2$ (0.15 g, 0.69 mmol) in the same solvent (25 ml). After 4 days stirring at room temperature, the white solid formed was filtered out, dried under reduced pressure, and identified as $[CdL^2_2]$. Single crystals of $[CdL^2_2(H_2O)]\cdot 2DMSO$ suitable for X-ray diffractometry were obtained by recrystallization from DMSO. Stirring the reagents in *1 : 1 mol ratio* for 6 h, at *room temperature* or under *reflux*, also gave $[CdL^2_2]$.

$M(OAc)_2$/$HTSC^3$ reaction. (a) M = Zn. *1 : 2 mol ratio.* To a solution of $HTSC^3$ (0.11 g, 0.53 mmol) in methanol (25 ml) at *room temperature* were added 0.06 g (0.27 mmol) of solid $Zn(OAc)_2\cdot 2H_2O$. After 6 h of stirring and further addition of 10 ml of water, the solution was cooled. The white solid formed, $[ZnL^3_2]$, was filtered out and dried under reduced pressure. The same product formed when the *1 : 2 mol ratio* reaction was carried out under *reflux* for 6 h. *1 : 1 mol ratio.* A solution of $Zn(OAc)_2\cdot 2H_2O$ (0.20 g, 0.90 mmol) in methanol (5 ml) was added to a solution of $HTSC^3$ (0.18 g, 0.90 mmol) in the same solvent (25 ml). After 48 h of stirring under *reflux*, the white solid formed, [$Zn(L^3$ − H)], was filtered out and dried under reduced pressure. The same complex was obtained when the

Table 1 Elemental analyses (%), melting points (°C), colour and mass spectra (*m/z*) of the new complexes

Compound	C	H	N	S	Zn	Mp	Colour	MS (%)
$[Zn(TSC^1)_2]$	44.4	4.7	17.3	10.6		210	White	623 (100.0) [M + H]
$(C_{24}H_{34}N_8O_4S_2Zn)$	(46.2)	(4.8)	(18.0)	(10.3)				500 (24.6) [M − NHPh(OCH$_3$)]
								343 (45.0) [Zn(TSC^1)]
$[Zn(L^2 - H]$	29.8	3.3	17.4	13.8	28.0	>300	White	
$(C_6H_7N_3OSZn)$	(30.7)	(3.0)	(17.9)	(13.7)	(27.9)			
$[CdL^2_2]$	31.0	3.2	18.3	15.1		220	White	455 (16.7) [M + H]
$(C_{12}H_{16}N_6O_2S_2Cd)$	(31.8)	(3.6)	(18.6)	(14.2)				394 (22.6) [M − C(S)NH$_2$]
								284 (13.7) [CdL^2]
$[ZnL^3_2]$	35.1	4.0	20.5	16.3		130	White	405 (55.8) [M + H]
$(C_{12}H_{16}N_6O_2S_2Zn)$	(35.5)	(4.0)	(20.7)	(16.1)				346 (33.0) [M − 2Et]
								315 (12.7) [M − C(S)NH$_2$ − Et]
								234 (7.6) [ZnL^3]
$[Zn(L^3 - H)]$	31.1	3.6	18.1			235	White	
$(C_6H_7N_3OSZn)$	(30.7)	(3.0)	(17.9)					
$[CdL^3_2]\cdot H_2O$	29.8	3.7	17.0	13.7		190	White	455 (100.0) [(M − H$_2$O) + H]
$(C_{12}H_{18}N_6O_3S_2Cd)$	(30.6)	(3.8)	(17.8)	(13.6)				394 (11.3) [M − H$_2$O − C(S)NH$_2$]
								284 (5.0) [CdL^3]
$[Zn(TSC^4)_2]$	33.6	4.7	16.8	12.4		145	White	501 (100.0) [M + H]
$C_{14}H_{24}N_6O_6S_2Zn$	(33.5)	(4.8)	(16.8)	(12.8)				469 (49.0) [M − (OCH$_3$)]
$[ZnL^4_2]$	32.1	3.8	18.2	14.0		130	White	437 (38.4) [M + H]
$C_{12}H_{16}N_6O_4S_2Zn$	(32.9)	(3.7)	(19.2)	(14.6)				250 (100.0) [ZnL^4].
$[Zn(L^4 - H)]$	28.2	2.8	16.2	12.9	24.7	>300	White	
$(C_6H_7N_3O_2SZn)$	(28.8)	(2.8)	(16.8)	(12.8)	(26.1)			
$[Cd(TSC^4)_2]$	29.5	4.4	14.6	12.0		170	White	551 (100.0) [M + H]
$C_{14}H_{24}N_6O_6S_2Cd$	(30.6)	(4.4)	(15.3)	(11.7)				519 (38.6) [M − (OCH$_3$)]
								332 (17.2) [Cd(TSC^4)]
$[CdL^4_2]\cdot H_2O$	28.0	3.9	16.0	12.1		185	White	487 (33.0) [(M − H$_2$O) + H]
$C_{12}H_{18}N_6O_5S_2Cd$	(28.7)	(3.6)	(16.7)	(12.7)				426 (22.4) [M − H$_2$O − C(S)NH$_2$]
								300 (60.0) [CdL^4]
$[ZnL^5_2]\cdot MeOH$	45.5	3.0	15.9	12.5		190	White	501 (78.0) [(M + H]
$C_{21}H_{20}N_6O_3S_2Zn$	(47.2)	(3.8)	(15.7)	(12.0)				440 (9.5) [M − C(S)NH$_2$]
$[CdL^5_2]\cdot MeOH$	41.7	4.0	14.1	10.4		180	White	551 (5.4) [(M − MeOH) + H]
$(C_{21}H_{20}N_6O_3S_2Cd)$	(43.4)	(3.5)	(14.5)	(11.0)				490 (6.3) [M − MeOH − C(S)NH$_2$]
								473 (100.0) [M − MeOH − Ph]
								332 (22.4) [CdL^5]

