Thiosemicarbazones as Co-ordinating Agents. Part 5.[1] Zinc Complexes derived from Methyl Pyruvate- and Pyridoxal-thiosemicarbazone *

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Reaction of zinc chloride or acetate with two ligands, methyl pyruvate thiosemicarbazone (Hmpt) and pyridoxal thiosemicarbazone (H_2L), lead to the formation of five novel complexes which have been characterized by spectroscopic methods. The crystal structures of three compounds: $[Zn(Hpt)_2]$ **1**, $[Zn(Hept)Cl_2]$ **2** and $[\{Zn(HL)Cl\}_2]\cdot 2H_2O$ **3** (H_2pt = pyruvic acid thiosemicarbazone, Hept = ethyl pyruvate thiosemicarbazone) have been determined by X-ray methods from diffractometer data and refined by least squares to *R* 0.054 (**1**), 0.034 (**2**) and 0.029 (**3**) for 1205, 1590 and 2134 observed reflections respectively. All the zinc complexes seem to be influenced significantly by the nature of the solvent and, consequently by the resulting pH. The transesterificated (Hept) and hydrolysed (H_2pt) forms of the original ligand (Hmpt) have been selectively isolated depending on the experimental conditions. In **1** the co-ordination geometry about zinc is distorted octahedral while in **2** and **3** the metal is five-co-ordinated, the geometry about zinc being better described as intermediate between an ideal square pyramid and trigonal bipyramid.

In several proteins the zinc atom has either a structural or a catalytic role, which seems to be connected with the following chemical features: (*a*) the ready formation of low-co-ordination-number sites which are more strongly acidic than high-co-ordination-number sites; (*b*) the easy deformation of the geometry of the ligands in the co-ordination sphere with consequent change of co-ordination number from four to five to six; (*c*) the relatively rapid exchange of the ligands in complexes; (*d*) the absence of redox chemistry;[2] and (*e*) the suggestion that zinc fingers may be a common feature in many protein–DNA (RNA) interactions.

On this basis, a part of a study to provide structural and spectroscopic models for zinc–sulfur centres in metalloproteins, and following our interest in the chemistry and in the pharmacological properties of thiosemicarbazones,[1,3–6] we report herein the preparation and the spectroscopic characterization of novel five-co-ordinated zinc complexes derived from zinc chloride or acetate by reaction with the ligands methyl pyruvate thiosemicarbazone (Hmpt) and pyridoxal thiosemicarbazone (H_2L). Also described are the X-ray structures of three compounds: $[Zn(Hpt)_2]$ **1**, $[Zn(Hept)Cl_2]$ **2** and $[\{Zn(HL)Cl\}_2]\cdot 2H_2O$ **3** (H_2pt = pyruvic acid thiosemicarbazone, Hept = ethyl pyruvate thiosemicarbazone).

Experimental

Measurements.—Elemental analyses (C, H, N and S) were made on a Perkin-Elmer 240 automatic instrument; IR spectra (4000–200 cm^{-1}) for KBr discs were recorded on a Perkin-Elmer 283 B spectrophotometer.

Materials.—Methyl pyruvate (98%), thiosemicarbazide, pyridoxal hydrochloride, anhydrous zinc chloride and zinc acetate were commercially available (Aldrich) and used without further purification.

Preparations.—Methyl pyruvate thiosemicarbazone (Hmpt) was prepared by treating methyl pyruvate and thiosemicarbazide in methanol using the published procedure.[5] Pyridoxal thiosemicarbazone (H_2L) was prepared from pyridoxal in its neutral form and thiosemicarbazide in absolute ethanol as previously described.[3]

$[Zn(Hpt)]_2$ **1**. An aqueous solution (40 cm^3) of Hmpt (0.25 g, 1.36 mmol) was treated at room temperature for *ca.* 1 h with zinc chloride (1:1 molar ratio, pH 4.5). After some days, yellow crystals were isolated (m.p. > 250 °C). The same compound was isolated when the reaction was carried out at 70 °C as well as when 1:2 or 2:1 molar ratios were used. Analytical data (C, 24.9; H, 3.2; N, 21.6%) disagree with the formula of a complex containing Hmpt as ligand. The X-ray diffraction analysis revealed the presence in the complex of the hydrolysed form of Hmpt, hereafter indicated as H_2pt. $C_8H_{12}N_6O_4S_2Zn$ requires C, 24.9; H, 3.1; N, 21.8%. The complex $[Zn(Hpt)_2]$ was also obtained from the reaction of Hmpt and zinc acetate in water (pH 6).

[Zn(mpt)Cl]. A methanol solution (30 cm^3) of Hmpt (0.20 g, 1.09 mmol) was treated for *ca.* 2 h with anhydrous zinc chloride (1:1 molar ratio, pH 5.5) dissolved in methanol (10 cm^3). After slow evaporation of the solvent at room temperature a pale yellow powder product was isolated (m.p. 225 °C). Analytical data agree with the formula Zn(mpt)Cl (Found: C, 21.9; H, 3.0; N, 15.3. $C_5H_8ClN_3O_2SZn$ requires C, 21.8; H, 2.9; N, 15.3%). The same compound was obtained when 1:2 or 2:1 molar ratios were used as well as when the reaction was carried out at reflux.

