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Coordination behaviour of sulfanilamide derivatives. Crystal structures of [Hg(sulfamethoxypyridazinato)$_2$], [Cd(sulfadimidinato)$_2$(H$_2$O)]·2H$_2$O and [Zn(sulfamethoxazolato)$_2$-(pyridine)$_2$(H$_2$O)$_2$]

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Abstract

Hg(II), Cd(II) and Zn(II) complexes with the ligands sulfadimethoxine, sulfamethoxypyridazine, sulfadiazine, sulfamerazine, sulfadimidine and sulfamethoxazole have been prepared and characterised by spectral data. ^{1}H and ^{13}C NMR have been used to interpret the structural characteristics of the complexes in solution. The X-ray crystal structures of [Hg(sulfamethoxypyridazinato)$_2$] (**2a**), [Cd(sulfadimidinato)$_2$(H$_2$O)]·2H$_2$O (**4b**) and [Zn(sulfamethoxazolato)$_2$(py)$_2$(H$_2$O)$_2$] (**6d**) have been determined. In complex **2a** the Hg(II) ion lies on an inversion centre and exhibits linear coordination by two sulfonamidic nitrogen atoms [Hg–N(1) = 2.071(4) Å] of the two deprotonated sulfamethoxypyridazinato ligands. The polymeric Cd(II) complex (**4b**) exhibits a high distorted-octahedral geometry, involving the sulfonamidic nitrogen [Cd–N(1) = 2.328(6); Cd–N(1′) = 2.326(6) Å] and the heterocyclic N(3)/N(2′) [Cd–N(3) = 2.307(6) Å; Cd–N(2′) = 2.426(6) Å] of two bidentate sulfadimidine ligands, the terminal amino N(4′b) [Cd–N(4′b) = 2.379(7) Å] of a third sulfadimidine which is bonded to an adjacent Cd(II), and the O(3) atom of a coordinated water molecule [Cd–O(3) = 2.334(6) Å]. In complex **6d** the geometry around the Zn(II) ion can be described as a slightly distorted compressed octahedron. Two pyridine [Zn–N(16) = 2.1841(17) Å] and two isoxazole N atoms [Zn–N(2) = 2.1736(15) Å] are located in the equatorial plane and two oxygen atoms of two water molecules [Zn–O(4) = 2.0984(14) Å] are placed in the apical positions. IR and NMR spectral studies suggest a similar behaviour of the Cd(II) and Zn(II) complexes, both in solid state and solution, and different to the corresponding Hg(II) complexes. Thus ^{1}H and ^{13}C NMR spectra, in DMSO-d_6, of Cd(II) and Zn(II) compounds show coordination mainly through the heterocyclic nitrogen while the corresponding Hg(II) derivatives seem to be coordinated through the sulfonamidic nitrogen.

Keywords: Cadmium complexes; Mercury complexes; Sulfamides; X-ray structure; Zinc complexes

1. Introduction

The synthesis of metal sulfanilamide compounds has received much attention due to the fact that sulfanilamides were the first effective chemotherapeutic agents to be employed for the prevention and cure of bacterial infections in humans (see Scheme 1). Although sulfamides present bacteriostatic activity [1–3] related to the inhibition of the bacterial enzyme DHPS (dihydropteroate synthetase) which catalyses the incorporation of *p*-aminobenzoic acid into the precursor of folic acid, 2-amino-4-hydroxy-6-hydroxymethyl dihydropteridine pyrophosphate (see Scheme 2) [4–7], the pharmacological activity of these types of molecules is often enhanced by complexation with metal ions [8,9]. Thus, rapid healing of skin disorders has been promoted by silver–sulfadiazine complex [10,11] in human topical burn therapy, and zinc–sulfadiazine complex [12,13] in the prevention of bacterial infection in burned animals, where the effectiveness of burn treatment seems to depend not only on the presence

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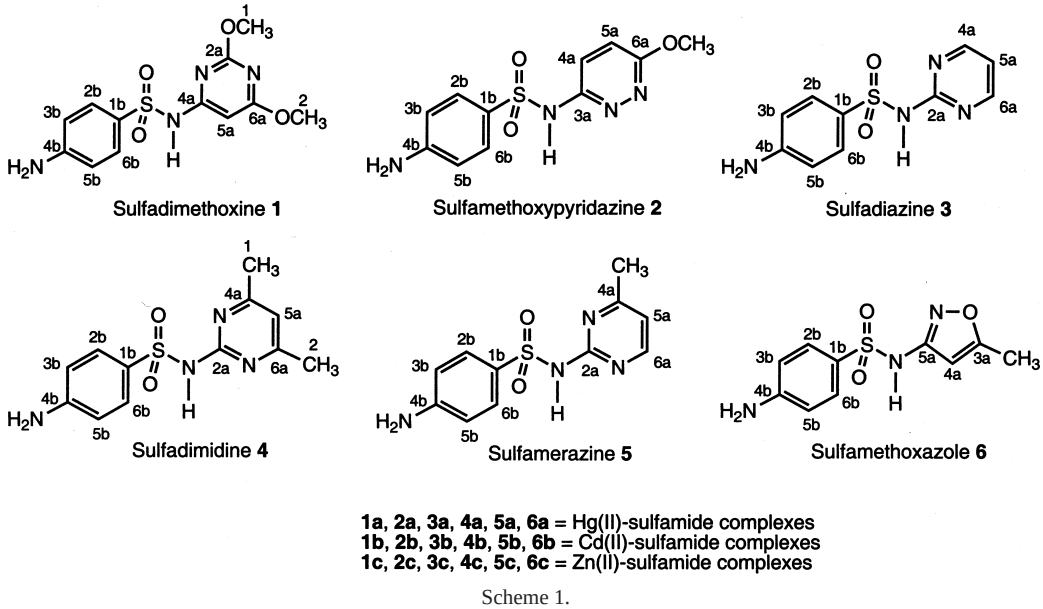


Scheme 1.

of a metal ion [slow release of the Ag(I) or Zn(II)], but also crucially on the nature of the material to which the metal ion is bound [12].

Morevoer, although interesting structural results have been described in the literature (sulfadiazine: Ag(I) [10,11,14], Zn(II) [12,13], Cu(II) [15] and Hg(II) [16]; sulfathiazole: Zn(II) [9], Cu(II) [17–20]; sulfadimetoxine: Co(II) [21]; sulfacetamide: Cu(II) [22]), no general studies related to the manner with which metal–sulfonamide interactions occur have been described. For this reason, in the present paper, we report on the synthesis and spectroscopic characterisation of the Zn(II), Cd(II) and Hg(II) complexes with six sulfonamides [sulfadimethoxine (**1**), sulfamethoxypyridazine (**2**), sulfadiazine (**3**), sulfadimidine (sulfamethazine) (**4**), sulfamerazine (**5**) and sulfamethoxazole (**6**)] and the X-ray structure determination of [Hg(sulfamethoxypyridazinato)$_2$] (**2a**), [Cd(sulfadimidinato)$_2$(H$_2$O)]·2H$_2$O (**4b**) and [Zn(sulfamethoxazolato)$_2$(py)$_2$(H$_2$O)$_2$] (**6d**) in order to show the general manner with which interactions between d^{10} metal ions and these ligands take place.

2. Experimental

2.1. Analysis and physical measurements

Satisfactory C, H, N and S analyses were obtained for all compounds and carried out using a Carlo-Erba Model 1106 microanalyser. The IR spectra in the solid state (KBr pellets) were recorded on a PE 683 spectrometer with a PE 1600 IR data station and on a Perkin-Elmer 843; electronic spectra were recorded on PE 552 and Shimadzu UV 2101PC spectrophotometers. 1D and 2D ^{1}H and ^{13}C NMR spectra were carried out on a Bruker AMX 300. Proton and carbon chemical shifts in DMSO-d_6 were referenced to DMSO-d_6 (^{1}H NMR, $\delta_{(DMSO)} = 2.60$ ppm; ^{13}C NMR, $\delta_{(DMSO)} = 43.5$ ppm). Solid state CP/MAS ^{13}C spectrum was recorded on a Varian Unity 300 spectrometer. Unequivocal C–H assignment was performed by 2D NMR experiments [HMQC [23] and HMBC [24]] or by comparison with spectra of related products. The 2D spectra were processed using commercial Bruker software and experimental characteristics are presented below.

2.1.1. ^{1}H-detected heteronuclear multiple quantum coherence spectroscopy (HMQC)

The one-bond ^{1}H–^{13}C shift correlation spectra resulted from a 502×2048 data matrix size with 48 scans (preceded by 16 dummy scans) per t_1 value. Predelay was 1.0 s, and a 10.3-μs 90° ^{13}C pulse width was used. A sine bell squared filter was used prior to Fourier transformation in the t_2 and t_1 dimensions.

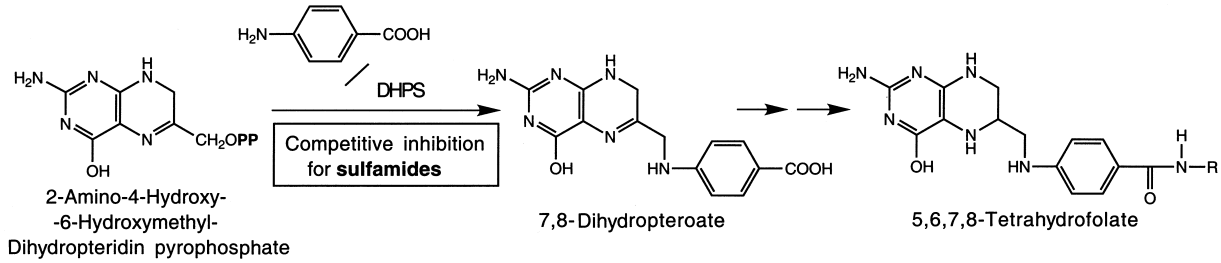
2.1.2. ^{1}H-detected multiple-bond heteronuclear multiple quantum coherence spectroscopy (HMBC)

The multiple-bond ^{1}H–^{13}C shift correlation spectra resulted from a 246×2048 matrix data size with 128 scans (preceded by 8 or 16 dummy scans) per t_1 value. Predelay was 1.0 s, and a 10.3-μs 90° ^{13}C pulse width were used. The delay between the first and the second 90° ^{13}C pulses was 75 ms. A sine bell squared filter was used prior to Fourier transformation in the t_2 and t_1 dimensions.

Sulfamides were used as received from Roig Farma. Zn(II), Cd(II) and Hg(II) acetates were supplied by Aldrich and used without purification.