1 : 1 mol ratio reaction was carried out *at room temperature*. (b) M = Cd. *1 : 1 mol ratio.* A solution of HTSC^3 (0.15 g, 0.74 mmol) in methanol (25 ml) was added to a solution of $Cd(OAc)_2\cdot 2H_2O$ (0.20 g, 0.74 mmol) in the same solvent (10 ml). After 6 h stirring at *room temperature*, the white solid formed, $[CdL^3_2]\cdot H_2O$, was filtered out and dried under reduced pressure. The same compound was obtained when this *1 : 1* mixture was *refluxed* for 6 h or when the *1 : 2 mol ratio* reaction was carried out at *room temperature* or under *reflux*.

M(OAc)$_2$/HTSC^4 reaction. (a) M = Zn. *1 : 2 mol ratio, room temperature.* A solution of HTSC^4 (0.15 g, 0.68 mmol) in methanol (20 ml) was added to a solution of $Zn(OAc)_2\cdot 2H_2O$ (0.07 g, 0.34 mmol) in the same solvent (10 ml). The mixture was stirred for 10 min, and after partial evaporation of the solvent the solid formed, $[Zn(TSC^4)_2]$ was filtered out and dried under reduced pressure. *Refluxing* the *1 : 2 mol ratio* mixture for 6 h, followed by partial evaporation of the solvent, gave $[ZnL^4_2]$ which was filtered out and dried under reduced pressure. The mother-liquor afforded single crystals of $[ZnL^4_2]\cdot 0.5H_2O$ suitable for X-ray study. $[ZnL^4_2]$ was also formed after 6 h stirring of the *1 : 2 mol ratio* mixture at *room temperature*. The reaction in *1 : 1 mol ratio*, at *room temperature* or under *reflux* always afforded the very insoluble compound $[Zn(L^4 - H)]$, which was filtered out and dried under reduced pressure. (b) M = Cd. *1 : 2 mol ratio.* A solution of HTSC^4 (0.15 g, 0.68 mmol) in methanol (25 ml) was added to a solution of $Cd(OAc)_2\cdot 2H_2O$ (0.09 g, 0.34 mmol) in the same solvent (5 ml) and the mixture was stirred for 6 h at *room temperature*. The white solid formed, $[Cd(TSC^4)_2]$, was filtered out and dried under reduced pressure. The *1 : 1 mol ratio* reaction *at room temperature* gave the same compound. When *refluxed* for 6 h, the *1 : 2* and *1 : 1* mixtures both gave $[CdL^4_2]\cdot H_2O$, which was filtered out and dried under reduced pressure.

M(OAc)$_2$/HTSC^5 reaction. (a) M = Zn. *1 : 2 mol ratio.* A solution of HTSC^5 (0.15 g, 0.57 mmol) in methanol (25 ml) was added to a solution of $Zn(OAc)_2\cdot 2H_2O$ (0.06 g, 0.28 mmol) in the same solvent (10 ml). The white solid $[ZnL^5_2]\cdot MeOH$, formed after 6 h of stirring at *room temperature*, was filtered out and dried under reduced pressure. The same complex was also obtained when this *1 : 2 mixture* was *refluxed*. In *1 : 1 mol ratio*, however, the result depended on the temperature: *refluxing* for 6 h gave first a white solid that has not yet been completely identified, and the mother-liquor then gave $[ZnL^5_2]\cdot MeOH$; while at *room temperature* the *1 : 1 mixture* gave only unidentified products. (b) M = Cd. *1 : 2 mol ratio.* A solution of $Cd(OAc)_2\cdot 2H_2O$ (0.07 g, 0.27 mmol) in methanol (5 ml) was added to a solution of HTSC^5 (0.15 g, 0.57 mmol) in the same solvent (25 ml). The white solid $[CdL^5_2]\cdot MeOH$ was formed after 3 h of stirring at *room temperature* and was filtered out and dried under reduced pressure. The same product was obtained under *reflux* and also when the *1 : 1 mol ratio* was used at *room temperature* or under *reflux*. Recrystallization from DMSO gave single crystals of $[CdL^5_2(DMSO)]\cdot 2DMSO$ suitable for X-ray study.

Table ST1 (ESI †) summarizes the syntheses described above.