$[Zn(Hept)Cl_2]$ **2**. To an ethanol solution of Hmpt (0.23 g, 1.25 mmol) in absolute ethanol (25 cm^3), an appropriate amount (1:1, 1:2 or 2:1 molar ratio) of anhydrous zinc chloride, dissolved in ethanol (10 cm^3), was added. The resulting solution (pH 5.5) was stirred at room temperature for *ca.* 2 h. By slow evaporation of the solvent a white product was isolated (m.p. 210 °C). Analytical data disagree with the formula of a complex containing Hmpt as ligand. The X-ray analysis revealed the presence of the ethyl pyruvate thiosemicarbazone (Hept) as ligand to the zinc atom (Found: C, 22.6; H, 3.5; N, 13.0. $C_6H_{11}Cl_2N_3O_2SZn$ requires C, 22.1; H, 3.4; N, 12.9%). A

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* Pyridoxal = 3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carbaldehyde.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Experimental data for the crystallographic analyses *

Compound	$[Zn(Hpt)_2]$ **1**	$[Zn(Hept)Cl_2]$ **2**	$[\{Zn(HL)Cl\}_2]\cdot 2H_2O$ **3**
Formula	$C_8H_{12}N_6O_4S_2Zn$	$C_6H_{11}Cl_2N_3O_2SZn$	$C_{18}H_{26}Cl_2N_8O_6S_2Zn_2$
M	385.7	325.5	716.2
Space group	*C*2/*c*	*C*2/*c*	$P\bar{1}$
a/Å	14.534(2)	18.358(2)	9.972(1)
b/Å	12.550(1)	11.601(1)	8.027(2)
c/Å	9.694(1)	13.991(1)	8.880(2)
α/°	90.0	90.0	83.04(1)
β/°	124.83(2)	122.79(2)	73.94(1)
γ/°	90.0	90.0	71.62(1)
$U/Å^3$	1451.4(4)	2504.9(7)	647.8(2)
Z	4	8	1
$D_c/Mg\ m^{-3}$	1.77	1.73	1.84
F(000)	784	1312	364
μ/mm^{-1}	5.28	8.25	6.14
Crystal size (mm)	0.20 × 0.33 × 0.05	0.10 × 0.16 × 0.20	0.13 × 0.13 × 0.26
θ range	2.50–70	2.50–60	3–70
No. measured reflections	3537	2369	2403
Condition for obs. reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Max./min. height in final difference map/e $Å^{-3}$	0.28, −0.49	0.22, −0.22	0.21, −0.30
No. refined parameters	96	136	225
No. unique reflections	1205	1590	2134
R	0.054	0.034	0.029
R'	0.064	0.038	0.033

* Data common to all three compounds: $T = 293 \pm 1$ K; unit weights used.

similar process of transesterification was observed when the reaction was carried out at reflux.

$[\{Zn(HL)Cl\}_2]\cdot 2H_2O$ **3**. An aqueous solution (50 cm^3) of H_2L (0.30 g, 1.02 mmol) was treated at reflux with zinc chloride (1:2 molar ratio) for *ca.* 1 h. The resulting solution (pH 4.5) was allowed to stand at room temperature; after slow evaporation of the solvent a yellow microcrystalline product was isolated. When a 1:1 molar ratio was used, the same zinc complex was obtained together with some unreacted H_2L. A template reaction between pyridoxal, thiosemicarbazide and zinc chloride (1:1:1 molar ratio) refluxed in aqueous solution (pH 4.5) for *ca.* 2 h led to the same zinc complex and unreacted H_2L.

$[Zn(H_2L)Cl_2]\cdot 2H_2O$. To a warm ethanol solution (40 cm^3) of H_2L (0.30 g, 1.02 mmol) an equimolar amount of zinc chloride, dissolved in absolute ethanol (10 cm^3) was added and the final solution was refluxed for *ca.* 1 h. A yellow powder product was then isolated (Found: C, 27.4; H, 3.7; N, 14.0, S, 7.7. $C_9H_{16}Cl_2N_4O_4SZn$ requires C, 26.1; H, 3.7; N, 13.6; S, 7.8%). A template reaction carried out with pyridoxal, thiosemicarbazide and zinc chloride (1:1:1 molar ratios) in absolute ethanol at reflux led to the same product.

X-Ray Analysis.—The relevant data concerning the crystal structure analyses are summarized in Table 1. All diffraction data were obtained on a Siemens-AED diffractometer, at room temperature, with Cu-Kα radiation (λ = 1.541 78 Å). The absorption correction was neglected in view of small or almost isotropic crystal dimensions. Only the observed reflections were used in the structure determinations. The structures were solved by Patterson and direct methods using the SHELX 86[7] system of computer programs. Refinements were carried out by full-matrix least-squares cycles using SHELX 76.[8] The hydrogen atoms, located on a difference map, were all refined isotropically.

The final atomic fractional coordinates are given in Table 2 for complexes **1**–**3**. Atomic scattering factors were taken from ref. 9.

All calculations were performed on the GOULD 6440 Powernode computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. (Parma), using the PARST[10] program for the geometrical description of the structure and ORTEP[11] and PLUTO[12] for the structure drawings.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Infrared Spectra.—Table 3 lists selected vibrational bands for Hmpt, H_2L and the zinc complexes.