2.2. Crystallographic studies

X-ray data from compounds **2a** and **4b** were collected on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (0.71069 Å). The cell parameters and space group were determined from a least-square refinement of 25 reflections



Scheme 2.

randomly searched. Data collection employed an ω–2θ scan technique. Three reflections were measured every hour as intensity controls; an intensity decay of 1.5% (**2a**) and 7.7% (**4b**) was observed and corrected. The MOLEN [25] package was used for applying Lorentz polarization correction and ψ-scan empirical absorption corrections. The structures were solved by direct methods using the SHELXS 86 program [26] and refined by least-squares using the SHELXL 93 program [27]. Hydrogen atoms were placed in calculated positions, except for those corresponding to water molecules (for **4b**), which were located in Fourier-difference maps, and refined with an isotropic thermal factor constrained to 1.2 times U_{eq} of their bonded atom [1.5 (**2a**) or 1.3 (**4b**) times in the case of methyl groups].

X-ray data from compound **6d** were collected on an Enraf-Nonius CAD4 automatic diffractometer [28] with Cu Kα radiation ($\lambda = 1.54184$ Å). Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections. Data collection employed an ω-scan technique and were corrected for Lorentz and polarisation effects [29]. A semi-empirical absorption correction (Ψ scan) was made [30]. The structure was solved by direct methods [26] which revealed the position of all non-hydrogen atoms and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [31]. The hydrogen atoms were located from difference maps and refined isotropically. Atomic scattering factors were from International Tables for X-Ray Crystallography [32]. Molecular graphics were from ZORTEP [33].

Details of the data collection and processing are summarised in Table 1.

2.3. Preparation of Hg(II)–sulfamidato complexes

2.3.1. General procedure

Hg(II) acetate (1 mmol) in methanol (20 ml) was added dropwise to a stirred solution of the corresponding sulfamide (2 mmol) in methanol (20 ml). A white precipitate begins to form and the reaction is stirred during 18 h at room temperature. The precipitate is filtered off and air dried. Crystallisation in different mixtures of NH_4OH–H_2O or DMSO–MeOH yields white crystals.

2.3.2. Hg(sulfadimethoxynato)$_2$ (**1a**)

White solid (87% yield). Found: C, 35.00; H, 3.09; N, 13.52; S, 7.89. Calc. for $C_{24}H_{26}N_8S_2O_8Hg$: C, 35.18; H, 3.17; N, 13.68; S, 7.82%. Selected IR data (cm^{-1}): 911m, 946w, 962vw, 984w, 1009m, 1090s, 1113s, 1141vs, 1211vs, 1294s, 1362vs, 1419s, 1575vs, 1635s, 3244m, 3367s, 3454m. UV (DMSO): λ 274 nm (ε 4.5×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 0.7. ^{1}H NMR (DMSO-d_6): δ 7.59d [2H, H(2b)/H(6b), J = 8.2 Hz], 6.57d [2H, H(3b)/H(5b), J = 8.2 Hz], 5.83s [1H, H(5a)], 5.80bs (2H, NH_2), 3.84s [3H, $OCH_3(1)$], 3.79s [3H, $OCH_3(2)$]. ^{13}C NMR (DMSO-d_6): δ 176.2 [C(6a)], 168.0 [C(2a)], 165.8 [C(4a)], 157.2 [C(4b)], 133.7 [C(2b)/C(6b)], 128.3 [C(1b)], 116.8 [C(3b)/C(5b)], 88.6 [C(5a)], 58.8 [$OCH_3(1)$], 58.0 [$OCH_3(2)$].

2.3.3. Hg(sulfamethoxypyridazinato)$_2$ (**2a**)

White solid (94% yield). White crystals in NH_4OH–H_2O (1:1). Found: C, 34.71; H, 2.88; N, 14.70; S, 8.33. Calc. for $C_{22}H_{22}N_8S_2O_6Hg$: C, 34.80; H, 2.90; N, 14.76; S, 8.44%. Selected IR data (cm^{-1}): 952s, 1016s, 1041m, 1091s, 1125m, 1153s, 1272vs, 1318m, 1351w, 1402vs, 1460s, 1503m, 1548w, 1602s, 3209m, 3363m. UV (DMSO): λ 273 nm (ε 3.5×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 3.3. ^{1}H NMR (DMSO-d_6): δ 7.82d [2H, H(2b)/H(6b), J = 8.6 Hz], 7.62d [1H, H(4a), J = 9.6 Hz], 7.31d [1H, H(5a), J = 9.6 Hz], 6.68d [2H, H(3b)/H(5b), J = 8.6 Hz], 6.06bs (2H, NH_2), 4.01s (3H, OCH_3). ^{13}C NMR (DMSO-d_6): δ 165.8 [C(6a)], 158.0 [C(3a)], 156.7 [C(4b)], 133.1 [C(2b)/C(6b)], 129.9 [C(1b)], 125.5 [C(4a)], 124.4 [C(5a)], 116.7 [C(3b)/C(5b)], 58.3 (OCH_3).

2.3.4. Hg(sulfadiazinato)$_2$·2DMSO (**3a**)

Previously described [16].

2.3.5. Hg(sulfadimidinato)$_2$ (**4a**)

White solid (83% yield). Found: C, 37.91; H, 3.43; N, 14.78; S, 8.48. Calc. for $C_{24}H_{26}N_8S_2O_4Hg$: C, 38.16; H, 3.45; N, 14.84; S, 8.48%. Selected IR data (cm^{-1}): 892m, 956vw, 992m, 1086m, 1150vs, 1302s, 1343m, 1371s, 1395sh, 1434m(br), 1503m, 1555m(br), 1597s, 1629m, 3348m. UV (DMSO): λ 275 nm (ε 5.2×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 0.3. ^{1}H NMR (DMSO-d_6): δ 7.88bd [2H, H(2b)/H(6b)], 6.66d

Table 1
Crystal data and structure refinements for complexes **2a**, **4b** and **6d**

	Hg(sulfamet)$_2$ (**2a**)	Cd(sulfadimid)$_2\cdot 3H_2O$ (**4b**)	Zn(sulfamoxaz)$_2$(py)$_2$(H$_2$O)$_2$ (**6d**)
Empirical formula	$C_{22}H_{22}HgN_8O_6S_2$	$C_{24}H_{32}CdN_8O_7S_2$	$C_{30}H_{38}N_8O_{10}S_2Zn$
Crystal size (mm)	0.18×0.20×0.55	0.14×0.17×0.28	0.30×0.15×0.10
Crystal system	monoclinic	monoclinic	triclinic
Space group	$C2/c$	$P2_1/a$	$P\bar{1}$
Unit cell dimensions			
a (Å)	22.424(4)	13.357(2)	9.0174(4)
b (Å)	10.642(1)	15.046(1)	9.8677(4)
c (Å)	11.222(2)	15.369(2)	10.4481(4)
α (°)			83.996(4)
β (°)	113.11(2)	97.60(1)	78.004(4)
γ (°)			86.455(3)
Volume (Å^3)	2463.1(7)	3061.6(6)	903.55(6)
Z	4	4	1
Formula weight	759.19	721.10	800.17
Density (calc.) (Mg m^{-3})	2.047	1.564	1.471
Absorption coefficient (mm^{-1})	6.477	0.905	2.587
$F(000)$	1480	1472	416
θ Range (°)	2.65–26.23	2.33–30.41	4.35–74.31
Index ranges	$-27\le h\le 23,\ -13\le k\le 0,\ 0\le l\le 13$	$0\le h\le 19,\ 0\le k\le 21,\ -21\le l\le 21$	$0\le h\le 11,\ -12\le k\le 12,\ -12\le l\le 13$
Reflections collected	2763	9623	3925
Independent reflections	2368 [$R_{int}=0.0255$]	9258 [$R_{int}=0.1088$]	3680 [$R_{int}=0.0111$]
Data/restraints/parameters	2368/0/179	9258/0/401	3680/0/309
Maximum, minimum transmission	0.999, 0.421	0.998, 0.823	0.981, 0.823
Final R indices [$I>2\sigma(I)$]	$R_1=0.0301$, $wR_2=0.0877$	$R_1=0.1125$, $wR_2=0.3007$	$R_1=0.0309$, $wR_2=0.0839$
R indices (all data)	$R_1=0.0398$, $wR_2=0.0921$	$R_1=0.2020$, $wR_2=0.3354$	$R_1=0.0365$, $wR_2=0.0875$
Goodness-of-fit on F^2	1.101	1.175	1.042
Largest difference peak, hole (e Å^{-3})	1.244, −1.114	2.081, −1.372	0.301, −0.351

[2H, H(3b)/H(5b), J=8.5 Hz], 6.85s [1H, H(5a)], 5.97bs (2H, NH_2), 2.37s (6H, CH_3). ^{13}C NMR (DMSO-d_6): δ 171.6 [C(4a)/C(6a)], 163.3 [C(2a)], 156.5 [C(4b)], 134.7 [C(2b)/C(6b)], 130.0 [C(1b)], 116.8 [C(5a)], 115.8 [C(3b)/C(5b)], 27.2 (CH_3).

2.3.6. Hg(sulfamerazinato)$_2\cdot 1.5H_2O$ (**5a**)

White solid (75% yield). Found: C, 35.05; H, 3.19; N, 14.62; S, 8.35. Calc. for $C_{22}H_{22}N_8S_2O_4Hg\cdot 1.5(H_2O)$: C, 35.03; H, 3.31; N, 14.86; S, 8.49%. Selected IR data (cm^{-1}): 917m, 944w, 975w, 1093s, 1143s, 1289s, 1312m, 1373s, 1391s, 1431m, 1457m, 1505m, 1557s, 1579vs, 1600s, 1638m, 3354s, 3450m. UV (DMSO): λ 272 nm (ε 4.9×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 0.7. ^{1}H NMR (DMSO-d_6): δ 8.41d [1H, H(6a), J=4.8 Hz], 7.87d [2H, H(2b)/H(6b), J=8.6 Hz], 6.96d [1H, H(5a), J=4.7 Hz], 6.66d [2H, H(3b)/H(5b), J=8.6 Hz], 5.98bs (2H, NH_2), 2.42s (3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 172.1 [C(4a)], 163.6 [C(2a)], 160.9 [C(6a)], 156.6 [C(4b)], 134.5 [C(2b)/C(6b)], 130.1 [C(1b)], 116.0 [C(3b)/C5b)], 117.7 [C(5a)], 27.4 (CH_3).