X-Ray crystallography

Crystal data were collected at room temperature on Enraf-Nonius CAD-4 or Bruker SMART diffractometers. Structures were solved using direct methods for the ligands and the Patterson method for the complexes, followed by normal difference Fourier techniques. Hydrogen atoms were included at ideal geometrical positions, except that of the water molecule in $[CdL^2_2(H_2O)]\cdot 2DMSO$, which was located. In this complex, one of the DMSO molecules is disordered. In $[ZnL^4_2]\cdot 0.5H_2O$ the occupancy of the water oxygen was fixed at 0.5 because its temperature factor was very high; and the hydrogen on this

Table 2 Selected crystallographic data for ligands and complexes

	HL^3	HL^5	$[ZnL^4_2]\cdot 0.5H_2O$	$[CdL^2_2(H_2O)]\cdot 2DMSO$	$[CdL^5_2(DMSO)]\cdot DMSO$
Empirical formula	$C_6H_9N_3OS$	$C_{10}H_9N_3OS$	$C_{12}H_{17}N_6O_{4.5}S_2Zn$	$C_{16}H_{30}N_6O_5S_4Cd$	$C_{24}H_{28}N_6O_4S_4Cd$
M	171.22	219.26	446.81	627.10	705.16
λ/Å	0.71073	1.54180	0.71073	0.71073	0.71073
Crystal size/mm	0.95 × 0.53 × 0.44	0.24 × 0.16 × 0.04	0.34 × 0.31 × 0.25	0.66 × 0.65 × 0.63	0.57 × 0.31 × 0.09
Crystal system	Monoclinic	Triclinic	Tetragonal	Monoclinic	Monoclinic
Space group	$C2/m$ (no. 12)	$P\bar{1}$ (no. 2)	$P4_12_12$ (no. 92)	$C2/m$ (no. 12)	$P2_1/c$ (no. 14)
a/Å	18.825(4)	6.0107(3)	9.3579(15)	15.665(3)	10.636(3)
b/Å	6.9385(14)	7.8604(13)	–	20.270(4)	13.317(3)
c/Å	6.1461(12)	11.2049(9)	22.554(5)	8.1761(17)	20.713(5)
α/°	–	94.399(12)	–	–	–
β/°	90.087(3)	100.733(7)	–	100.030(3)	91.174(5)
γ/°	–	95.417(11)	–	–	–
Z	4	2	4	4	4
Refl. collec./uniq.	2519/890	2270/2065	11298/2052	5924/2696	14594/5964
R_{int}	0.0338	0.0354	0.0372	0.0158	0.0432
R_1 [$I > 2\sigma(I)$]	0.0578	0.0438	0.0327	0.0261	0.0448
R_w [$I > 2\sigma(I)$]	0.1661	0.1242	0.0920	0.0718	0.1041

Table 3 Selected bond lengths (Å) and angles (°) in ligands and complexes

	HL^3	HL^5	$[ZnL^4_2]\cdot 0.5H_2O$ [a]	$[CdL^2_2(H_2O)]\cdot 2DMSO$ [b]	$[CdL^5_2(DMSO)]\cdot DMSO$ [c]
M(1)–S(1)			2.3731(10)	2.5733(7)	2.5908(15)
Cd(1)–S(11)					2.5910(15)
M(1)–N(3)			1.971(3)	2.2342(18)	2.392(4)
Cd(1)–N(13)					2.355(4)
Cd(1)–O(1D)					2.499(4)
Cd(1)–O(1W)				2.319(3)	
Cd(1)–O(1)^i					2.374(4)
S(1)–C(1)	1.659(3)	1.663(2)	1.703(3)	1.705(2)	1.687(5)
N(1)–C(1)	1.329(3)	1.326(3)	1.315(5)	1.308(3)	1.312(6)
C(1)–N(2)	1.379(3)	1.388(3)	1.359(4)	1.370(3)	1.385(6)
N(2)–N(3)	1.379(3)	1.392(2)	1.387(4)	1.391(3)	1.405(5)
N(3)–C(2)	1.323(3)	1.358(3)	1.316(4)	1.327(3)	1.342(6)
C(2)–C(3)	1.372(4)	1.369(3)	1.413(5)	1.391(3)	1.390(7)
C(3)–C(4)	1.403(4)	1.409(3)	1.384(5)	1.390(3)	1.381(7)
C(4)–O(1)	1.248(3)	1.251(2)	1.244(4)	1.266(3)	1.266(6)
C(4)–N(2)	1.410(3)	1.412(2)	1.448(4)	1.436(3)	1.421(6)
C(1)–N(2)–N(3)	121.9(2)	121.14(15)	120.2(3)	120.88(17)	120.3(4)
N(2)–N(3)–C(2)	108.8(2)	107.09(15)	106.4(3)	105.23(17)	103.3(4)
N(3)–C(2)–C(3)	110.0(2)	110.27(17)	111.9(3)	113.1(2)	113.5(4)
C(2)–C(3)–C(4)	107.9(2)	108.24(18)	107.5(3)	106.90(19)	107.1(5)
S(1)–Cd(1)–S(11)					152.61(5)
S(1)–M(1)–S(1)^i			106.83(6)	122.18(4)	
S(1)–M(1)–N(3)			84.93(8)	77.38(5)	74.24(10)
S(1)–M(1)–N(3)^i			126.43(9)	104.75(5)	
S(1)–Cd(1)–O(1)^i					85.57(9)
S(11)–Cd(1)–O(1D)					76.53(10)
N(3)–Cd(1)–N(13)					84.37(14)
N(3)–M(1)–N(3)^i			129.82(16)	175.71(10)	
N(3)–Cd(1)–O(1W)				87.85(5)	
S(1)–Cd(1)–O(1W)				118.910(19)	

[a] i = $-y + 1, -x + 1, -z + 3/2$. [b] i = $-x, y, -z$. [c] i = $-x, y - 1/2, -z + 1/2$.

atom was not included. The program used was SHELX97.[4] Molecular graphics were obtained with ORTEP-3.[5] Crystal and refinement data are listed in Table 2, and selected bond lengths and angles are included in Table 3. Bond lengths and angles in hydrogen bonds in ligands and complexes are included as ESI † in Table ST5.