As regards the Hmpt series, in analogy with the copper(II) complexes[5] a comparison between the vibrational bands in the spectrum of the free ligand and the zinc complexes is difficult owing to the modification that Hmpt has undergone during complex formation. The most significant shifts are observed in the 1700–1500 cm^{-1} region; in particular only one absorption, at 1685 cm^{-1}, is observed in the spectrum of $[Zn(Hept)Cl_2]$ ($\Delta\nu$ = 35 cm^1 with respect to the free Hmpt). A more negative shift ($\Delta\nu = 90\ cm^{-1}$) was found in the dimeric copper complex $[\{Cu(ept)Cl\}_2]$, where the ligand is deprotonated.[5]

As previously found in the spectrum of $[\{[Cu(Hpt)Cl]\cdot 2H_2O\}_n]$,[5] a split ν(CO) band is observed for $[Zn(Hpt)_2]$, while three intense absorptions are present in the spectrum of [Zn(mpt)Cl] in the 1700–1600 cm^{-1} region.

As far as the absorptions involving the CN and CS groups are concerned, the variations of the frequency values upon co-ordination suggest an ONS terdentate ligand behaviour, in agreement with previously reported data.[5,13–15]

In both the H_2L complexes the main vibrational bands agree well with those previously found in metal complexes showing a similar stoichiometry.[4,16] Points of interest are the lack of the ν(NH) absorption in $[\{Zn(HL)Cl\}_2]\cdot 2H_2O$, the presence of bands in the 2950–2850 cm^{-1} region, which confirm the dipolar nature of the pyridoxal moiety,[3] and the shifts in frequencies of the absorptions of CN and CS groups as a consequence of co-ordination of the nitrogen and sulfur atoms to the metal.

Crystal and Molecular Structures.—$[Zn(Hpt)_2]$ **1**. The structure of the compound is shown in Fig. 1 and consists of discrete molecular units. The complex has crystallographically imposed C_2 symmetry with the metal atom lying on the crystallographic two-fold rotational axis. Unusually the co-

Table 2 Fractional atomic coordinates (× 10^4) for non-hydrogen atoms

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Compound **1**							
Zn	0(0)	−1596(1)	2500(0)	N(3)	1234(3)	−1897(4)	5083(5)
S	1429(1)	−270(2)	3036(2)	C(1)	2420(5)	−672(5)	5005(7)
O(1)	−680(3)	−2809(4)	3271(5)	C(2)	1043(4)	−2525(4)	5907(7)
O(2)	−342(4)	−3739(4)	5457(7)	C(3)	−100(5)	−3081(5)	4794(8)
N(1)	3461(4)	−276(5)	5868(8)	C(4)	1779(6)	−2770(7)	7717(9)
N(2)	2261(4)	−1385(4)	5872(6)				
Compound **2**							
Zn	3543(1)	2501(1)	4197(1)	N(3)	2291(3)	1759(4)	3541(4)
Cl(1)	4609(1)	3043(1)	5958(1)	C(1)	1688(3)	3597(4)	2857(4)
Cl(2)	3922(1)	2016(1)	2982(1)	C(2)	2195(3)	680(4)	3599(4)
S	2667(1)	4243(1)	3610(1)	C(3)	3052(4)	105(5)	4388(5)
O(1)	3728(1)	649(3)	4868(4)	C(4)	3809(4)	−1632(6)	5210(6)
O(2)	2986(2)	−1005(3)	4462(3)	C(5)	3618(6)	−2862(7)	4947(10)
N(1)	972(3)	4187(4)	2199(4)	C(6)	1367(4)	23(6)	3019(7)
N(2)	1592(3)	2438(4)	2880(4)				
Compound **3**							
Zn	3160(0)	1359(1)	735(0)	C(1)	1087(3)	2438(4)	3844(4)
Cl	5400(1)	1839(1)	466(1)	C(2)	1370(3)	5179(4)	564(3)
S	2018(1)	350(1)	3105(1)	C(3)	1995(3)	5157(4)	−1123(3)
O(1)	2739(2)	1995(3)	−1318(2)	C(4)	1902(3)	6780(4)	−1979(3)
O(2)	1358(3)	9945(3)	−2219(3)	C(5)	2426(3)	6799(4)	−3576(3)
O(3)	4113(4)	5447(4)	2483(3)	C(6)	3196(3)	3696(4)	−3597(4)
N(1)	415(3)	2527(3)	5363(3)	C(7)	2638(3)	3581(4)	−1960(3)
N(2)	943(3)	3972(3)	3029(3)	C(8)	4013(4)	2100(4)	−4535(4)
N(3)	1634(3)	3795(3)	1476(3)	C(9)	1188(3)	8501(4)	−1169(4)
N(4)	3056(3)	5273(3)	−4329(3)				

Table 3 Selected vibrational bands (cm^{-1})

	ν(NH_2), ν(OH)	ν(NH)	ν(CO)	ν(NH^+), ν(OH)	ν(CN), ring	ν(NCS)	ν(CS)
Hmpt·0.5H_2O	3510m 3290m(br) 3230ms	3150ms	1720vs		1625s 1610s	1435s 1290vs 1260vs 1210m	965m 860ms
[Zn(Hpt)$_2$]	3490ms 3290m(br)	3170s	1655s 1630vs(br)		1580s	1420m 1230s 1195s	870ms
[Zn(Hept)Cl_2]	3310m 3250m	3140ms	1685s		1620(sh) 1610vs(br) 1550vs	1430m 1230s 1180vs	850m
[Zn(mpt)Cl]	3380m 3240ms 3120ms(br)		1700vs 1660vs 1630s		1595s	1435ms 1280mw 1250mw 1220ms	860ms
H_2L	3390m 3250m	3160m		2860m	1600s	1250s 1220m	920m
[{Zn(HL)Cl}$_2$]·2H_2O	3520m 3460m 3360m 3280m			2880m 2850m	1640s 1605m(br)	1240m 1220ms	920m
[Zn(H_2L)Cl_2]·2H_2O	3460w 3280m 3230m	3130m		2950m 2860m	1620vs	1245m 1205ms	925m

ordination is distorted octahedral due to the metal being bonded to two monodeprotonated ligand molecules. Each ligand is terdentate co-ordinating through sulfur, nitrogen of the hydrazinic chain and carboxylate oxygen. The large steric constraints in the two five-membered chelate rings distort the co-ordination of this complex [O(1)–Zn–N(3) 73.3(2), S–Zn–N(3) 80.2(1), S–Zn–O(1) 153.3(1)°].