2.3.7. Hg(sulfamethoxazolato)$_2$ and Hg(sulfamethoxazolato)$_2\cdot 1.5$DMSO (**6a**)

White solid (89% yield). Found: C, 33.93; H, 2.84; N, 11.75; S, 9.08. Calc. for $C_{20}H_{20}S_2O_6Hg$: C, 34.06; H, 2.84; N, 11.92; S, 9.05%. White crystals in DMSO–MeOH. Found: C, 33.80; H, 3.54; N, 9.99; S, 13.67. Calc. for $C_{20}H_{20}S_2O_6Hg\cdot 1.5$DMSO: C, 33.59; H, 3.53; N, 10.22; S, 13.63%. Selected IR data (cm^{-1}): 903m, 952s, 1012m, 1061m, 1091s, 1136vs, 1288m(br), 1266s, 1296s, 1378w, 1416s, 1432s, 1472vs, 1504s, 1598s, 1613s, 1630s, 3378s, 3474m. UV (DMSO): λ 274 nm (ε 4.5×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 0.6. ^{1}H NMR (DMSO-d_6): δ 7.76d [2H, H(2b)/H(6b), J=8.5 Hz], 6.69d [2H, H(3b)/H(5b), J=8.5 Hz], 6.13 s[1H, H(4a)], 6.11bs (2H, NH_2), 2.38s (3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 174.7 [C(3a)], 165.9 [C(5a)], 157.0 [C(4b)], 133.4 [C(2b)/C(6b)], 129.2 [C(1b)], 116.7 [C(3b)/C(5b)], 99.4 [C(4a)], 16.4 (CH_3).

2.4. Preparation of Cd(II) and Zn(II)–sulfamidato complexes

2.4.1. General procedure

Cd(II) or Zn(II) acetate (1 mmol) in distilled water (20 ml) was added dropwise to a stirred solution of sodium sulfamidato (2 mmol) in distilled water (20 ml). A white precipitate begins to form and the reaction is stirred during 18 h at room temperature. The precipitate is filtered off and air dried. Crystallisation in different mixtures of NH_4OH–H_2O or DMSO–MeOH yields white crystals.

*2.4.2. Cd(sulfadimethoxynato)$_2$·1/2(NH_3)·H_2O and Cd(sulfadimethoxynato)$_2$·DMSO (**1b**)*

White solid (83% yield). White crystals in NH_4OH–H_2O (1:1). Found: C, 37.92; H, 3.84; N, 15.57; S, 8.37. Calc. for $C_{24}H_{26}N_8S_2O_8Cd \cdot 1/2(NH_3) \cdot H_2O$: C, 38.05; H, 3.89; N, 15.72; S, 8.46%. White crystals in DMSO–MeOH. Found: C, 38.41; H, 3.95; N, 13.72; S, 11.87. Calc. for $C_{24}H_{26}N_8S_2O_8Cd \cdot DMSO$: C, 38.59; H, 3.96; N, 13.85; S, 11.87%. Selected IR data (cm^{-1}): 881s, 932w, 961w, 989w, 1086s, 1145s, 1180m, 1215s, 1263s, 1363s, 1369s, 1396m, 1425s, 1461m, 1489m, 1558s, 1585vs, 1602vs, 2953m, 3337m(br), 3491m(br). UV (DMSO): λ 274 nm (ε 8.6×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 10.2. ^{1}H NMR (DMSO-d_6): δ 7.59d [2H, H(2b)/H(6b), J = 8.2 Hz], 6.57d [2H, H(3b)/H(5b), J = 8.2 Hz], 5.83s [1H, H(5a)], 5.80bs (2H, NH_2), 3.84s [3H, OCH_3(1)], 3.79s [3H, OCH_3(2)]). ^{13}C NMR (DMSO-d_6): δ 175.7 [C(6a)], 169.6 [C(2a)], 167.6 [C(4a)], 155.6 [C(4b)], 132.6 [C(2b)/C(6b)], 132.3 [C(1b)], 116.4 [C(3b)/C(5b)], 87.7 [C(5a)], 58.3 [OCH_3(1)], 57.6 [OCH_3(2)].

*2.4.3. Zn(sulfadimethoxinato)$_2$·3/4(NH_3)·3/4(H_2O) (**1c**)*

White solid (90% yield). White crystals in NH_4OH–H_2O (1:9). Found: C, 40.45; H, 3.98; N, 17.35; S, 8.91. Calc. for $C_{24}H_{26}N_8S_2O_8Zn \cdot 3/4(NH_3) \cdot 3/4(H_2O)$: C, 40.58; H, 4.19; N, 17.26; S, 9.02%. IR (cm^{-1}): 883s, 996m, 1008sh, 1058s,s 1069w, 1144s, 1181m, 1213s, 1275s, 1362s, 1369s, 1394m, 1431m, 1461w, 1488m, 1599vs, 2953m, 3168m, 3259m, 3373m(br), 3472m(br). UV (DMSO): λ 275 nm (ε 4.6×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 11.0. ^{1}H NMR (DMSO-d_6): δ 7.58d [2H, H(2b)/H(6b), J = 8.4 Hz], 6.59d [2H, H(3b)/H(5b), J = 8.6 Hz], 5.86s [H, H(5a)], 5.77bs (2H, NH_2), 3.81s [3H, OCH_3(1)], 3.73s [3H, OCH_3(2)]. ^{13}C NMR (DMSO-d_6): δ 175.4 [C(6a)], 170.1 [C(2a)], 167.6 [C(4a)], 155.7 [C(4b)], 132.8 [C(2b)/C(6b)], 132.8 [C(1b)], 116.5 [C(3b)/C(5b)], 88.4 [C(5a)], 58.2 [OCH_3(1)], 57.6 [OCH_3(2)].

*2.4.4. Cd(sulfamethoxypyridazinato)$_2$·2(H_2O) (**2b**)*

White solid (90% yield). Found: C, 37.34; H, 3.50; N, 15.71; S, 8.55. Calc. for $C_{22}H_{22}N_8S_2O_6Cd \cdot 2(H_2O)$: C, 37.37; H, 3.68; N, 15.85; S, 9.06%. Selected IR data (cm^{-1}): 836s, 971s, 1016s, 1047m, 1087s, 1138s, 1182m, 1254s, 1299s, 1367m, 1422vs, 1469s, 1503m, 1540m, 1601s, 1637m, 3264m, 3364s. UV (DMSO): λ 270 nm (ε 3.5×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 5.1. ^{1}H NMR (DMSO-d_6): δ 7.65 d[2H, H(2b)/H(6b), J = 8.4 Hz], 7.42 d [1H, H(4a), J = 9.6 Hz], 7.16 d [1H, H(5a), J = 9.6 Hz], 6.55 d [2H, H(3b)/H(5b), J = 8.4 Hz], 5.72 bs (2H, NH_2), 3.95 s (3H, OCH_3). ^{13}C NMR (DMSO-d_6): δ 164.1 [C(6a)], 162.3 [C(3a)], 155.4 [C(4b)], 133.9 [C(1b)], 132.6 [C(2b)/C(6b)], 125.8 [C(4a)], 124.9 [C(5a)], 116.7 [C(3b)/C(5b)], 58.1 (OCH_3).

*2.4.5. Zn(sulfamethoxypyridazinato)$_2$·2.5(H_2O) (**2c**)*

White solid (55% yield). Found: C, 39.41; H, 3.90; N, 16.61; S, 9.84. Calc. for $C_{22}H_{22}N_8S_2O_6Zn \cdot 2.5(H_2O)$: C, 39.49; H, 4.04; N, 16.76; S, 9.57%. Selected IR data (cm^{-1}): 750m, 840m, 945m, 1015s, 1091s, 1133s, 1185m, 1293s, 1417vs, 1469vs, 1503m, 1599s, 1629m, 3240m(br), 3368m, 3446m(br). UV (DMSO): λ 271 nm (ε 3.5×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 5.5. ^{1}H NMR (DMSO-d_6): δ 7.51d [2H, H(2b)/H(6b), J = 8.4 Hz], 7.49d [1H, H(4a), J = 9.7 Hz], 7.11d [1H, H(5a), J = 9.7 Hz], 6.51d [2H, H(3b)/H(5b), J = 8.4 Hz], 5.67bs (2H, NH_2), 3.90s (3H, OCH_3). ^{13}C NMR (DMSO-d_6): δ 163.0 [C(6a)], 162.1 [C(3a)], 155.2 [C(4b)], 134.3 [C(1b)], 132.2 [C(2b)/C(6b)], 127.6 [C(4a)], 124.6 [C(5a)], 116.5 [C(3b)/C(5b)], 58.0 (OCH_3).

*2.4.6. Cd(sulfadiazinato)$_2$·2(NH_3) (**3b**)*

White solid (80% yield). White crystals in NH_4OH–H_2O (1:1). Found: C, 37.29; H, 3.66; N, 21.56; S, 9.79. Calc. for $C_{20}H_{18}N_8S_2O_4Cd \cdot 2(NH_3)$: C, 37.24; H, 3.72; N, 21.72; S, 9.93%. Selected IR data (cm^{-1}): 725m, 785m, 806s, 846s, 964s, 980s, 1008s, 1090s, 1108m, 1262s, 1277s, 1352m, 1413vs, 1442s, 1501m, 1554s, 1584s, 1598s, 3154m, 3244m, 3315s, 3460m(br). UV (DMSO): λ 271 nm (ε 4.5×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 5.1. ^{1}H NMR (DMSO-d_6): δ 8.37d [2H, H(6a), J = 4.9 Hz], 7.64d [2H, H(2b)/H(6b), J = 8.6 Hz], 6.77t [1H, H(5a)], 6.53d [2H, H(3b)/H(5b), J = 8.6 Hz], 5.64s (2H, NH_2). ^{13}C NMR (DMSO-d_6): δ 166.3 [C(2a)], 162.2 [C(4a)/C(6a)], 155.0 [C(4b)], 134.1 [C(1b)], 132.9 [C(2b)/C(6b)], 116.0 [C(3b)/C5b)], 115.1 [C(5a)].

*2.4.7. Zn(sulfadiazinato)$_2$·2(NH_3) (**3c**)*

Only small quantities of the complex have been obtained using the experimental procedure previously described [12] or the general procedure described in the present paper. Under these conditions, a mixture of neutral sulfadiazine and $Zn(OH)_2$ is present [14].

Improved results have been obtained by means of the following procedure. Zn(II) nitrate (1 mmol) in NH_4OH–H_2O (1:9) (20 ml) is added dropwise to a stirred solution of sulfadiazine (2 mmol) in NH_4OH–H_2O (1:9) (20 ml). The resulting solution is heated (60°C) until a white precipitate begins to form; the solution is then filtered and crystals are obtained after cooling (24–48 h). The crystalline complex is filtered off and air dried (65% yield). Selected IR data (cm^{-1}): 836m, 978m, 994m, 1014m, 1024m, 1082s, 1102s, 1124s, 1141s, 1182m, 1230s, 1269s, 1282m, 1296m, 1363m, 1418vs, 1426vs, 1453vs, 1502m, 1554s, 1597s, 1635m, 3226m, 3340s, 3459m. ^{1}H NMR (DMSO-d_6): δ 8.30d [2H, H(6a), J = 4.5 Hz], 7.65d [2H, H(2b)/H(6b), J = 8.2 Hz], 6.73t [1H, H(5a)], 6.56d [2H, H(3b)/H(5b), J = 8.4 Hz], 5.68s (2H, NH_2). ^{13}C NMR (DMSO-d_6): δ 166.1 [C(2a)], 161.9 [C(4a)/C(6a)], 155.0 [C(4b)], 134.1 [C(1b)],

133.1 [C(2b)/C(6b)], 116.0 [C(3b)/C5b)], 115.0 [C(5a)].