CCDC reference numbers 230381–230385.

See http://www.rsc.org/suppdata/dt/b4/b401674b/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and identification of the ligands

All the thiosemicarbazones HTSC^n and pyrazolones HL^n were characterized by elemental analysis, mass spectrometry, and IR and ^{1}H and ^{13}C NMR spectroscopy (ESI, † SM1), and HL^3 and HL^5 were also studied by X-ray diffractometry. All except HTSC[4], which is ochre in colour, are white solids, and all melt without decomposition at temperatures between 80 and 198 °C.

Fig. 1(a) and (b) show the molecular structures of HL^3 and HL^5 together with the atomic numbering schemes used. Selected bond lengths and angles are listed in Table 3. In both ligands, the bond lengths and angles are similar to those found in the two pyrazolone ligands previously studied by X-ray diffraction,[2c,6] the major difference being that HL^3 has a significantly shorter C(2)–N(3) bond. Both ligands adopt the keto-thione form. In the HL^3 molecule all the atoms, with the exception of hydrogens on C5 and C6, are in the same plane. In HL^5 the plane containing the pyrazolone ring and the carbothioamide group (rms = 0.03) forms an angle of 21° with the phenyl ring. Both ligands have an N(1)H ··· O(1) intramolecular hydrogen bond [N(1) ··· O(1) = 2.634(4) Å in HL^3 and 2.664(3) Å in HL^5] and two intermolecular hydrogen bonds

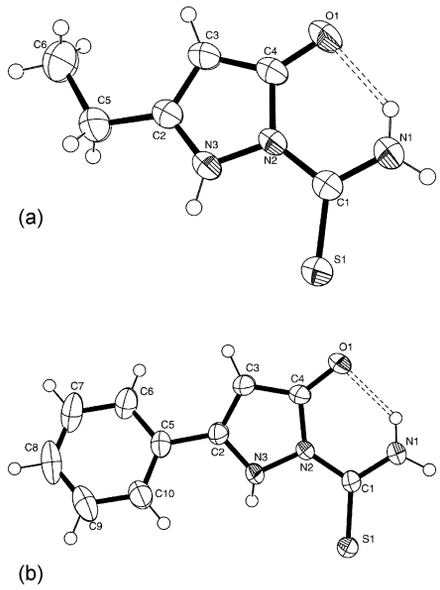


Fig. 1 Molecular structures and numbering scheme of ligands (a) HL^3 and (b) HL^5.

(see Table ST5 in ESI†). One of the latter links the N(3)–H group and the carbonyl oxygen atom of a neighbouring molecule [N(3) ··· O(1)^{ii} = 2.746(3) Å in HL^3 (ii = x, y, $z - 1$), 2.924(2) Å in HL^5 (ii = $x - 1$, y, z)] and gives rise to a polymeric chain parallel to the z axis in HL^3 and the x axis in HL^5. The other intermolecular hydrogen bond, between the N(1)–H(1B) group and the S^i atom [N(1) ··· S^i = 3.413(4) Å in HL^3 (i = $-x$, y, $-z + 2$), 3.404(2) Å in HL^5 (i = $-x$, $-y$, $-z + 1$)], links the chains in pairs. The distance between molecules in the same chain is somewhat longer in HL^5, probably because of steric hindrance by the phenyl group.

Synthesis of the complexes

Depending on the metal, the ligand and the reaction conditions, the reactions of Cd(II) and Zn(II) acetates with the selected thiosemicarbazones (Scheme 2) led to three types of complex: thiosemicarbazonates [M(TSC^n)$_2$] (**II** in Scheme 1), pyrazolonates with monodeprotonated ligands [ML$^n_2$] (**V** in Scheme 1), and pyrazolonates with dideprotonated pyrazolones, [Zn(L^n − H)].

Thiosemicarbazonate complexes were only obtained in reactions with $HTSC^1$ and $HTSC^4$ (Table ST1 in ESI†). [Zn(TSC^1)$_2$] was isolated when zinc(II) acetate was reacted with $HTSC^1$ in 1 : 2 mol ratio at room temperature or under reflux, or in 1 : 1 mol ratio at room temperature. The reaction of zinc(II) acetate with $HTSC^4$ gave the thiosemicarbazonate only when carried out in 1 : 2 mol ratio and interrupted after 10 min, with the solid formed being filtered off immediately. [Cd(TSC^4)$_2$] was easily formed at room temperature from $Cd(OAc)_2$ and $HTSC^4$ in both 1 : 1 and 1 : 2 mol ratio, but was not obtained when the reaction mixture was refluxed. In keeping with earlier work,[2b,c] these results suggest that stabilization of the thiosemicarbazonate complexes is probably easier with Zn(II) than with Cd(II). In fact, [Cd(TSC^4)$_2$] is the first Cd(II) complex of this type to have been isolated, and its readiness to undergo cyclization is shown by the fact that heating it for 1 h at 90 °C in DMSO-d_6 led to its ^{1}H NMR spectrum showing signals for both thiosemicarbazonate and pyrazolonate complexes (Fig. SF2 in ESI†); in the same conditions, [Zn(TSC^1)$_2$] underwent no such evolution. The stabilization of [M(TSC^n)$_2$] seems also to depend on the leaving group R_3 (*vide infra*), the identity of R_1 (possibly because its inductive effect influences the deprotonation of N(3)H), and the temperature. It seems plausible that all the $HTSC^n$ ligands would have been cyclized by both metals given a long enough reaction time.