An isostructural nickel compound [crystallographic parameters: a = 12.416(1), b = 14.677(2), c = 9.844(1) Å, β = 126.32(2)°] was also obtained from the reaction of $NiCl_2$ with a new ligand H_2mpipt (methyl pyruvate hydrazinopyruvoylthiosemicarbazone) which, in aqueous solution, yielded Hpt as a result of hydrolysis.

[Zn(Hept)Cl_2] **2**. Like **1** this complex is also monomeric. Although it can be formally described as having a square-pyramidal co-ordination, the distortion around the zinc centre gives it a structure intermediate between the five-co-ordinated extremes of an ideal square pyramid and trigonal bipyramid.[17] The same distortion is present in **3** (see below and Table 4).[19] The metal is surrounded by two chlorine atoms and three donors O, N and S of the non-deprotonated ethyl pyruvate thiosemicarbazone (Fig. 2). The

Table 4 Comparison of bond angles (°) relative to ideal trigonal-bipyramidal and square pyramidal geometries[17]

Trigonal bipyramid	$[Zn(Hept)Cl_2]$ **2**		$[\{Zn(HL)Cl\}_2]\cdot 2H_2O$ **3**		Square pyramid
120	Cl(2)–Zn–N(3)	106.1(1)	Cl–Zn–O(1)	105.2(1)	100
90	Cl(2)–Zn–S	112.0(1)	Cl′–Zn–Cl	89.0(0)	100
90	Cl(2)–Zn–O(1)	92.1(1)	N(3)–Zn–Cl	103.3(1)	100
120	Cl(2)–Zn–Cl(1)	117.3(1)	S–Zn–Cl	118.9(0)	100
90	Cl(1)–Zn–S	99.3(1)	N(3)–Zn–S	83.3(1)	88.4
90	S–Zn–N(3)	80.2(1)	Cl′–Zn–O(1)	84.5(1)	88.4
90	N(3)–Zn–O(1)	71.7(2)	Cl′–Zn–S	95.8(0)	88.4
90	O(1)–Zn–Cl(1)	88.0(1)	Cl′–Zn–Cl	89.0(0)	88.4
120	Cl(1)–Zn–N(3)	132.6(1)	N(3)–Zn–O(1)	86.8(1)	160
180	S–Zn–O(1)	147.2(1)	S–Zn–O(1)	135.9(1)	160

Average deviation from trigonal bipyramid is 12.6° for **2** and 8.1° for **3**
Average deviation from square pyramid is 12.0° for **2** and 8.7° for **3**

Variation of the dihedral angle δ_{24} with the angles θ_{15} and θ_{24} at zinc.[18]

Complex	δ_{24}*	θ_{15}*	θ_{24}*
2	16.3	147.2	132.6
3	25.2	166.5	135.9

* The subscripts 1,2,4,5 indicate the atoms as follows: **2** 1, S; 5, O(1); 2, Cl(1); and 4, N(3); **3** 1, N(3); 5, Cl′; 2, S; and 4, O(1). Parameters θ_{15} and θ_{24} are respectively the axial and equatorial angles. The subscripts on δ refer to the common edge connecting the two triangular faces whose normals give the dihedral angle.

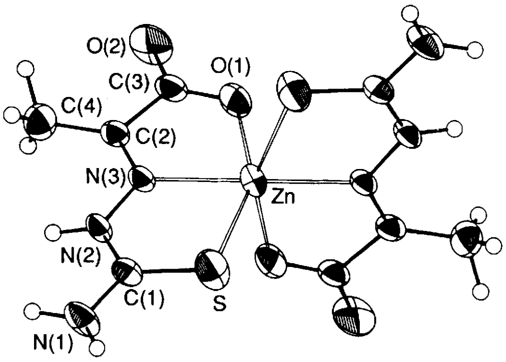

Fig. 1 Perspective view of $[Zn(Hpt)_2]$ which has crystallographically imposed C_2 symmetry (thermal ellipsoids at 50% probability level

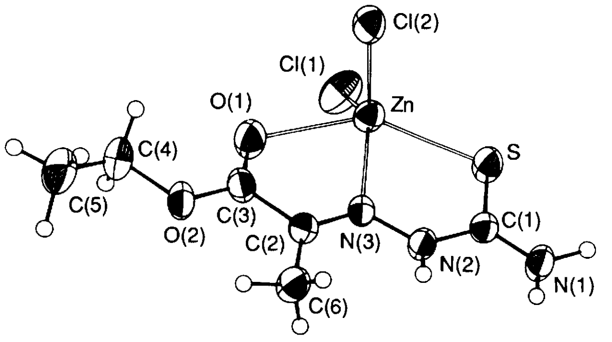

Fig. 2 Perspective view of $[Zn(Hept)Cl_2]$ with thermal ellipsoids at 50% probability level

complex is isostructural with the corresponding iron(II) compound.[20]