*2.4.8. [Cd(sulfadimidinato)$_2$(H$_2$O)]·2H$_2$O (**4b**)*

White solid (80% yield). White crystals in NH_4OH–H_2O (3:9). Found: C, 40.09; H, 4.49; N, 15.48; S, 8.67. Calc. for $C_{24}H_{26}N_8S_2O_4Cd\cdot 3H_2O$: C, 39.98; H, 4.44; N, 15.55; S, 8.88%. Selected IR data (cm^{-1}): 885s, 982m, 1082s, 1128vs, 1144s, 1184m, 1248s, 1347m, 1380vs, 1398m, 1434s, 1499m, 1564m, 1586s, 1601s, 1641m, 3160m, 3288m, 3371m, 3465m, 3545m. UV (DMSO): λ 273 nm (ε 6.7×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 3.5. ^{1}H NMR (DMSO-d_6): δ 7.67bd [2H, H(2b)/H(6b)], 6.51bd [2H, H(3b)/H(5b)], 6.49s [1H, H(5a)], 5.62bs (2H, NH_2), 2.18s (6H, CH_3). ^{13}C NMR (DMSO-d_6): δ 171.2 [C(4a)/C(6a)], 166.1 [C(2a)], 154.9 [C(4b)], 134.2 [C(1b)], 133.5 [C(2b)/C(6b)], 115.6 [C(3b)/C5b)], 114.0 [C(5a)], 27.0 (CH_3).

*2.4.9. Zn(sulfadimidinato)$_2$·1.75(NH$_3$)·0.25(H$_2$O) (**4c**)*

White solid (71% yield). White crystals in NH_4OH–H_2O (1:9). Found: C, 43.87; H, 4.84; N, 20.90; S, 9.40. Calc. for $C_{24}H_{26}N_8S_2O_4Zn\cdot 1.75(NH_3)\cdot 0.25(H_2O)$: C, 44.06, H, 4.86; N, 20.88; S, 9.79%. Selected IR data (cm^{-1}): 886s, 984m, 1014m, 1058m, 1082s, 1128vs, 1144s, 1186m, 1274s, 1304w, 1349m, 1380s, 1400m, 1436s, 1501m, 1650m, 1588s, 1602s, 1644m, 3158m, 3281m(br), 3368m, 3456m, 3550m UV (DMSO): λ 273 nm (ε 2.1×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 2.7. ^{1}H NMR (DMSO-d_6): δ 7.68d [2H, H(2b)/H(6b), J = 7.9 Hz], 6.53d [2H, H(3b)/H(5b), J = 7.6 Hz], 6.46s [1H, H(5a)], 5.62bs (2H, NH_2), 2.18s (6H, CH_3). ^{13}C NMR (DMSO-d_6): δ 170.9 [C(4a)/C(6a)], 165.9 [C(2a)], 155.0 [C(4b)], 133.6 [C(1b)], 133.6 [C(2b)/C(6b)], 115.7 [C(3b)/C5b)], 114.3 [C(5a)], 26.8 (CH_3).

*2.4.10. Cd(sulfamerazinato)$_2$·2H$_2$O (**5b**)*

White solid (83% yield). Found: C, 39.05; H, 3.67; N, 16.40; S, 9.26. Calc. for $C_{22}H_{22}N_8S_2O_4Cd\cdot 2H_2O$: C, 39.14; H, 3.85; N, 16.60; S, 9.48%. Selected IR data (cm^{-1}): 867m, 906m, 978m, 1086m, 1104m, 1113m, 1138s, 1253s, 1328m, 1391s, 1414s, 1436s, 1460m, 1498m, 1558m, 1566m, 1581s, 1597s, 3161m, 3257m, 3292m, 3360m, 3496m, 3553m. UV (DMSO): λ 271 nm (ε 4.8×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 3.3. ^{1}H NMR (DMSO-d_6): δ 8.21bd [1H, H(6a)], 7.64d [2H, H(2b)/H(6b)], 6.63d [1H, H(5a)], 6.51bd [2H, H(3b)/H(5b)], 5.62bs (2H, NH_2), 2.18s (3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 171.6 [C(4a)], 166.2 [C(2a)], 161.9 [C(6a)], 154.9 [C(4b)], 134.1 [C(1b)], 133.1 [C(2b)/C(6b)], 115.8 [C(3b)/C5b)], 114.7 [C(5a)], 26.9 (CH_3).

*2.4.11. Zn(sulfamerazinato)$_2$·2H$_2$O (**5c**)*

White solid (84% yield). Found: C, 41.76; H, 4.11; N, 17.46; S, 10.29. Calc. for $C_{22}H_{22}N_8S_2O_4Zn\cdot 2H_2O$: C, 42.07; H, 4.14; N, 17.85; S, 10.20%. Selected IR data (cm^{-1}): 865m, 980m, 981m, 1014m, 1087s, 1104m, 1113m, 1138s, 1252s, 1327m, 1398s, 1419vs, 1433s, 1462s, 1499m, 1566s, 1582s, 1598vs, 1624m, 3156m, 3247m, 3286m, 3366m, 3491m, 3554m. UV (DMSO): λ 272 nm (ε 5.0×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 3.2. ^{1}H NMR (DMSO-d_6): δ 8.13s [1H, H(6a)], 7.67d [2H, H(2b)/H(6b), J = 8.2 Hz], 6.60s [1H, H(5a)], 6.54d [2H, H(3b)/H(5b), J = 8.2 Hz], 5.62bs (2H, NH_2), 2.19s (3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 172.3 [C(4a)], 165.8 [C(2a)], 160.9 [C(6a)], 155.2 [C(4b)], 134.2 [C(1b)], 133.5 [C(2b)/C(6b)], 116.0 [C(3b)/C5b)], 114.8 [C(5a)], 27.3 (CH_3).

*2.4.12. Cd(sulfamethoxazolato)$_2$·2(H$_2$O) (**6b**)*

White solid (89% yield). Found: C, 37.11; H, 3.69; N, 12.80; S, 9.78. Calc. for $C_{20}H_{20}S_2O_6Cd\cdot 2(H_2O)$: C, 36.78; H, 3.67; N, 12.87; S, 9.80%. Selected IR data (cm^{-1}): 792m, 835s, 930s, 942s, 1090s, 1111vs, 1174s, 1216s, 1222s, 1264m, 1302m, 1320m, 1377w, 1418s, 1445m, 1477vs, 1506m, 1604m, 1628s, 3379m, 3431m, 3476m. UV (DMSO): λ 267 nm (ε 3.4×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 12.4. ^{1}H NMR (DMSO-d_6): δ 7.58d [2H, H(2b)/H(6b), J = 8.6 Hz], 6.58d [2H, H(3b)/H(5b), J = 8.6 Hz], 5.89s [1H, H(4a)], 5.71bs (2H, NH_2), 2.26s (3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 172.7 [C(3a)], 168.4 [C(5a)], 155.8 [C(4b)], 133.2 [C(1b)], 133.2 [C(2b)/C(6b)], 117.0 [C(3b)/C(5b)], 100.7 [C(4a)], 16.5 (CH_3).

*2.4.13. Zn(sulfamethoxazolato)$_2$·2(H$_2$O) (**6c**)*

White solid (79% yield). Found: C, 39.52; H, 3.96; N, 13.72; S, 10.52. Calc. for $C_{20}H_{20}S_2O_6Zn\cdot 2(H_2O)$: C, 39.64; H, 3.96; N, 13.87; S, 10.57%. Selected IR data (cm^{-1}): 818s, 838s, 884sh, 920s, 951s, 1010m, 1055m, 1086s, 1131vs, 1261s, 1274s, 1305m, 1323m, 1426s, 1476s, 1504m, 1577m, 1601s, 1636s, 1661m, 3071m, 3225s, 3365s, 3496s. UV (DMSO): λ 267 nm (ε 3.3×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO, 25°C) = 10.2. ^{1}H NMR (DMSO-d_6): δ 7.60d [2H, H(2b)/H(6b), J = 8.6 Hz], 6.58d [2H, H(3b)/H(5b), J = 8.6 Hz], 5.97s [1H, H(4a)], 5.78s (2H, NH_2), 2.28s (3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 172.8 [C(3a)], 167.3 [C(5a)], 156.2 [C(4b)], 133.2 [C(1b)], 132.2 [C(2b)/C(6b)], 116.9 [C(3b)/C(5b)], 100.9 [C(4a)], 16.4 (CH_3).

*2.4.14. Zn(sulfamethoxazolato)$_2$(py)$_2$(H$_2$O)$_2$ (**6d**)*

A solution of $ZnCl_2$ containing 10 mmol in 50 ml H_2O–py (3:1) was added to a solution of sulfamethoxazole (5 mmol in 50 ml H_2O–py, 1:1) with continuous stirring. Immediately, a white solid was obtained. The precipitate was isolated by filtration and the filtrate was left to stand at room temperature. From the filtrate colourless prismatic crystals suitable for X-ray measurement appeared after a month. Selected IR data (cm^{-1}): 670s, 700s, 750m, 800–820m, 840m, 900m, 930s, 1000m, 1040s, 1060m, 1080s, 1130vs, 1220s, 1250s, 1270s, 1315m, 1410s, 1440s, 1460s, 1500s, 1590s, 1600s, 1630s,

3350s, 3480s. UV (solid): 258 nm. UV (DMSO): λ 273 nm (ε 4.5×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in DMSO at 25°C) = 10.0. ^{1}H NMR (DMSO-d_6): δ 8.69dt [2H, H(o-) py, J = 4.2 and 1.7 Hz], 7.96tt [1H, H(p-) py, J = 7.7 and 1.7 Hz], 7.57m [4H, H(2b)/H(6b) + H(m-) py], 6.61d [2H, H(3b)/H(5b), J = 8.6 Hz], 6.05s [1H, H(4a)], 5.87s (2H, NH_2), 2.30s (3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 172.4 [C(3a)], 167.5 [C(5a)], 155.9 [C(4b)], 153.2 [C(o-) py], 142.1 [C(p-) py], 132.7 [C(2b)/C(6b)], 132.1 [C(1b)], 128.7 [C(m-) py], 116.5 [C(3b)/C(5b)], 100.6 [C(4a)], 16.2 (CH_3). Solid ^{13}C NMR (ppm) tentative assignment: 168.2 [(C(3a)], 163.0 [C(5a)], 150.3 [C(4b) and C(o-) py], 140.1 [C(p-) py], 131.1 [C(1b)], 127.0 and 123.1 [C(2b) or C(6b) + C(m-) py and C(6b) or C(2b)], 115.3 and 111.0 [C(5b) and C(3b)], 99.3 [C(4a)], 12.0 (CH_3).