It is noteworthy that of the five zinc thiosemicarbazonates derived from β-keto amides and β-keto esters that have been isolated so far (two in this work and three previously[2b]), the least prone to cyclization are the three derived from β-keto amides. Their higher stability may be due to nucleophilic attack by N(2) on C(4)=O (see Scheme 1) being slowed down or prevented by the involvement of the N(2) lone pair in an N(4)–H ··· N(2) intramolecular hydrogen bond, the presence of which has been shown by X-ray crystallography in the case of [Zn(TSC)$_2$]·DMSO (HTSC = *o*-acetoacetanisidide thiosemicarbazone).[2b]

Complexes [ML$^n_2$] were obtained, normally without heating, in all the $Cd(OAc)_2$/$HTSC^n$ reactions except those of $HTSC^4$ at room temperature, which afforded [Cd(TSC^4)$_2$]. The reactions of zinc acetate with $HTSC^n$ in 1 : 2 mol ratio also gave [ML$^n_2$] complexes for n = 2–5 (Table ST1 in ESI†).

The reactions of $Zn(OAc)_2$ with $HTSC^n$ in 1 : 1 mol ratio (n = 2, 3 and 4) afforded a third, previously unreported type of complex, [Zn(L^n − H)] (ST1 in ESI†). No reaction of cadmium(II) acetate gave a [Cd(L^n − H)] complex. It was found that the [Zn(L^n − H)] derivatives can also be prepared by stirring [ZnL$^n_2$] for 48 h with zinc acetate in 1 : 1 mol ratio at room temperature, but not by refluxing [ZnL$^n_2$] in the absence of $Zn(OAc)_2$; this suggests that 1 : 1 metal : ligand mol ratio is essential for preparation of the complexes containing dideprotonated pyrazolones. The fact that the [Zn(L^n − H)] compounds are insoluble in water and in the common organic solvents, which prevents their crystallization, suggests that they are polymeric in nature. They are nevertheless soluble in trifluoroacetic acid, in which they react releasing the free pyrazolone ligand.

Structures of the complexes

(a) [M(TSC^n)$_2$]. The main change in the IR spectra of $HTSC^1$ and $HTSC^4$ upon coordination to the metal in the complexes [Zn(TSC^1)$_2$], [Zn(TSC^4)$_2$] and [Cd(TSC^4)$_2$] is that one of the ν(C=S) absorptions vanishes or shifts to lower wavenumbers, suggesting coordination through the S atom (see Table ST2 in ESI†). Comparison of these spectra with those of similar compounds studied by X-ray diffractometry[2b,c] also suggests coordination *via* the lone pair of N(3), since in these compounds the ν(C=N) absorptions suffer small but significant changes in its position respect to the free ligands.

The ^{1}H and ^{13}C NMR spectra of these complexes show signals for only one conformer (Tables ST3 and ST4 in ESI†). Deprotonation of the ligand was confirmed by the absence of N(2)H signals. In the ^{13}C NMR spectra the major changes upon coordination are the shielding of C(1) and C(3) (in the former case due to thione-to-thiol evolution), and the deshielding of C(2) [due to N(3)-coordination]. In the cadmium complex, the main ^{113}Cd NMR signal appears at lower field (448 ppm) than in thiosemicarbazonate complexes with [N_4S_2]-coordination (420 ppm),[7] in keeping with the [N_2S_2]-coordination proposed for [Cd(TSC^4)$_2$]. Nevertheless, the presence of two weak signals at higher field (439 and 371 ppm) suggests the presence of minor species, possibly involving DMSO molecules. These species are presumably uncyclized, since the signal of the cyclized complex appears at 280 ppm (*vide infra*).

(b) [ML$^n_2$]. The structures of [ZnL$^4_2$]·0.5H_2O, [CdL$^2_2$(H_2O)]·2DMSO and [CdL$^5_2$(DMSO)]·DMSO were established by X-ray diffractometry.

Fig. 2(a) shows the solid-state molecular structure of [ZnL$^4_2$]·0.5H_2O and the atomic numbering scheme used in this paper. Selected bond lengths and angles are listed in Table 3. In the crystal structure the Zn and O1W atoms lie on a two-fold axis. Two S,N-bidentate ligands chelate the zinc atom, giving rise to a distorted tetrahedral coordination polyhedron with an S(1)–Zn(1)–N(3) angle of only 85°. The O(2) and O(2)^i atoms (i = $-y + 1$, $-x + 1$, $-z + 3/2$), are located 2.74 Å from the zinc