$[\{Zn(HL)Cl\}_2]\cdot 2H_2O$ **3**. The pyridoxal thiosemicarbazone (H_2L) co-ordinates to the Zn atom through the phenolic oxygen O(1), imine nitrogen N(3) and sulfur atom of the Schiff base. A chlorine atom completes the co-ordination, bridging two zinc atoms to form a centrosymmetric dimeric structure (Fig. 3). Therefore the metal can be considered five-co-ordinated and the distortions in the co-ordination sphere give it a structure intermediate between trigonal bipyramidal and square pyramidal (Table 4). Assuming the structure to be that of a distorted trigonal bipyramid (rather than a square pyramid), the axial donors can be defined as nitrogen N(3) and chlorine of the centrosymmetrically related molecule, and equatorial donors as chlorine, sulfur and phenolic oxygen O(1). The stereochemical non-rigidity of five-co-ordinated complexes allows the interchange of axial and equatorial donors (Berry pseudorotation [18]) and is more probably in accordance with the role of the metal in biological systems. The angular distortions present in these complexes can be considered as the result either of steric constraints or of electronic effects.

The ligand is monodeprotonated and the Zn ··· Zn distance [3.595(1) Å] is similar to that found by Miyamae *et al.* [3.545 Å] in $Zn(S_2CNPr^i{}_2)_2$.[21]

For the complexes with the aliphatic ligands, Hpt and Hept, two five-membered chelate rings are present. In **1** they are characterized by a torsion axis across C(3) and N(2) respectively to give a twist conformation, while in **2** the chelate rings show an envelope conformation with folds across the lines S ··· N(3) and O(1) ··· N(3) respectively. In **3** the five- and six-membered chelate rings show an envelope and twist-boat conformation respectively.

The co-ordination distances are reported in Table 5 for complexes **1** and **2** and in Table 6 for complex **3**.

In **1** the Zn–O [2.167(6) Å] and Zn–N [2.120(4) Å] distances are comparable with the values found in the literature for octahedral geometry,[23,24] but Zn–O(carboxylate) is larger than the sum of the Pauling covalent radii, 2.05 Å. The Zn–S bond distance [2.474(2) Å] is very long (the sum of the Pauling covalent radii for zinc and sulfur is 2.35 Å). Unfortunately too few examples of octahedral compounds containing Zn–S bonds have been studied to permit a comparison.

In **2**, owing to the lack of deprotonation of the ligand, two chlorine atoms are present. The two Zn–Cl distances are in accord with values reported in the literature,[25,26] and their difference, Zn–Cl(1) being slightly longer than Zn–Cl(2), may be related to the fact that Cl(1) accepts two hydrogen bonds (Table 9). Also in this compound the Zn–S distance is greater [2.432(2) Å] than most values found in zinc(II) complexes with sulfur-donor ligands[25–28] but are slightly shorter than those in **1**. The Zn–N distance is normal, but the Zn–O (carbonylic) bond is significantly longer [2.295(4) Å] than in **1** (Table 5). This difference is probably due to the negative charge present on the carboxylate oxygen.

In **3** the ligand is monodeprotonated pyridoxal thiosemicarbazone (HL). A centrosymmetrically related chlorine

Table 5 Comparison of bond distances (Å) for Hmpt and for the complexes obtained by reaction with $ZnCl_2$, $Zn(CH_3CO_2)_2·2H_2O$, $FeCl_2$, $CuCl_2·2H_2O$ and $CuSO_4·5H_2O$

	Hmpt[5]	[Zn(Hpt)$_2$] **1**[a]	[{[Cu(Hpt)Cl]·2H$_2$O}$_n$][5]	[{Cu(Hpt)(OH$_2$)·0.5SO$_4$}$_2$][22]	[Zn(Hept)Cl$_2$] **2**[a]	[Fe(Hept)Cl$_2$][19]	[{Cu(ept)Cl}$_2$][5]
M–S		2.474(2)	2.277(2)	2.296(3)	2.432(2)	2.439(4)	2.245(3)
M–O(1)		2.167(6)	1.986(3)	1.967(6)	2.295(4)	2.251(11)	2.054(5)
M–O(aq)		—	—	2.263(9)	—	—	—
M–N(3)		2.120(4)	1.956(3)	1.975(6)	2.139(4)	2.133(12)	1.975(6)
M–Cl		—	2.226(1)	—	2.252(2)–2.230(2)	2.261(6)–2.314(4)	2.236(2)–2.819(2)
S–C(1)	1.684(4)	1.684(5)	1.710(3)	1.713(6)	1.689(5)	1.683(14)	1.745(8)
C(1)–N(1)	1.325(5)	1.337(7)	1.301(4)	1.284(9)	1.316(6)	1.338(17)	1.321(11)
C(1)–N(2)	1.363(4)	1.336(9)	1.355(5)	1.365(8)	1.359(7)	1.361(21)	1.327(10)
N(2)–N(3)	1.367(4)	1.385(6)	1.358(4)	1.341(8)	1.355(5)	1.362(14)	1.346(8)
N(3)–C(2)	1.285(4)	1.261(9)	1.291(5)	1.291(8)	1.274(7)	1.290(19)	1.297(9)
C(2)–C(4)	1.498(5)[b]	1.469(8)	1.488(5)	1.491(9)	1.488(8)[c]	1.465(20)[c]	1.496(15)[c]
C(2)–C(3)	1.506(6)	1.537(7)	1.523(6)	1.501(10)	1.502(7)	1.503(19)	1.455(11)
C(3)–O(1)	1.208(4)	1.259(8)[d]	1.224(7)	1.291(8)[d]	1.220(7)	1.219(19)	1.258(10)
C(3)–O(2)	1.337(4)	1.216(10)	1.273(6)[d]	1.229(9)	1.302(2)	1.318(19)	1.318(9)
C(4)–O(2)	1.457(5)	—	—	—	1.481(7)	1.483(17)	1.465(11)
C(5)–C(4)	—	—	—	—	1.467(10)	1.530(23)	1.496(15)