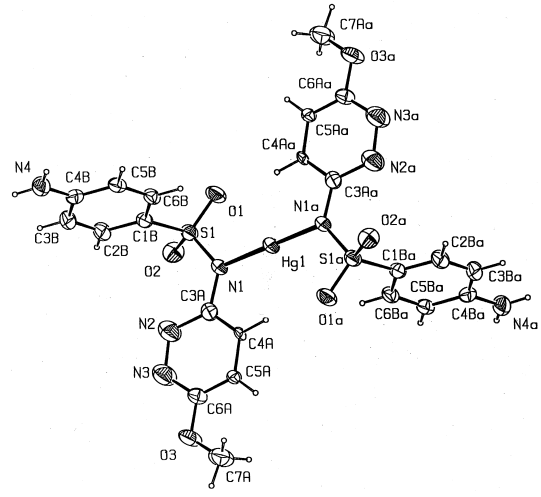


Fig. 1. ORTEP plot of [Hg(sulfamethoxypyridazinato)$_2$] (**2a**).

3. Results and discussion

3.1. Crystal structures

3.1.1. [Hg(sulfamethoxypyridazinato)$_2$] (*2a*)

The molecular structure of complex **2a** and the atom numbering scheme are shown in Fig. 1. The two sulfamethoxypyridazinato ligands are bound to the mercury atom via the sulfonamidic nitrogen N(1) in a linear arrangement. The Hg atom is at the centre of symmetry of the unit complex. The Hg–N bond distance [Hg–N(1) = 2.071(4) Å] (Table 2) is similar to previously reported distances in other Hg–N systems [16]. The bond lengths and angles of the benzene ring, the distances C(4b)–N(4b) = 1.392(7) Å, S(1)–N(1) = 1.625(4) Å, N(1)–C(3a) = 1.403(7) Å and the angle S(1)–N(1)–C(3a) conform well to those found in the free ligand. Sensitive changes in bonds and angles of the heterocyclic ring are observed by comparison with those of the free sulfamethoxypyridazine, as a consequence of a new restructuring of the ring charge. The trigonal arrangement around the sulfonamidic nitrogen is similar to those observed in the free ligand and the Hg–sulfadiazine complex [16]. The *gauche* conformation between the two rings regarding the S(1)–N(sulfonamidic) bond, the torsion angle [C(1b)–S(1)–N(sulfonamidic)–C(3a) = 74.59°] and the dihedral [O(1)–S(1)–N(sulfonamidic)–metal = 20.13°] are quite different to those observed in the Hg–sulfadiazine complex (dihedral 5.80°). The monomeric units are held through weak intermolecular hydrogen bonds between the SO_2 group and the NH_2 of an adjacent unit [N(4b)–H···OSO = 3.04°].

3.1.2. [Cd(sulfadimidinato)$_2$(H_2O)]·2H_2O (*4b*)

The molecular structure of compound **4b** and the atom numbering scheme are shown in Fig. 2. The Cd(II) ion in complex exhibits a high distorted-octahedral geometry, being coordinated to the sulfonamidic N(1) [Cd–N(1) = 2.328(6) Å; Cd–N(1′) = 2.326(6) Å] and the heterocyclic N(3)/N(2′) [Cd–N(3) = 2.307(6) Å; Cd–N(2′) = 2.426(6) Å] of two bidentate sulfadimidine ligands generating two four-membered rings. The terminal amino N(4′b) [Cd–N(4′b) = 2.379(7) Å] of a third sulfadimidine, which is bonded to an adjacent Cd(II), and the O(3) [Cd–O(3) = 2.334(6) Å] atom of a water molecule complete the coordination sphere. Although both ligands are bound in a bidentate form to the metal, only one sulfadimidine presents two equivalent Cd–N distances. The N(4)–C(4b) and N(4′)–C(4b′) distances are 1.393(11) and 1.413(9) Å, respectively, greater than the corresponding distances in the free ligand [N(4)–C(4b) = 1.384(6) Å], which is consistent with the coordination of the terminal amino group to the adjacent Cd(II). The bond lengths and angles of the benzene ring conform well to those found in the free sulfadimidine [34], whereas distances S(1)–N(1) = 1.609(7) Å, S(1′)–N(1′) = 1.578(7) Å, N(2)–C(3a) = 1.338(10) Å and N(2′)–C(3a′) = 1.348(9) Å are shorter in the Cd(II) complex. In this case the trigonal arrangement around the sulfonamidic nitrogen is similar to those observed in the Zn(II) and Cu(II)–sulfadiazine complexes [16]. The *gauche* conformation between the two rings regarding the S(1)–N(sulfonamidic) bond, with a torsion angle of [C(1b)–S(1)–N(sulfonamidic)–C(3a) = 65.51°] is similar to that of the Ag–sulfadiazine complex [10,11,14]. The packing of the complex units is governed by long chains formed by the bridging sulfadimidine ligands which are bound to Cd(1) via N(1)/N(3) and Cd(2) via NH_2 [N(4′b)–Cd = 2.379(7) Å]. Stacking interactions are present in the crystal structure involving benzene and heterocyclic rings (3.6 Å). In the complex units there are intramolecular hydrogen bonds between the NH_2 group and SO_2 of different ligands, and between SO_2 and coordinated H_2O molecules.

3.1.3. [Zn(sulfamethoxazolato)$_2$(py)$_2$(H_2O)$_2$] (*6d*)

The structure consists of centrosymmetric units of Zn(sulfamethoxazolato)$_2$·(py)$_2$(H_2O)$_2$ (Fig. 3). The geometry around the Zn(II) ion, placed at a crystallographic symmetry centre, can be described as a slightly distorted

Table 2
Selected bond lengths (Å) and angles (°) for complexes **2a**, **4b** and **6d**

Hg(sulfamethoxypyridazinato)$_2$ (**2a**)			
Hg(1)–N(1)	2.071(4)	Hg(1)–N(1) [a]	2.071(4)
N(1) [a]–Hg(1)–N(1)	180.0(3)		
C(3A)–N(1)–Hg(1)	114.4(3)	S(1)–N(1)–Hg(1)	120.8(2)
Cd(sulfadimidinato)$_2$ (**4b**)			
Cd(1)–N(3)	2.307(6)	Cd(1)–N(4′) [b]	2.379(7)
Cd(1)–N(1′)	2.326(6)	Cd(1)–N(2′)	2.426(6)
Cd(1)–N(1)	2.328(6)	Cd(1)–O(3)	2.334(6)
N(4′)–Cd(1) [c]	2.379(7)		
N(3)–Cd(1)–N(1′)	115.1(2)	N(1)–Cd(1)–N(2′)	120.7(2)
N(3)–Cd(1)–O(3)	97.6(2)	N(1)–Cd(1)–O(3)	95.7(2)
N(1′)–Cd(1)–O(3)	86.5(2)	N(3)–Cd(1)–N(2′)	96.6(2)
N(3)–Cd(1)–N(1)	56.7(2)	N(2′)–Cd(1)–N(1′)	56.4(2)
O(3)–Cd(1)–N(2′)	142.8(2)	N(1′)–Cd(1)–N(1)	171.7(2)
N(3)–Cd(1)–N(4′) [b]	144.1(2)	N(4′) [b]–Cd(1)–N(2′)	91.5(2)
N(1′)–Cd(1)–N(4′) [b]	98.5(2)	N(1)–Cd(1)–N(4′) [b]	89.3(2)
O(3)–Cd(1)–N(4′) [b]	96.7(3)		
C(3A)–N(1)–Cd(1)	96.1(5)	C(3A′)–N(1′)–Cd(1)	97.2(4)
S(1)–N(1)–Cd(1)	140.9(4)	S(1′)–N(1′)–Cd(1)	136.1(4)
C(3A)–N(3)–Cd(1)	98.5(5)	C(3A′)–N(2′)–Cd(1)	93.7(4)
C(6A)–N(3)–Cd(1)	144.5(6)	C(4A′)–N(2′)–Cd(1)	147.6(5)
C(4B′)–N(4′)–Cd(1) [c]	114.3(4)		
Zn(sulfamethoxazolato)$_2$(pyridine)$_2$(H_2O)$_2$ (**6d**)			
Zn–O(4)	2.0984(14)	Zn–O(4) [d]	2.0984(14)
Zn–N(2)	2.1736(15)	Zn–N(2) [d]	2.1736(15)
Zn–N(16)	2.1841(17)	Zn–N(16) [d]	2.1841(17)
N(16) [d]–Zn–N(16)	180.0	N(2)–Zn–N(2) [d]	180.0
N(2) [d]–Zn–N(16) [d]	92.50(6)	N(2)–Zn–N(16)	92.50(6)
N(2) [d]–Zn–N(16)	87.50(6)	N(2)–Zn–N(16) [d]	87.50(6)
O(4) [d]–Zn–N(2)	90.98(6)	O(4)–Zn–N(2) [d]	90.98(6)
O(4) [d]–Zn–N(2) [d]	89.02(6)	O(4)–Zn–N(2)	89.02(6)
O(4) [d]–Zn–N(16) [d]	92.35(7)	O(4)–Zn–N(16)	92.35(7)
O(4) [d]–Zn–N(16)	87.65(7)	O(4)–Zn–N(16) [d]	87.65(7)
O(4) [d]–Zn–O(4)	180.0		
C(5A)–N(2)–Zn	133.61(12)	C(11)–N(16)–Zn	121.84(15)
O(3)–N(2)–Zn	119.24(10)	C(15)–N(16)–Zn	120.74(16)

[a] Symmetry transformations used to generate equivalent atoms: $-x+1/2, -y+1/2, -z$.
[b] Symmetry transformations used to generate equivalent atoms: $-x+1/2, y+1/2, -z$.
[c] Symmetry transformations used to generate equivalent atoms: $-x+1/2, y-1/2, -z$.
[d] Symmetry transformations used to generate equivalent atoms: $-x+1, -y, -z+1$.

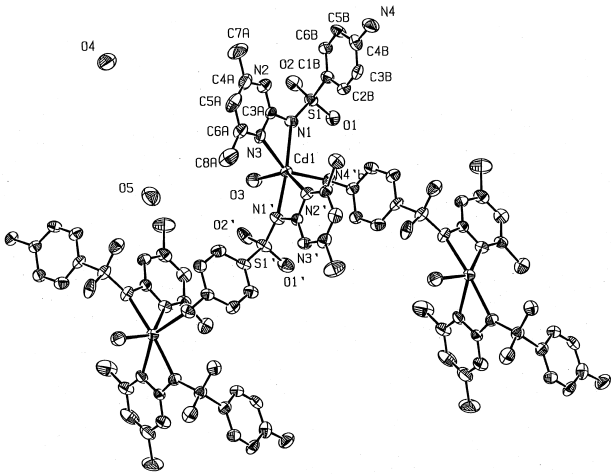


Fig. 2. ORTEP plot of [Cd(sulfadimidinato)$_2$(H_2O)·2H_2O (**4b**). All hydrogen atoms have been omitted for clarity.