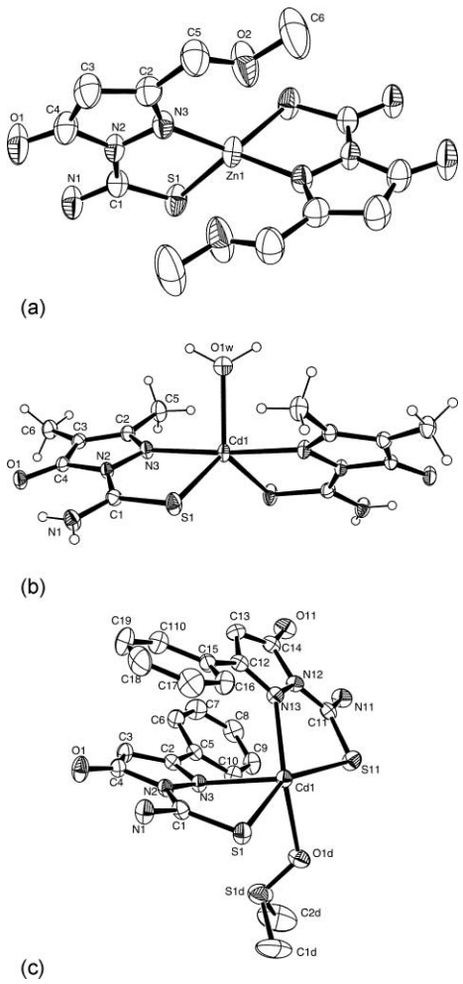


Fig. 2 Molecular structures of complexes: (a) $[ZnL^4_2]\cdot 0.5H_2O$; (b) $[CdL^2_2(H_2O)]\cdot 2DMSO$; (c) $[CdL^5_2(DMSO)]\cdot DMSO$

atom, a distance that is less than the sum of the van der Waals radii (2.90 Å[8]) and suggests the existence of a very weak interaction with the metal centre. Be that as it may, the positions of O(2) and O(2)^{i} are probably responsible for keeping the water molecule outside the coordination sphere and so preventing a coordination number higher than four. Except for the O(2) and C(6) atoms, the pyrazolone ligands are almost planar [rms = 0.0185 for S(1)C(1)N(1)N(2)N(3)C(2)C(3)C(4)-C(5)O(1); O(2) and C(6) lie about 0.27 and 0.29 Å, respectively, from this plane], and their planes form a dihedral angle of 78°. The N(1) atom is involved in two hydrogen bonds with O(1) atoms (see Table ST5 in ESI†), one of them being intramolecular [N(1) ··· O(1), 2.696(4) Å] and one intermolecular [N(1) ··· O(1)^{ii} (ii = $-x + 5/2$, $y - 1/2$, $-z + 5/4$), 2.804(4) Å]. This latter hydrogen bond gives rise to a three-dimensional network. The water molecule seems not to interact with other components of the lattice, OW1 lying 3.235 Å from the closest atom [O(1)^{iii}, iii = $x - 1$, y, z].

The solid-state molecular structure of $[CdL^2_2(H_2O)]\cdot 2DMSO$ is shown in Fig. 2(b) together with the atomic numbering scheme, and selected bond lengths and angles are listed in Table 3. In the crystal structure the Cd and O1W atoms lie on a two-fold axis. Cd(II) is pentacoordinated by two N(3),S-bidentate ligands and a water molecule, which create a distorted trigonal bipyramidal coordination geometry (τ = 0.89[9]) with the N atoms apical [N(3)−Cd−N(3)^{i} 175.71°]. The pyrazolonate rings are planar [rms = 0.056 Å] and the dihedral angle between the planes is about 55.9°. Deprotonation and coordination promote a thione-to-thiol transition (the C(1)–S(1) bond is longer than in the free pyrazolone[6]) and also cause delocalization of π-charge in the ring. The intramolecular N(1)H ··· O(1) hydrogen bond of the free ligand persists in the complex, but is weaker [N(1) ··· O(1), 2.711(3) Å]. An intermolecular hydrogen bond between the water molecule and O(1)^{ii} [O(1w) ··· O(1)^{ii} 2.807(2) Å, ii = $-x + 1/2$, $-y + 1/2$, $-z$] gives rise to polymeric chains. The two DMSO molecules bridge between chains through hydrogen bonds with the NH_2 groups, making a three-dimensional network [N(1) ··· O(1D) 2.961(3) Å; N(1) ··· O(2D) 2.902(3) Å]. This compound is isostructural with the complex of Zn(II) with the same ligand.[2b]

Fig. 2(c) shows the molecular structure of $[CdL^5_2(DMSO)]\cdot$DMSO and the atomic numbering scheme (for clarity, the DMSO molecule that is not coordinated to the cadmium is not represented). Selected bond lengths and angles are listed in Table 3. The metal atom has coordination number six, a trigonal prismatic coordination geometry being created by the two N,S-bidentate thiosemicarbazone ligands, a DMSO oxygen (O1D), and a carbonyl oxygen belonging to a neighbouring molecule [O(1)^{i}, i = $-x$, $y - 1/2$, $-z + 1/2$]. This Cd(1)–O(1)^{i} bond links the molecules in chains along the y axis (Fig. SF1 in ESI†). Each NH_2 group is involved in one intra- and one intermolecular hydrogen bond (Table ST5 in ESI†), the former with the oxygen of a carbonyl group [N(1)–O(1) 2.617(6) Å; N(11) ··· O(11) 2.646(6) Å] and the latter with either a DMSO molecule [N(11) ··· O(2D) 2.749(7) Å] or a carbonyl oxygen atom belonging to a neighbouring molecule [N(1) ··· O(11)^{ii} (ii = $x - 1$, y, z) 2.770(5) Å]. These N(1) ··· O(11)^{ii} bonds link the above-mentioned chains along the x axis. The major modifications in bond lengths with respect to the free ligand are the lengthening of S(1)–C(1) from 1.663(2) to 1.687(5) Å and of C(2)–C(3) from 1.369(3) to 1.390(7) Å, and the shortening of C(3)–C(4) from 1.409(3) to 1.381(7) Å due to the new charge distribution in the anion. In each ligand the plane containing the pyrazolone ring and the thioamide group [rms = 0.015, S(1)N(1)C(1)N(2)N(3)C(2)C(3)C(4)O(1)] makes a dihedral angle of 22° with the plane of the phenyl group. The two pyrazolone planes form an angle of about 20°.

