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Different coordinative behaviour of methyl-substituted 2-pyridylsulfonamide derivatives as ligands in zinc complexes

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Abstract

Neutral zinc complexes [ZnL_2L'] of a series of methyl-substituted *N*-2-pyridylsulfonamide ligands (HL) and 1,10-phenanthroline or 2,2′-bipyridine (L′) have been synthesised by electrochemical oxidation of anodic zinc metal in an acetonitrile solution of the ligand and the coligand. The compounds obtained have been characterised by microanalysis, IR and ^{1}H NMR spectroscopy, LSI mass spectrometry studies and some of the mixed complexes by single-crystal X-ray diffraction. The crystal structures show different octahedral environments around the metal (N6 or N4O2) depending on the position of the substituent on the pyridine ring.

Keywords: Zinc complexes; Sulfonamide ligands; Electrochemical synthesis; Crystal structures

1. Introduction

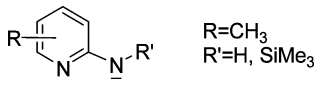
Recently, the chemistry of metal complexes containing amide ligands has been a subject of great interest. The reason for this interest stems from the fact that such complexes can be easily made and variation of the substituents is facile. These characteristics provide the possibility of tailoring the bite angle and degree of steric hindrance present in the ligand. The chemistry of metal complexes containing pyridine-functionalised amido ligands of the type shown below (Scheme 1) has received a great deal of attention [1–5].

It is believed that the presence of bulky substituents on these ligands stabilises the metal complexes.

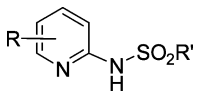
Consequently, it was decided to study the chemistry of the metal complexes of sulfonyl-2-pyridine-amines. These ligands, which are represented in Scheme 2, contain a bulky sulfonyl group as a substituent on the exocyclic nitrogen atom. In addition, the electron-withdrawing effect of this substituent increases the acid character of the NH group and makes the process of ligand deprotonation easier.

It has been found that these ligands can coordinate to the metal in a number of different ways (see Scheme 3).

Coordination modes I has been found in zinc compounds. However, it is worth noting that a weak interaction between the metal and the exocyclic nitrogen atom is present [6]. Coordination mode II is the most common, and this has been found in cobalt(II) [7], nickel(II) [8] and cadmium(II) [9] complexes. Coordination mode III has been found in cadmium(II) compounds [11]. To date, coordination mode IV has only



Scheme 1.



Scheme 2.

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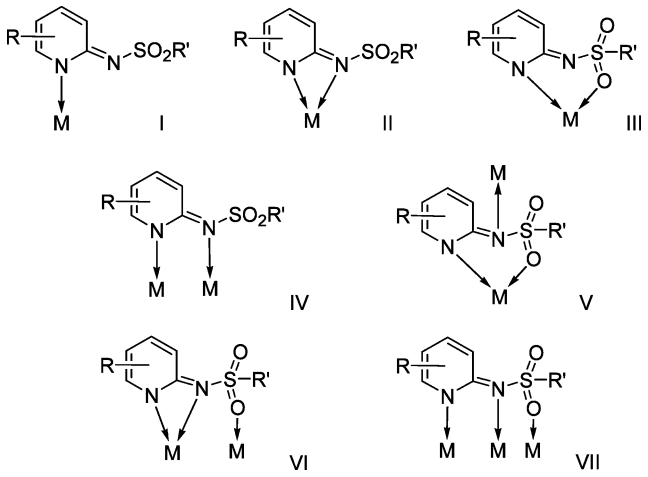
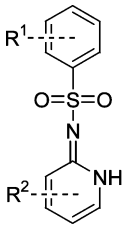


Scheme 3.

been found in copper(II) [11,12] and silver(I) [11,13] complexes. Coordination modes V and VI were found in a polymer compound of cadmium(II) [9] and coordination mode VII has thus far only been found in silver(I) complexes [11].