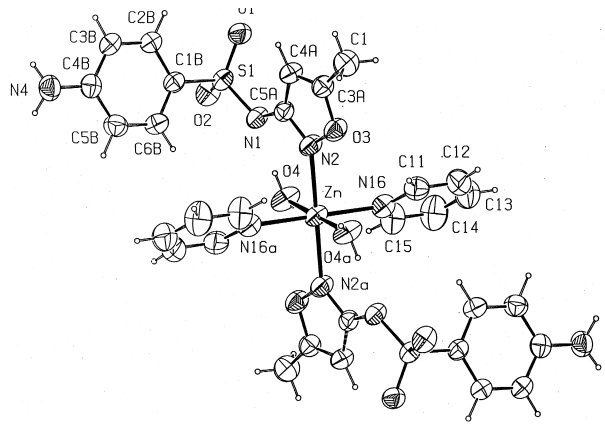


Fig. 3. ORTEP plot of [Zn(sulfamethoxazolato)$_2$(pyridine)$_2$(H_2O)$_2$] (**6d**).

compressed octahedron. The equatorial plane is formed by two pyridine N atoms [N(16) and N(16A)] and two isoxazole N atoms [N(2) and N(2A)] from two sulfamethoxazolate anions. Two oxygen atoms of two water molecules are placed in the apical positions. The equatorial M–N distances [2.1841(17) and 2.1736(15) Å] are almost equal and markedly longer than the axial M–OW ones [2.0984(14) Å]. The coordination angles around the metal, which range from 87.50(6) to 92.50(6)°, do not deviate significantly from a regular octahedron.

It should be noted that the coordination behaviour of the sulfamethoxazolate anion contrasts with that exhibited by the related sulfathiazolate in the Zn(sulfathiazolato)$_2 \cdot H_2O$ compound [18] in spite of the structural similarity between both sulfonamides. The sulfamethoxazolate acts as monodentate through the $N_{isoxazole}$, whereas the sulfathiazolate anion behaves as a bridge linking two metal ions through the $N_{thiazole}$ and N_{amino}.

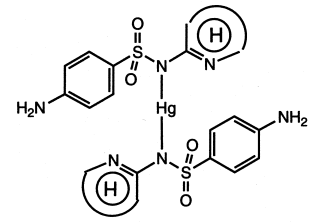
When comparing the bond lengths of the sulfamethoxazolate anion with those of the free sulfamethoxazole [35] a remarkable similarity of all bond distances is found. The most significant changes are: a small shortening of the N(1)–C(5A) distance [from 1.393(4) to 1.370(2) Å], a slight lengthening of the C(1B)–S(1) bond distance [from 1.734(3) to 1.7650(18) Å] and a marked shortening of the S(1)–N(1) length [from 1.645(3) to 1.5675(15) Å]. It must be noted that the S(1)–N(1) bond distance is very close to those of the S=N double bond (1.494–1.580 Å) [36]. Since these distances are comparable to the corresponding ones in the sulfamethoxazole sodium salt [36] and the sulfonamido group does not interact with the metal ion, these changes are ascribed to the deprotonation of this moiety. Moreover, the C(4B)–N(4) bond distance is longer than the corresponding one in the free sulfamethoxazole [1.394(3) Å in the complex, 1.358(5) Å in the ligand]. The lack of interaction of the amino N atom of the sulfamethoxazole with Zn(II) leads us to propose that this lengthening is determined by the intermolecular hydrogen bonds involving the amino group [N(4)–H···OW and N(4)···H–OW = 2.09 and 2.20 Å, respectively, N(4)–H···OSO = 2.20 Å]. The crystal structure is stabilised by an extensive network of intra- and intermolecular hydrogen bonds involving the water molecules, the sulfonamido N and O atoms and the terminal amino group. To be noticed the strong intramolecular interaction between a coordinated water molecule and the sulfonamido N(1) atom [N(1)···H–O(4) = 1.92 Å]. As found in metal complexes with other sulfonamides [18], the coordination through the heteroaromatic N atom does not significantly modify the bond lengths and bond angles of the ring. The isoxazole ring is planar and perpendicular to the benzene ring (angle between planes, 78.28°).

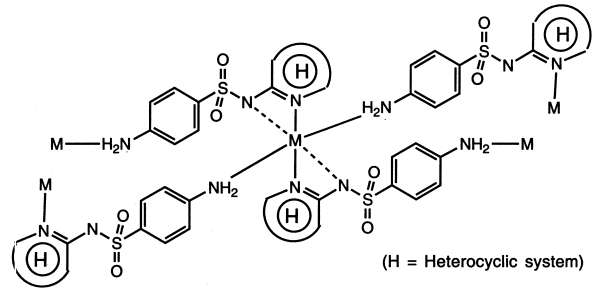
3.2. Infrared spectra

The infrared spectra of the complexes in the far-IR region to 200 cm^{-1} were compared with those of the free ligands. Similar modifications are observed in Zn(II)/Cd(II) complexes which are different to those in Hg(II) complexes. The bands that appear near 3500 and 3400 cm^{-1} due to $\nu_{asym}(NH_2)$ and $\nu_{sym}(NH_2)$ vibrations of the NH_2 group [16] are modified with respect to those of the free respective ligands. In general, these vibration modes appear at higher and lower wavenumbers, compared with those of the free ligand. When the amino N atom does not interact with the metal ion (this excludes the **4b** complex) these modifications are consequently due to the hydrogen bonds involving the amino group. The frequency ν(N–H) of the sulfonamido group, which in the free ligands is found at about 3125 cm^{-1}, is not present in the spectra of the complexes, confirming the deprotonation of the $–SO_2NH–$ moiety. Moreover, for the **6d** complex, in agreement with the coordination of the ligand through the isoxazole N atom, deduced from the crystal structure, the characteristic ring vibration is shifted from 1460 cm^{-1} in the free ligand to 1410 cm^{-1} in the complex. The strong band at (1370–1330 cm^{-1}) related to $\nu_{asym}(SO_2–N)$ [9,16,18] in each free ligand is also changed in frequency or split in the same way in Zn(II) and Cd(II) compounds and differently in Hg(II) derivatives. The 920–975 cm^{-1} band in the ligand is assigned to ν(S–N) [9,16] and changed to higher frequencies in all cases as a consequence of coordination to the metal. This shift to higher frequencies is in accordance with the shortening of the S–N bond lengths, which have been observed in the crystal structures of compounds **2a**, **4b** and **6d**. In complex **6d**, the bands at 1600, 1460, 1440, 1220, 760 and 700 cm^{-1} are assigned to vibrations of the pyridine rings [37,38].

3.3. NMR spectra

^1H and ^{13}C NMR of the complexes **1**–**6** are presented in Tables 3–14.





oligomeric or polymeric M(sulfamidato)$_2$ [M=Cd(II) or Zn(II)]

Proposed structures of M(sulfamidato)$_2$ in DMSO solution

Scheme 3.

Table 3
^{1}H NMR shift assignments of sulfadimethoxine (sulfadime-H, **1**) and its Hg (**1a**), Cd (**1b**) and Zn (**1c**) complexes in DMSO-d_6 [a]

Assignment	^{1}H (**1**)	^{1}H (**1a**)	$\Delta\delta$ (H) [b]	^{1}H (**1b**)	$\Delta\delta$ (H) [b]	^{1}H (**1c**)	$\Delta\delta$ (H) [b]
N(4a)–H	11.23						
C(5a)–H	6.03	5.94	**−0.09**	5.83	**−0.20**	5.86	**−0.17**
C(2b)–H	7.65	7.85	**+0.20**	7.59	−0.06	7.58	−0.07
C(3b)–H	6.69	6.72	+0.03	6.57	**−0.12**	6.59	**−0.10**
OCH_3(1)	3.89	3.95	+0.06	3.84	−0.05	3.81	−0.07
OCH_3(2)	3.88	3.89	+0.01	3.79	**−0.09**	3.73	**−0.15**
NH_2	6.21	6.18	−0.03	5.80	**−0.41**	5.77	**−0.44**

[a] Relative to TMS with DMSO-d_6 peak as reference (^{1}H, 2.60 ppm; ^{13}C, 43.5 ppm).
[b] $\Delta\delta = \delta_{(\text{sulfamide complex})} - \delta_{(\text{sulfamide})}$.

Table 4
^{13}C NMR shift assignments of sulfadimethoxine (sulfadime-H, **1**) and its Hg (**1a**), Cd (**1b**) and Zn (**1c**) complexes in DMSO-d_6 [a]

Assignment	^{13}C (**1**)	^{13}C (**1a**)	$\Delta\delta$ (C) [b]	^{13}C (**1b**)	$\Delta\delta$ (C) [b]	^{13}C (**1c**)	$\Delta\delta$ (C) [b]
C(2a)	168.4	168.0	−0.4	169.6	**+1.2**	170.1	**+1.7**
C(4a)	164.2	165.8	**+1.6**	167.6	**+3.4**	167.6	**+3.4**
C(5a)	88.3	88.6	+0.3	87.7	−0.6	88.4	+0.1
C(6a)	175.6	176.2	−0.4	175.7	+0.1	175.4	−0.2
C(1b)	128.2	128.3	+0.1	132.3	**+4.1**	132.8	**+4.6**
C(2b)/C(6b)	133.4	133.7	+0.3	132.6	−0.8	132.8	−0.6
C(3b)/C(5b)	116.5	116.8	+0.3	116.4	−0.1	116.5	+0.0
C(4b)	157.4	157.2	−0.2	155.6	**−1.8**	155.7	**−1.7**
OCH_3(1)	58.4	58.8	+0.4	58.3	−0.1	58.2	−0.2
OCH_3(2)	57.7	58.0	+0.3	57.6	−0.1	57.6	−0.1

[a] Relative to TMS with DMSO-d_6 peak as reference (^{1}H, 2.60 ppm; ^{13}C, 43.5 ppm).
[b] $\Delta\delta = \delta_{(\text{sulfamide complex})} - \delta_{(\text{sulfamide})}$.

Table 5
^{1}H NMR shift assignments of sulfamethoxypyridazine (sulfamet-H, **2**) and its Hg (**2a**), Cd (**2b**) and Zn (**2c**) complexes in DMSO-d_6 [a]

Assignment	^{1}H (**2**)	^{1}H (**2a**)	$\Delta\delta$ (H) [b]	^{1}H (**2b**)	$\Delta\delta$ (H) [b]	^{1}H (**2c**)	$\Delta\delta$ (H) [b]
N(3a)–H	11.8 (br)						
C(4a)–H	7.66	7.62	−0.04	7.42	**−0.24**	7.49	**−0.17**
C(5a)–H	7.35	7.31	−0.04	7.16	**−0.19**	7.11	**−0.24**
C(2b)–H	7.56	7.82	**+0.26**	7.65	+0.09	7.51	−0.05
C(3b)–H	6.65	6.68	+0.03	6.55	**−0.10**	6.51	**−0.14**
NH_2	6.03	6.06	+0.03	5.72	**−0.31**	5.67	**−0.36**
OCH_3	3.96	4.01	+0.05	3.95	−0.01	3.90	−0.06

[a] Relative to TMS with DMSO-d_6 peak as reference (^{1}H, 2.60 ppm; ^{13}C, 43.5 ppm).
[b] $\Delta\delta = \delta_{(\text{sulfamide complex})} - \delta_{(\text{sulfamide})}$.