The above structures show that in $[ML^n_2]$ complexes the four bonds with the two pyrazolone ligands can be increased to five or six by incorporation of additional donor molecules when the R substituents on the pyrazolone ring do not block access to the metal centre as they do in $[Zn(L^4)_2]\cdot 0.5H_2O$. This suggests that in some of the complexes formulated in Table 1 as hydrates or solvates the water or organic solvent molecule may in fact occupy a position in the inner coordination sphere of the metal.

In the IR spectra of most of the $[ML^n_2]$ compounds, the ν(C=O) absorption has shifted to significantly lower wavenumbers than in the spectrum of the free ligand (SM1 and Table ST2 in ESI†), presumably either because of coordination of the carbonyl group to the metal atom (as in $[CdL^5_2(DMSO)]\cdot$DMSO) or because the oxygen atom is involved in stronger hydrogen bonds than in the free ligand. The possible exceptions are $[ZnL^4_2]$ and $[ZnL^5_2]\cdot$MeOH, which have spectra in which very broad absorptions hinder interpretation. The ν(C–N) absorption, located at 1340–1300 cm^{-1} in the ligand spectra shifts to wavenumbers 30–90 cm^{-1} higher in the spectra of all the complexes due to the redistribution of the π charge upon coordination. The ligand absorptions associated with the ν(C=S) mode, one near 1100 cm^{-1} and the other near 900–850 cm^{-1}, either shift to lower wavenumbers in the spectra of the complexes or, in the case of the higher-energy absorption, disappear. $[CdL^3_2]\cdot H_2O$ is an exception to this rule because in this case the absorption at higher wavenumber disappears upon complexation and the lower-energy absorption shifts to higher wavenumber and becomes weaker.

As expected, the ^{1}H NMR spectra of $[ML^n_2]$ show no N(3)H signal, due to deprotonation. In the ^{13}C NMR spectra almost all the signals lie downfield of their positions in the free ligands, the only exception being that C(3) is shielded (see SM1 and ST4 in ESI†). The ^{113}Cd NMR spectra all show a single signal at *ca.* 280 ppm, a chemical shift almost identical to that previously

Table 4 Solid-state ^{13}C NMR data

Compound	δ[C(1)]	δ[C(2)]	δ[C(3)]	δ[C(4)]	δ[R_1]
[ZnL^4_2]	175.5	157.8	85.1	165.6	67.2 [C(5)], 57.9 [C(6)]
[Zn(L^4 − H)]	176.6	153.5	89.8, 87.5	163.6	68.4 [C(5)], 60.2 [C(6)]

Table 5 Theoretical and experimental atomic ratios for [ZnL^4_2]·0.5H_2O and [Zn(L^4 − H)]

	Theoretical atomic ratios				Surface atomic ratio (XPS)			
Sample	O/Zn	S/Zn	N/Zn	C/Zn	O/Zn	S/Zn	N/Zn	C/Zn
[ZnL^4_2]·0.5H_2O	4.50	2.00	6.00	12.00	4.32	2.01	5.83	13.58
[Zn(L^4 − H)]	2.00	1.00	3.00	6.00	2.17	1.31	3.04	7.93

Table 6 Binding energies, in eV, of Zn $2p_{3/2}$, Zn_{LMN}, S 2p, N 1s and O 1s, and the Auger parameter α, for [ZnL^4_2]·0.5H_2O and [Zn(L^4 − H)]

Complex	Zn $2p_{3/2}$	Zn_{LMN}	α	S 2p	N 1s	O 1s
[ZnL^4_2]·0.5H_2O	1022.3	265.4	2010.5	162.6	398.8 399.8 400.9	530.9 532.6
[Zn(L^4 − H)]	1022.3	265.4	2010.5	162.8	398.5 399.7 400.9	531.5 532.9

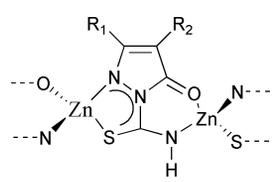
found for [CdL^1_2]·3H_2O (281 ppm).[2c] As in this latter case, δ(^{113}Cd) is larger than expected for an [N_2S_2] kernel;[10] this may be due to an increase in coordination number due to the coordination of solvent molecules (as seen in the solid state for [CdL^2_2] and [CdL^5_2]).

(c) [Zn(L^n − H)]. The very poor solubility of these complexes, which suggests a polymeric structure, severely hindered their characterization. Although the presence of the metal is guaranteed by the elemental analyses (see Experimental section), the LDI and MALDI MS experiments only produced signals for small organic fragments, which might reflect either the desorption of polymers that then break up under the laser radiation, or the existence of a polymeric structure from which polymeric fragments are not desorbed. Other MS methods (ESI) gave no additional clues. The results of the solid-state ^{13}C NMR experiments (Table 4) suggest that the organic moiety has a cyclic structure similar to that of $(L^n)^-$, the signals of all the pyrazolone ring carbons of the monodeprotonated ligands having counterparts within 4 ppm in the [Zn(L^n − H)] spectra. Furthermore, all the [Zn(L^n − H)] complexes afforded the free pyrazolone when treated with trifluoroacetic acid.