As a continuation of our work on different sulfonamide compounds [6–10], here we report the synthesis of a series of neutral zinc complexes through an electrochemical procedure in which the metal is the anode in a cell containing an acetonitrile solution of different substituted *N*-2-pyridyl-benzenesulfonamide ligands. These ligands are characterised by the presence of an additional donor nitrogen atom in the α-position belonging to a picoline group. With the aim of investigating whether the position of the methyl group on the pyridine ring has any influence on the coordinative behaviour of these compounds, the 3- and 6-methyl derivatives were chosen for this study. The benzene ring is also substituted by one methyl group (*p*-toluene group) or, alternatively, by three methyl groups (mesityl group) (see Scheme 4, HL).



Scheme 4.

Code	R1	R2
HTs3mepy	4-Me	3-Me
HTs6mepy	4-Me	6-Me
HMs6mepy	2,4,6-Me3	6-Me

2. Experimental

Acetonitrile, dichloromethane, 2-amino-3-picoline, 2-amino-6-picoline, *p*-toluenesulfonyl chloride, 2-mesitylsulfonyl chloride, 2,2′-bipyridine, 1,10-phenanthroline monohydrate, sodium carbonate, anhydrous magnesium sulfate, and all other reagents were commercial products and were used as supplied. Zinc (Aldrich) was used as 2 × 2 cm plates.

2.1. Preparation of ligands

The ligands were prepared by reaction of the corresponding 2-aminopyridine and the sulfonyl chloride (1:1) in dichloromethane as described previously [8,10]. Experimental details are given for a representative example.

2.1.1. HTs3mepy

This ligand was synthesised by dissolving 2-amino-3-picoline (2 g, 18.4 mmol) and 4-methylphenylsulfonyl chloride (3.51 g, 18.4 mmol) in dichloromethane. To this solution was added dropwise 20 cm^3 of an aqueous solution containing sodium carbonate (1.95 g, 18.4 mmol). The reaction mixture was stirred overnight and water (100 cm^3) was added. The organic layer was dried with anhydrous magnesium sulfate, the solvent was evaporated and the resulting crude oil was treated with ethanol. The resulting white precipitate was isolated by filtration and identified as HTs3mepy: *Anal.* C, 58.7; H, 5.7; N, 10.2; S, 11.8%. *Calc.* for $C_{13}N_2H_{14}O_2S$: C, 59.5; H, 5.4; N, 10.7; S, 12.2%. ^{1}H NMR ($CDCl_3$, ppm): 2.15 [s, 3H, CH_3(py)]; 2.35 [s, 3H, CH_3(tolyl)]; 6.50 (t, $J = 6.6$ Hz, 1H, py); 7.22 (d, $J = 8.2$ Hz, 2H, tolyl); 7.39 (d, $J = 6.6$ Hz, 1H, py); 7.49 (d, $J = 6.6$ Hz, 1H, py); 7.84 (d, $J = 8.2$ Hz, 2H, tolyl); 12.14 (b, 1H, NH). IR (KBr, cm^{-1}): 3248(m), 2951(w), 1.632(m), 1594(s), 1544(s), 1399(m), 1371(m), 1342(m), 1126(s), 1127(m), 1080(s), 964(m), 828(m), 767(m) 682(s), 570(m), 552(m), 424(w). EI MS: *m*/*z*: 262 (8%, M^+); 108 (20%, M^+—{O_2S-tolyl}).

2.1.2. HTs6mepy

Anal. C, 58.8; H, 5.6; N, 10.6; S, 12.3%. *Calc.* for $C_{13}N_2H_{14}O_2S$: C, 59.5; H, 5.4; N, 10.7; S, 12.2%. ^{1}H NMR ($CDCl_3$, ppm): 2.36 [s, 3H, CH_3(tolyl)]; 2.41 [s, 3H, CH_3(py)]; 6.60 (d, $J = 7.3$ Hz, 1H, py); 7.05 (d, $J = 8.5$ Hz, 1H, py); 7.21 (d, $J = 8.2$ Hz, 2H, tolyl); 7.46 (dd, $J = 7.3$ and 8.5 Hz, 1H, py); 7.79 (d, $J = 8.2$ Hz, 2H, tolyl); 9.95 (b, 1H, NH). IR (KBr, cm^{-1}): 3231(w), 3092(m), 2958(w), 1612(vs), 1534(m), 1369(s), 1253(m), 1135(s), 1089(m), 855(m), 787(m), 661(m), 572(m), 554(m), 440(w). EI MS: *m*/*z*: 262 (6%, M^+); 108 (3%, M^+—{O_2S-tolyl}).