All Hg(sulfamidato)$_2$ complexes (**1a–6a**) present a similar NMR pattern with two equivalent sulfamide groups. Thus, upon complexation, a downfield shift (+1.0 to +4.0 ppm) is observed for the carbon directly bonded to the sulfonamidic nitrogen [C(4a) for complex **1a**, C(3a) for complex **2a**, C(2a) for complexes **3a–5a** and C(5a) for complex **6a**]. Moreover, the downfield shift for H(2b)/H(6b) resonance (+0.14 to +0.26 ppm) could be related to the proximity of the Hg(II) which can be explained by a direct interaction, as in solid state, between the metallic ion and the sulfonamidic nitrogen (Scheme 3).

Cd(II) (**1b–6b**) and Zn(II) (**1c–6c**) complexes also show similar NMR patterns with two equivalent sulfamide groups. In these cases, important downfield shifts, higher than in the corresponding Hg(II) compounds, of the carbons directly bonded to the sulfonamidic moiety [C(4a) for complex **1a**, C(3a) for complex **2a**, C(2a) for complexes **3a–5a** and C(5a) for complex **6a** (+3.4 to +6.4 ppm) and C(1b) (+3.1 to 5.1 ppm)] together with different $\Delta\delta$ (H or C) of the resonances presented in the heterocyclic ring suggest a main metal–heterocyclic nitrogen interaction. However, secondary interaction with the sulfonamidic nitrogen cannot be completely discarded. On the other hand, the upfield shifts of the NH_2 (−0.31 to −0.47 ppm), H(3b)/H(5b) (−0.10 to −0.15 ppm) and C(4b) (−1.3 to −2.2 ppm) indicate that NH_2–metal(II) binding is also present, yielding equivalent

Table 6
^{13}C NMR shift assignments of sulfamethoxypyridazine (sulfamet-H, **2**) and its Hg (**2a**), Cd (**2b**) and Zn (**2c**) complexes in DMSO-d_6 [a]

Assignment	^{13}C (**2**)	^{13}C (**2a**)	Δδ (C) [b]	^{13}C (**2b**)	Δδ (C) [b]	^{13}C (**2c**)	Δδ (C) [b]
C(3a)	156.3	158.0	**+1.3**	162.3	**+6.0**	162.1	**+5.8**
C(4a)	128.8	125.5	**−3.3**	125.8	**−3.0**	127.6	**−1.2**
C(5a)	126.8	124.4	**−2.4**	124.9	**−1.9**	124.6	**−1.9**
C(6a)	163.9	165.8	**+1.9**	164.1	+0.2	163.0	−0.9
C(1b)	130.8	129.9	**−0.9**	133.9	**+3.1**	134.3	**+3.5**
C(2b)/C(6b)	132.7	133.1	+0.4	132.6	−0.1	132.2	−0.5
C(3b)/C(5b)	116.8	116.7	−0.1	116.7	−0.1	116.5	−0.3
C(4b)	156.7	156.7	+0.0	155.4	**−1.3**	155.2	**−1.5**
OCH_3	58.5	58.3	−0.2	58.1	−0.4	58.0	0.5

[a] Relative to TMS with DMSO-d_6 peak as reference (^{1}H, 2.60 ppm; ^{13}C, 43.5 ppm).
[b] $\Delta\delta = \delta_{(\text{sulfamide complex})} - \delta_{(\text{sulfamide})}$.

Table 7
^{1}H NMR shift assignments of sulfadiazine (sulfadia-H, **3**) and its Hg (**3a**), Cd (**3b**) and Zn (**3c**) complexes in DMSO-d_6 [a]

Assignment	^{1}H (**3**)	^{1}H (**3a**)	Δδ (H) [b]	^{1}H (**3b**) [c]	Δδ (H) [b]	^{1}H (**3c**) [c]	Δδ (H) [b]
N(2a)–H	11.35						
C(4a)–H	8.57	8.59	+0.02	8.37	**−0.19**	8.30	**−0.27**
C(5a)–H	7.11	7.08	−0.03	6.77	**−0.34**	6.73[c]	**−0.38**
C(2b)–H	7.70	7.87	**+0.17**	7.64	−0.06	7.64	−0.06
C(3b)–H	6.65	6.67	+0.02	6.53	**−0.12**	6.55	**−0.10**
NH_2	6.11	6.01	**−0.10**	5.64	**−0.47**	5.68	**−0.43**

[a] Relative to TMS with DMSO-d_6 peak as reference (^{1}H, 2.60 ppm; ^{13}C, 43.5 ppm).
[b] $\Delta\delta = \delta_{(\text{sulfamide complex})} - \delta_{(\text{sulfamide})}$.
[c] Spectrum presents broad peaks.

Table 8
^{13}C NMR shift assignments of sulfadiazine (sulfadia-H, **3**) and its Hg (**3a**), Cd (**3b**) and Zn (**3c**) complexes in DMSO-d_6 [a]

Assignment	^{13}C (**3**)	^{13}C (**3a**)	Δδ (C) [b]	^{13}C (**3b**)	Δδ (C) [b]	^{13}C (**3c**)	Δδ (C)
C(2a)	161.2	163.7	**+2.5**	166.3	**+5.1**	166.1	**+4.9**
C(4a)/C(6a)	162.2	162.4	+0.2	162.2	+0.0	161.9	−0.3
C(5a)	119.5	118.4	**−1.1**	115.1	**−4.4**	115.0	**−4.5**
C(1b)	128.8	129.8	**+1.0**	134.1	**+5.3**	134.1	**+5.3**
C(2b)/C(6b)	133.8	134.3	+0.5	132.9	−0.9	133.1	−0.7
C(3b)/C(5b)	116.1	116.0	+0.1	116.0	−0.1	116.0	−0.1
C(4b)	157.0	156.6	−0.4	155.0	**−2.0**	155.0	**−2.0**

[a] Relative to TMS with DMSO-d_6 peak as reference (^{1}H, 2.60 ppm; ^{13}C, 43.5 ppm).
[b] $\Delta\delta = \delta_{(\text{sulfamide complex})} - \delta_{(\text{sulfamide})}$.

Table 9
^{1}H NMR shift assignments of sulfadimidine (sulfadim-H, **4**) and its Hg (**4a**), Cd (**4b**) and Zn (**4c**) complexes in DMSO-d_6 [a]

Assignment	^{1}H (**4**)	^{1}H (**4a**)	Δδ(H) [b]	^{1}H (**4b**) [c]	Δδ (H) [b]	^{1}H (**4c**) [c]	Δδ (H) [b]
N(2a)–H	11.15 (br)						
C(5a)–H	6.84	6.85	+0.01	6.49 [d]	**−0.35**	6.46	**−0.38**
C(2b)–H	7.74	7.88	**+0.14**	7.67	−0.07	7.68	−0.06
C(3b)–H	6.65	6.66	+0.01	6.51	**−0.14**	6.53	**−0.12**
NH_2	6.06	5.97	**−0.09**	5.61	**−0.45**	5. 62	**−0.44**
CH_3	2.34	2.37	+0.03	2.18	**−0.16**	2.18	**−0.16**

[a] Relative to TMS with DMSO-d_6 peak as reference (^{1}H, 2.60 ppm; ^{13}C, 43.5 ppm).
[b] $\Delta\delta = \delta_{(\text{sulfamide complex})} - \delta_{(\text{sulfamide})}$.
[c] Spectrum presents broad peaks.
[d] Estimated.

Table 10
^{13}C NMR shift assignments of sulfadimidine (sulfadim-H, **4**) and its Hg (**4a**), Cd (**4b**) and Zn (**4c**) complexes in DMSO-d_6 [a]

Assignment	^{13}C (**4**)	^{13}C (**4a**)	$\Delta\delta$ (C) [b]	^{13}C (**4b**)	$\Delta\delta$ (C) [b]	^{13}C (**4c**)	$\Delta\delta$ (C) [b]
C(2a)	160.7	163.3	**+2.6**	166.1	**+5.4**	165.9	**+5.2**
C(4a)/C(6a)	171.3	171.6	+0.3	171.2	−0.1	170.9	−0.4
C(5a)	117.7	116.8	**−0.9**	114.0	**−3.7**	114.3	**−3.4**
C(1b)	129.0	130.0	**+1.0**	134.2	**+5.2**	133.6	**+4.6**
C(2b)/C(6b)	134.3	134.7	+0.3	133.5	−0.7	133.6	−0.7
C(3b)/C(5b)	115.9	115.8	−0.1	115.6	−0.3	115.7	−0.2
C(4b)	156.9	156.5	−0.4	154.9	**−2.0**	155.0	**−1.9**
CH_3	27.1	27.2	+0.1	27.0	−0.1	26.8	−0.3

[a] Relative to TMS with DMSO-d_6 peak as reference (^1H, 2.60 ppm; ^{13}C, 43.5 ppm).
[b] $\Delta\delta = \delta_{(\text{sulfamide complex})} - \delta_{(\text{sulfamide})}$.

Table 11
^1H NMR shift assignments of sulfamerazine (sulfamer-H, **5**) and its Hg (**5a**), Cd (**5b**) and Zn (**5c**) complexes in DMSO-d_6 [a]

Assignment	^1H (**5**)	^1H (**5a**)	$\Delta\delta$ (H) [b]	^1H (**5b**) [c]	$\Delta\delta$ (H) [b]	^1H (**5c**) [c]	$\Delta\delta$ (H) [b]
N(2a)–H	11.22 (br)						
C(5a)–H	6.98	6.96	−0.02	6.63	**−0.35**	6.60	**−0.38**
C(6a)–H	8.40	8.41	+0.01	8.21	**−0.19**	8.13	**−0.27**
C(2b)–H	7.72	7.87	**+0.15**	7.64	−0.08	7.67	−0.05
C(3b)–H	6.66	6.66	+0.00	6.51	**−0.15**	6.54	**−0.12**
NH_2	6.09	5.98	**−0.11**	5.62	**−0.47**	5.62	**−0.47**
CH_3	2.41	2.42	+0.01	2.18	**−0.23**	2.19	**−0.22**

[a] Relative to TMS with DMSO-d_6 peak as reference (^1H, 2.60 ppm; ^{13}C, 43.5 ppm).
[b] $\Delta\delta = \delta_{(\text{sulfamide complex})} - \delta_{(\text{sulfamide})}$.
[c] Spectrum presents broad peaks.