[a] This work. [b] C(2)–C(5). [c] C(2)–C(6). [d] Co-ordinated oxygen.

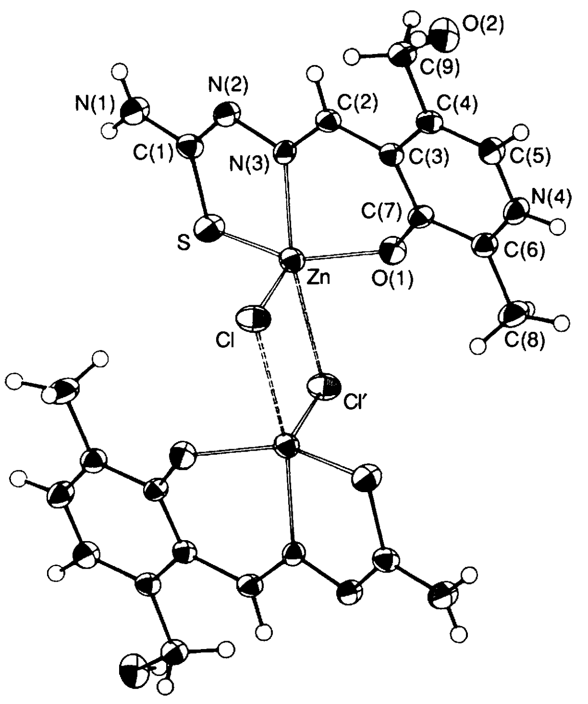

Fig. 3 Perspective view of the centrosymmetric dimeric complex [{Zn(HL)Cl}$_2$] in **3**

atom bridging the two zinc atoms completes the co-ordination sphere leading to five-co-ordination at each zinc atom in the binuclear complex. The two Zn–Cl distances are very different [2.328(1), 2.698(1) Å] with the lower value larger than those found in **2**, reflecting the bridging interaction. The Zn–O and Zn–S distances are much lower than the corresponding values in complexes **1** and **2**, probably as a consequence of the different electronic structure of the HL ligand due to charge delocalization in the heterocyclic derivative.[3] So the weaker zinc–ligand binding in the complexes with the aliphatic molecules (H_2pt and Hept) leads to a smaller perturbation in the ligand bonds; in fact (for example) the C–S bonds retain a large degree of double-bond character as found in the free ligands (Tables 5 and 6). Comparisons of bond distances of methyl pyruvate thiosemicarbazone and pyridoxal thiosemicarbazone with some of their complexes are shown in Tables 5 and 6 respectively. As previously observed,[3] with regard to the free ligands, it can be seen that the charge delocalization is higher in the heterocyclic derivative, while in the complexes obtained with Hmpt deprotonation on the hydrazine nitrogen is more important. For the H_2pt derivatives, the metal in general reaches the greatest co-ordination number permitted by its electronic configuration, probably as a consequence of the small steric requirement of the ligand. The zinc complexes with H_2pt and Hept are monomeric, while the analogous copper(II) compounds are polymeric and dimeric respectively. In all complexes with H_2L the pyridoxal thiosemicarbazone corresponds to a dipolar ion, owing to the shift of the proton from O(1) to N(4).

Both the Hmpt and H_2L ligands can be described as consisting of three systems: the thiourea moiety, the hydrazinic chain and the pyruvic group or the pyridoxal ring respectively. The dihedral angles between these planes and the chelate rings are reported in Tables 7 and 8.

In compound **1** the organic molecule deviates considerably from planarity. In fact the thiourea moiety and the pyruvic group are planar, but the dihedral angle between them is 10.3(2)°, as previously found in the polymer complex [{[Cu(Hpt)Cl]·2H$_2$O}$_n$].[5]

In **2** the ligand is nearly planar, the largest deviation from the best plane being for the terminal ethyl carbon C(5), but Fig. 2 illustrates that the bites of the ligand leave the zinc ion in an exposed position as is illustrated by the dihedral angles between the ligand parts and the chelate rings (Table 7).

In **3** the displacement from coplanarity of the ligand is indicated by the dihedral angles (Table 8) and the non-planarity of the hydrazinic chain gives a curvature to the whole molecule which assumes a boat-like conformation.[1]

In all the complexes the packing interactions are very important. The hydrogen bonds in **1** link the hydrazinic nitrogen atoms and the carboxylic oxygen atoms, and in **2** involve the chlorine atoms so forming layers of complex molecules nearly parallel to the $(20\bar{2})$ planes (Fig. 4). In **3** the dimers are joined together through N–H···N double hydrogen bonding to form polymeric ribbons parallel to (202) planes. The ribbons are interlinked by other hydrogen bonds involving the water molecules (Table 9 and Fig. 5).