The pyrazolonate ligand $(L^n)^-$ can only lose an additional proton from the –NH_2 group. Although the acidity of the amine group is very low, it is well documented that in certain Zn(II) complexes with similar coordination to the present compounds the metal cation is bound to a deprotonated –NH_2 group.[11,12] It is nevertheless interesting that whereas in the synthesis of these latter complexes the deprotonation of –NH_2 had been induced by a basic reagent (hydride ion) or a basic solvent (DMF), the presence of the metal ion and the acetate group seems to suffice in the formation of [Zn(L^n − H)].

The IR spectra of [Zn(L^3 − H)] and [Zn(L^4 − H)], the former especially, are quite similar to those of [ZnL^3_2] and [ZnL^4_2] everywhere except in the region corresponding to ν(N–H) absorptions, as is to be expected if the only significant structural change is deprotonation of the –NH_2 group. The IR spectrum of [Zn(L^2 − H)] also differs from that of [$ZnL^2_2(H_2O)$][2b] in this region, although in this case the absorptions due to the water molecule of the latter complex hinder direct comparison. Except in the case of the HL^3 derivatives, the ν(C=O) absorption shifts to lower wavenumbers, suggesting coordination of the oxygen atom to the metal, although once more an alternative explanation might be a strengthening of hydrogen bonds involving the oxygen atom. In the solid state ^{13}C NMR spectrum (Table 4), the carbonyl carbon [C(4)] is shielded by 2 ppm when the second deprotonation of the pyrazolone occurs, which is also compatible with O–Zn(II) interaction.

In view of the probable polymeric nature of these [Zn(L^n − H)] complexes and the deprotonation of their amine group, and assuming that the carbonyl oxygen atom does coordinate to the zinc(II) atom, we hypothesize that they may have the structure shown in Scheme 3.



Scheme 3

To support this assumption, samples of [ZnL^4_2]·0.5H_2O and [Zn(L^4 − H)] were studied by XPS. Table 5 shows the theoretical and the experimental atomic ratios. There is very good agreement between the theoretical and experimental surface compositions, confirming that the surfaces of both samples have chemical compositions similar to the bulk. The higher observed C/Zn atomic ratios can be attributed to adventitious carbon. To determine the redox state of Zn, the Auger parameter α was calculated from the equation

$$\alpha = \mathrm{KE}(\mathrm{Zn_{LMN}}) + \mathrm{BE}(\mathrm{Zn}\,2p_{3/2})$$

where KE (Zn_{LMN}) is the kinetic energy of the Zn_{LMN} Auger electron [KE(Zn_{LMN}) = 1253.6 − BE(Zn_{LMN}), 1253.6 being the energy of the Mg-Kα X-ray source, in eV] and BE(Zn $2p_{3/2}$) is the binding energy of the Zn $2p_{3/2}$ photoelectron. Both complexes have the same Auger parameter, 2010.5 eV, a value that is intermediate between the 2009.8 eV of ZnO and the 2011.3 eV of ZnS,[13] and a Wagner plot (not shown here) indicates that in both cases Zn is present as Zn(II).

Table 6 lists the binding energies of the elements studied by XPS. The S 2p signal appears at 162.6 and 162.8 eV for [ZnL^4_2]·0.5H_2O and [Zn(L^4 − H)], respectively, indicating that only S(−II) is present in these complexes. The N 1s signal is very broad for both compounds, and can be decomposed into three contributions at 398.8, 399.8 and 400.9 eV (FWHM = 2.76 eV) for [ZnL^4_2]·0.5H_2O and 398.5, 399.7 and 400.9 eV (FWHM =

3.45 eV) for [Zn(L^4 − H)]. These contributions are assigned to the three types of nitrogen atom of the ligand, and the greater breadth of the [Zn(L^4 − H)] signal is attributed to the co-ordination of the amine group to Zn(II). [ZnL^4_2]·0.5H_2O has three types of oxygen atom, two belonging to the ligand and the third to the water molecule. However, [Zn(L^4 − H)] has only two types of oxygen atom according to the proposed structure. The O 1s spectrum for [ZnL^4_2]·0.5H_2O shows a broad signal centred at 532.3 eV (FWHM = 3.45 eV) that can be decomposed into two signals at 530.9 and 532.6 eV (Fig. SF3 in ESI†). The former is assigned to the oxygen of the carbonyl group and the latter, more intense signal, to the oxygen of the methoxy group (there may also be a contribution from the oxygen of the water molecule). In the case of [Zn(L^4 − H)], the O 1s signal is narrower (FWMH = 2.85 eV) and can be decomposed into two signals of similar intensity at 531.5 and 532.9 eV (Figure SF3 in ESI†). The O 1s binding energy of the oxygen of the carbonyl group is shifted from 530.9 to 531.5 eV as a consequence of its binding to zinc, which reduces the partial negative charge of the oxygen atom. The XPS data, therefore, seem to support the proposed structure for solid [Zn(L^4 − H)].

The smaller size of Zn(II), its tendency to tetracoordination and its "hard" acid character probably explain why this kind of polymerization is induced by Zn(II) but not by Cd(II).

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