Table 12
^{13}C NMR shift assignments of sulfamerazine (sulfamer-H, **5**) and its Hg (**5a**), Cd (**5b**) and Zn (**5c**) complexes in DMSO-d_6 [a]

Assignment	^{13}C (**5**)	^{13}C (**5a**)	$\Delta\delta$ (C) [b]	^{13}C (**5b**)	$\Delta\delta$ (C) [b]	^{13}C (**5c**)	$\Delta\delta$ (C) [b]
C(2a)	161.0	163.6	**+2.6**	166.2	**+5.2**	165.8	**+4.8**
C(4a)	172.1	172.1	+0.0	171.6	−0.5	172.3	+0.2
C(5a)	118.9	117.7	**−1.2**	114.7	**−4.2**	114.8	**−4.1**
C(6a)	161.7	162.0	+0.3	161.9	+0.2	160.9	−0.8
C(1b)	129.0	130.1	**+1.1**	134.1	**+5.1**	134.2	**+5.2**
C(2b)/C(6b)	134.2	134.5	+0.3	133.1	**−1.1**	133.5	−0.7
C(3b)/C(5b)	116.1	116.0	−0.1	115.8	−0.3	116.0	−0.1
C(4b)	157.1	156.6	−0.5	154.9	**−2.2**	155.2	**−1.9**
CH_3	27.4	27.4	+0.0	26.9	−0.5	27.3	−0.1

[a] Relative to TMS with DMSO-d_6 peak as reference (^1H, 2.60 ppm; ^{13}C, 43.5 ppm).
[b] $\Delta\delta = \delta_{(\text{sulfamide complex})} - \delta_{(\text{sulfamide})}$.

Table 13
^1H NMR shift assignments of sulfamethoxazole (sulfamoxaz-H, **6**) and its Hg (**6a**), Cd (**6b**) and Zn (**6c**) complexes, and [Zn(sulfamethoxazolato)$_2$(py)$_2$(H_2O)$_2$] (**6d**) in DMSO-d_6 [a]

Assignment	^1H (**6**)	^1H (**6a**)	$\Delta\delta$ (H) [b]	^1H (**6b**)	$\Delta\delta$ (H) [b]	^1H (**6c**)	$\Delta\delta$ (H) [b]	^1H (**6d**)	$\Delta\delta$ (H) [b]
N(2a)–H	11.04								
C(4a)–H	6.18	6.13	−0.05	5.89	**−0.29**	5.97	**−0.21**	6.05	**−0.13**
C(2b)–H	7.58	7.76	**+0.18**	7.58	+0.00	7.60	+0.02	7.57(m)	−0.01
C(3b)–H	6.67	6.69	+0.02	6.58	**−0.09**	6.58	**−0.09**	6.60	−0.07
NH_2	6.18	6.11	−0.07	5.71	**−0.47**	5.78	**−0.40**	5.87	**−0.31**
CH_3	2.38	2.38	+0.00	2.26	**−0.12**	2.28	**−0.10**	2.30	−0.08

[a] Relative to TMS with DMSO-d_6 peak as reference (^1H, 2.60 ppm; ^{13}C, 43.5 ppm).
[b] $\Delta\delta = \delta_{(\text{sulfamide complex})} - \delta_{(\text{sulfamide})}$.

Table 14
^{13}C NMR shift assignments of sulfamethoxazole (sulfamoxaz-H, **6**) and its Hg (**6a**), Cd (**6b**) and Zn (**6c**) complexes and [Zn(sulfamethoxazolato)$_2$(py)$_2$(H_2O) (**6d**) in DMSO-d_6 [a]

Assignment	^{13}C (**6**)	^{13}C (**6a**)	$\Delta\delta$ (C) [b]	^{13}C (**6b**)	$\Delta\delta$ (C) [b]	$1^{13}C$ (**6c**)	$\Delta\delta$ (C) [b]	^{13}C (**6d**)	$\Delta\delta$ (C) [b]
C(3a)	174.0	174.7	+0.3	172.7	**−1.3**	172.8	**−1.2**	172.4	**−1.6**
C(4a)	99.4	99.4	+0.0	100.7	**+1.3**	100.9	**+1.5**	100.6	**+1.2**
C(5a)	162.0	165.9	**+3.9**	168.4	**+6.4**	167.3	**+5.3**	167.5	**+5.5**
C(1b)	128.2	129.2	**+1.0**	133.2	**+5.0**	133.2	**+5.0**	132.1	**+3.9**
C(2b)/C(6b)	132.9	133.4	+0.5	133.2	+0.3	132.2	−0.7	132.9	+0.0
C(3b)/C(5b)	116.7	116.7	+0.0	117.0	+0.3	116.9	+0.2	116.5	−0.2
C(4b)	157.4	157.0	−0.4	155.8	**−1.6**	156.2	**−1.2**	155.9	**−1.5**
CH_3	16.1	16.4	+0.3	16.5	+0.4	16.4	+0.3	16.2	+0.1

[a] Relative to TMS with DMSO-d_6 peak as reference (^1H, 2.60 ppm; ^{13}C, 43.5 ppm).
[b] $\Delta\delta = \delta_{(\text{sulfamide complex})} - \delta_{(\text{sulfamide})}$.

structures to the previously described polymeric Zn(sulfothiazolato)$_2$ [9] (Scheme 3). Similar results are obtained for compound **6d**. Moreover, the solid ^{13}C NMR spectrum shows the non-equivalence of the aromatic carbons of the bencenic moiety as can be observed in the crystal structure (Fig. 3).

The Λ_M (10^{-3} mol dm^{-3}) values in DMSO at 25°C imply the presence of non-electrolyte type species for all the complexes described in this work [39].

4. Conclusion

Spectral and X-ray data of the complexes show a general pathway for the interaction between the six sulfamides studied and the d^{10} metal ions. Thus, Cd(II) and Zn(II) compounds present coordination mainly through heterocyclic nitrogen whereas the corresponding Hg(II) derivatives seem to be coordinated through sulfonamidic nitrogen (Scheme 3).

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request, quoting the deposition numbers: 137958 (**2a**), 137959 (**4b**) and 137960 (**6d**).

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References

[1] T. Nogrady, Medicinal Chemistry, Oxford University Press, Oxford, 2nd edn., 1988.
[2] R.B. Silverman, The Organic Chemistry of Drug Design and Drug Action, Academic Press, New York, 1992.
[3] C.J. Coulson, Molecular Mechanisms of Drug Action, Taylor and Francis, London, 2nd edn., 1994, p. 30.
[4] G.M. Brown, Adv. Biochem. 35 (1971) 35.
[5] G.H. Miller, P.H. Doukas, J.K. Seydal, J. Med. Chem. 15 (1972) 700.
[6] P. Narula, M. Haridas, T.P. Singh, Indian J. Phys., Sect. A 61 (1987) 132.
[7] Catálogo de Especialidades Farmacológicas, Consejo General de Colegios Oficiales de Farmaceúticos, Spain, 1997.
[8] A. Bult, H. Sigel, Metal Ions in Biological Systems, vol. 16, Marcel Dekker, New York, 1983, p. 261.
[9] J. Casanova, G. Alzuet, S. Ferrer, J. Borrás, S. García-Granda, E. Perez-Carreño, J. Inorg. Biochem. 51 (1993) 689 and Refs. therein.
[10] N.C. Baezinger, A.W. Strauss, Inorg. Chem. 15 (1976) 1807.
[11] D.S. Cook, M.F. Turner, J. Chem. Soc., Perkin Trans. 2 (1975) 1021.
[12] N.C. Baezinger, S.L. Modak, C.L. Fox Jr., Acta Crystallogr., Sect. C 39 (1983) 1620.
[13] C.J. Brown, D.S. Cook, L. Sengier, Acta Crystallogr., Sect. C 41 (1985) 718.
[14] A. Bult, N. Hulsing, J.N. Weyland, J. Pharm. Pharmacol. 33 (1981) 171.
[15] C.J. Brown, D.S. Cook, L. Sengier, Acta Crystallogr., Sect. C 43 (1987) 2332.
[16] A. García-Raso, J.J. Fiol, G. Martorell, A. López-Zafra, M. Quirós, Polyhedron 16 (1997) 613.
[17] J. Casanova, G. Alzuet, J. Borrás, J.M. Amigó, T. Debaerdemaeker, Z. Kristallogr. 209 (1994) 271.
[18] J. Casanova, G. Alzuet, J. Borrás, J. Timoneda, S. García-Granda, I. Cándano-González, J. Inorg. Biochem. 56 (1994) 65.
[19] J. Casanova, G. Alzuet, J. Borrás, O. Carugo, J. Chem. Soc., Dalton Trans. (1996) 2239.
[20] J. Casanova, G. Alzuet, J. Latorre, J. Borrás, Inorg. Chem. 36 (1997) 2052.
[21] Y.A. Simonov, M.D. Mazus, I.A. Popa, V.N. Shafranskii, T.I. Malinovskii, Zh. Strukt. Khim. 31 (1990) 77.
[22] F. Blasco, R. Ortiz, L. Perelló, J. Borrás, J. Amigó, T. Debaerdemaeker, J. Inorg. Biochem. 53 (1994) 117.
[23] A. Bax, S. Subramanian, J. Magn. Reson. 67 (1986) 565.

[24] A. Bax, M.F. Summers, J. Am. Chem. Soc. 108 (1986) 2093.
[25] C.K. Fair, MOLEN. An Interactive Intelligent System for Crystal Structure Analysis, Enraf-Nonius, Delft, 1990.
[26] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
[27] G.M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.
[28] Enraf-Nonius, CAD4-Express Software, Version 5.1, Enraf-Nonius, Delft, The Netherlands, 1995.
[29] A.L. Spek, HELENA. A Program for Data Reduction of CAD4 Data, University of Utrecht, The Netherlands, 1997.
[30] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, University of Utrecht, The Netherlands, 1997.
[31] G.M. Sheldrick, SHELXL 97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[32] International Tables for X-ray Crystallography, Vol. C, Kluwer, Dordrecht, The Netherlands.
[33] L. Zsolnai, ZORTEP, A Program for the Presentation of Thermal Ellipsoids, University of Heidelberg, Germany, 1997.
[34] R.K. Tiwari, M. Haridas, T.P. Singh, Acta Crystallogr., Sect. C 40 (1984) 655.
[35] L. Maury, J. Rambaud, B. Pauvert, Y. Lasserre, G. Berge, M. Audran, Can. J. Chem. 63 (1985) 3012.
[36] H. Nakai, M. Takasuka, M. Shiro, J. Chem. Soc., Perkin Trans 2 (1984) 1459.
[37] M. Cressey, E.D. McKenzie, S. Yates, J. Chem. Soc., Sect. A (1977) 2677.
[38] D.L. Arora, L. Kenti, S.P. Gupta, S.K. Sahni, Polyhedron 5 (1986) 1499.
[39] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.