The adenine, guanine and cytosine also have amine groups adjacent to unprotonated ring nitrogen atoms and are thus well equipped to form similar double hydrogen bonds with the thiosemicarbazone complexes. In fact some workers[29] investigating the biological activity of similar compounds suggest that hydrogen bonding may be an important factor in the antitumour mechanism.

Table 6 Comparison of bond distances (Å) for H_2L and for some of its complexes in which it is monodeprotonated

	H_2L[3]	$[\{Zn(HL)Cl\}_2]\cdot 2H_2O$ **3***	$[Fe(HL)Cl_2]$[20]	$[\{Cu(HL)(OH_2)\}_2]Cl_2\cdot 2H_2O$[4]
M–S	—	2.286(1)	2.337(4)	2.226(2)
M–O(1)	—	1.955(2)	1.889(8)	1.875(4)
M–O(aq)	—	—	—	1.941(5)
M–N(3)	—	2.110(2)	2.197(11)	1.943(6)
M–Cl	—	2.328(1)–2.698(1)	2.248(3)–2.287(4)	—
S–C(1)	1.70(1)	1.746(3)	1.730(13)	1.719(7)
C(1)–N(1)	1.33(1)	1.329(4)	1.340(14)	1.333(8)
C(1)–N(2)	1.35(1)	1.338(4)	1.330(16)	1.324(8)
N(2)–N(3)	1.40(1)	1.363(4)	1.377(12)	1.368(7)
N(3)–C(2)	1.30(1)	1.294(4)	1.303(16)	1.298(8)
C(2)–C(3)	1.45(1)	1.455(4)	1.436(15)	1.435(8)
C(3)–C(4)	1.42(1)	1.417(4)	1.428(18)	1.432(8)
C(4)–C(5)	1.37(1)	1.369(4)	1.347(16)	1.350(8)
C(5)–N(4)	1.36(1)	1.350(4)	1.377(16)	1.338(9)
C(6)–N(4)	1.34(1)	1.336(4)	1.334(16)	1.335(9)
C(6)–C(8)	1.50(1)	1.491(4)	1.508(18)	1.463(10)
C(6)–C(7)	1.42(1)	1.408(4)	1.391(15)	1.420(9)
C(7)–C(3)	1.44(1)	1.420(4)	1.407(18)	1.396(9)
C(7)–O(1)	1.29(1)	1.316(4)	1.320(15)	1.301(8)
C(4)–C(9)	1.52(1)	1.507(4)	1.526(18)	1.497(10)
C(9)–O(2)	1.43(1)	1.420(4)	1.408(16)	1.421(8)

* This work.

Table 7 Comparison of dihedral angles (°) between planes in the complexes obtained with Hmpt

	Planes					
	A–B	A–C	B–C	A–D	B–D	C–D
$[Zn(Hpt)_2]$ **1***	5.8	1.9	4.5	10.3	8.1	8.5
$[Zn(Hept)Cl_2]$ **2***	11.6	9.8	16.2	2.2	10.9	11.9
$[Fe(Hept)Cl_2]$[20]	13.0	11.4	19.6	2.4	11.4	13.6
$[\{Cu(ept)Cl\}_2]$[5]	6.2	5.4	2.0	1.0	0.7	1.1
$[\{[Cu(Hpt)Cl]\cdot 2H_2O\}_n]$[5]	11.0	6.7	4.4	10.2	2.7	4.5
$[\{Cu(Hpt)(OH_2)\cdot 0.5SO_4\}_2]$[22]	6.7	6.0	2.0	7.4	5.6	7.2

A = pyruvic moiety; B = five-membered chelate ring with sulfur; C = five-membered chelate ring with oxygen; D = thiourea moiety.
* This work.

Table 8 Comparison of dihedral angles (°) between planes in the complexes with H_2L

	$[\{Zn(HL)Cl\}_2]\cdot 2H_2O$ **3***	$[Fe(HL)Cl_2]$[19]	$[\{Cu(HL)(OH_2)\}_2]Cl_2\cdot 2H_2O$[4]
A–B	157.9	17.1	5.7
A–C	17.9	19.0	5.5
B–C	146.6	15.6	1.8
A–D	6.7	4.9	5.9
A–E	10.2	5.9	5.7
D–E	5.0	5.5	1.4
B–D	156.8	19.3	1.7
B–E	160.0	17.1	3.0
C–D	12.0	14.2	0.5
C–E	13.4	14.3	1.1

A = pyridine ring; B = six-membered chelate ring; C = five-membered chelate ring; D = thiourea moiety; E = hydrazine chain.
* This work.

Conclusion

All the zinc complexes seem to be influenced significantly by the nature of the solvent and, consequently, the resulting pH, independent of the metal : ligand molar ratio and the reaction temperature. In fact, as previously reported on a series of copper(II) complexes,[5] the transesterificated (Hept) and hydrolysed (H_2pt) forms of the original ligand (Hmpt) have been isolated depending on the experimental conditions, Hept and H_2pt being obtained when absolute ethanol and water respectively have been used as solvents.

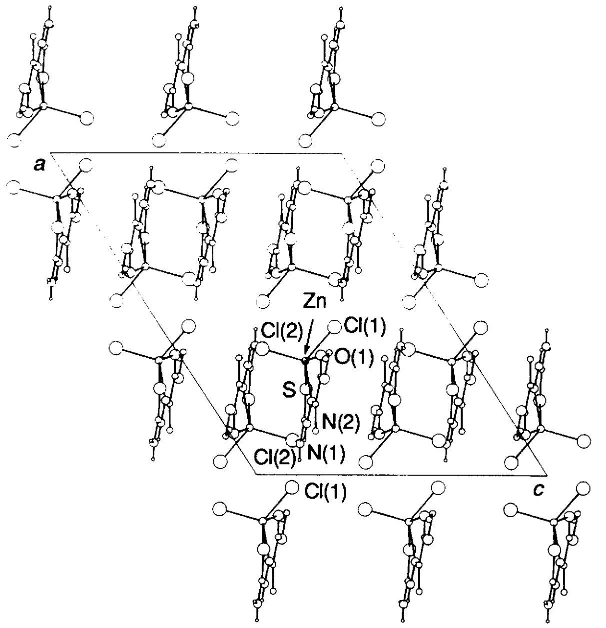

Fig. 4 Projection of the structure of complex **2** on the (010) plane. The hydrogen atoms have been omitted for clarity

As far as H_2L is concerned, the zinc complexes contain the monodeprotonated or neutral form of the ligand, when water or ethanol has been used respectively.

A comparison of the structures of the zinc complexes with both ligands, Hmpt and H_2L, and those of similar copper(II) and iron(II,III) compounds suggests the following considerations: (*a*) a greater variation in the bonding geometry of the zinc complexes is observed; (*b*) the different configurations can be a compromise resulting from competing energetic and geometrical factors such as the retention of resonance energy by the planar ligands, the bite of the ligand and the facility of the zinc atom to change its co-ordination number; (*c*) the weaker zinc–ligand bonds could determine, for $[Zn(Hpt)_2]$ and $[Zn(Hept)Cl_2]$, a lower stability than that of analogous copper(II) complexes, in accord with relatively rapid exchange of the ligands hypothesized for the catalytic role of the metal in biological systems, while a greater likeness can be observed between zinc and iron complexes with either Hept or H_2L; (*d*) the terdentate

Table 9 Relevant hydrogen bonds distances (Å) and angles (°); D = donor atom, A = acceptor atom

D–H ··· A	D ··· A	D–H ··· A
Compound **1**		
N(1)–H(11) ··· O(1^{i})	3.072(8)	134.8 (5.2)
N(2)–H(1) ··· O(1^{i})	2.727(5)	143.0 (6.0)
N(1)–H(21) ··· O(2^{ii})	2.775(10)	148.1 (6.4)
Compound **2**		
N(2)–H(1) ··· Cl(1^{i})	3.193(4)	159.7 (4.4)
N(1)–H(21) ··· Cl(1^{ii})	3.356(5)	149.0 (5.3)
N(1)–H(11) ··· Cl(2^{ii})	3.306(5)	174.7 (5.3)
Compound **3**		
O(3)–H(13) ··· Cl	3.299(3)	173.3 (4.6)
O(3)–H(23) ··· Cl^{i}	3.228(3)	159.6 (4.3)
N(1)–H(11) ··· O(2^{ii})	2.993(4)	149.7 (3.9)
N(1)–H(21) ··· N(2^{iii})	3.045(3)	173.1 (4.1)
N(4)–H(4) ··· O(3^{iv})	2.737(4)	171.6 (3.6)
O(2)–H(5) ··· O(1^{v})	2.757(4)	165.6 (4.0)

Symmetry operations. **1**: i $x + \frac{1}{2}$, $-y - \frac{1}{2}$, $z + \frac{1}{2}$; ii $x + \frac{1}{2}$, $y + \frac{1}{2}$, z. **2**: i $x - \frac{1}{2}$, $\frac{1}{2} - y$, $z - \frac{1}{2}$; ii $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$. **3**: i $1 - x$, $1 - y$, $-z$; ii x, $y - 1$, $z + 1$; iii $-x$, $1 - y$, $1 - z$; iv x, y, $z - 1$; v x, $1 + y$, z.

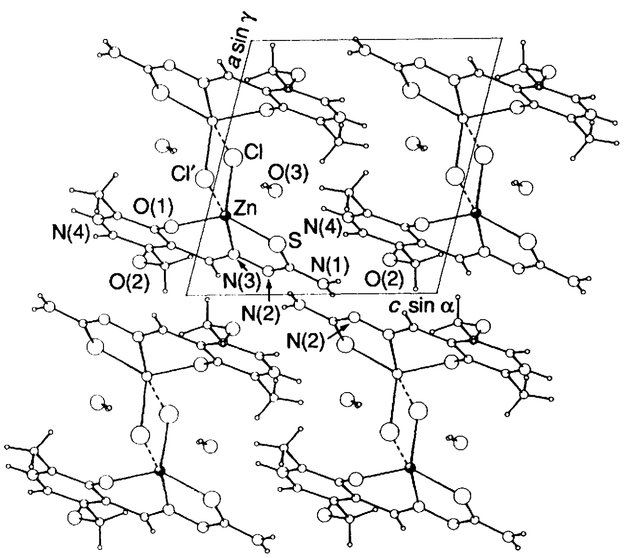

Fig. 5 The packing arrangement of complex **3** showing polymeric ribbons of dimers parallel to (202) planes

chelating nature of both ligands yields complexes with different stoichiometry dependent on the inorganic ion or on the ligand whether it is in neutral or monoanionic form; (*e*) all the zinc complexes are monomeric or dimeric but not polymeric; (*f*) all the metal complexes containing the terdentate system ONS show a potential biological activity with a wide range of pharmacological properties.[30]

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