2.1.3. HMs6mepy

Anal. C, 61.3; H, 6.4; N, 9.5; S, 10.9% *Calc.* for $C_{15}N_2H_{18}O_2S$: C, 62.1; H, 6.2; N, 9.6; S, 11.0%. ^{1}H NMR ($CDCl_3$, ppm): 2.23 [s, 3H, CH_3(*p*-tolyl)]; 2.37 [s, 3H, CH_3(py)]; 2.69 [s, 6H, CH_3(*o*-tolyl)]; 6.54 (d, $J = 7.6$ Hz, 1H, py); 6.74 (d, $J = 8.4$ Hz, 1H, py); 6.88 (s, 2H, tolyl); 7.37 (dd, $J = 7.6$ and 8.4 Hz, 1H, py); 9.40 (b, 1H, NH). IR (KBr, cm^{-1}): 3237(w), 3028(w), 2932(m), 1617(vs), 1533(m), 1457(m), 1362(vs), 1289(m), 1137(vs), 1064(m), 834(m), 790(m), 748(m), 656(m), 579(m), 527(m). EI MS: *m*/*z*: 291 (4%, M^+); 108 (13%, M^+—{O_2S-mesityl}).

2.2. Preparation of complexes

The complexes were prepared by an electrochemical method. The cell consisted of zinc foil suspended from a platinum wire as the anode and a platinum wire as the cathode. The sulfonamide ligand (HL) and the corresponding coligand, 2,2′-bipyridine or 1,10-phenanthroline (L′), were dissolved in acetonitrile and a small amount of tetraethylammonium perchlorate was added to the solution as a supporting electrolyte. Applied voltages of 8–15 V allowed sufficient current flow for smooth dissolution of the metal. Nitrogen was bubbled through the solution during electrolysis to stir the reaction mixture. The cell can be summarised as $Zn_{(+)}/CH_3CN + HL + L'/Pt_{(-)}$. At the end of the reaction colourless crystals were filtered off, washed with acetonitrile and diethyl ether and dried at room temperature. In some cases air concentration was required to obtain a crystalline solid.

*2.2.1. [Zn(Ts3mepy)$_2$bipy] (**1**)*

Electrolysis of a solution of the ligand (0.15 g, 0.56 mmol) and 2,2′-bipyridine (0.04 g, 0.28 mmol) in acetonitrile (50 cm^3) at 15 V and 10 mA for 1.5 h dissolved 16.5 mg of zinc, $E_f = 0.45$ mol F^{-1}. A colourless solid was obtained and identified as [Zn(Ts3mepy)$_2$bipy] CH_3CN. *Anal. Calc.* for $C_{38}H_{37}N_7O_4S_2Zn$: C, 58.1; H, 4.7; N, 12.5; S 8.2%. Found: C, 57.6; H, 4.6; N, 11.8; S, 8.4%. IR (KBr, cm^{-1}): 3037(w), 2916 (w), 1600 (m), 1442(m), 1413 (s), 1324 (m), 1243(m), 1186(w), 1117(m), 1064(m), 1001(w), 984(w), 845(w), 812(m), 771(m), 742(m), 662(m), 590(m), 546(w), 419(w). ^{1}H NMR ($CDCl_3$, ppm): δ 8.64–6.57 (m, 22H), 2.15 [s, 6H, *p*-Me(Tos)], 1.99 [s, 6H, Me(py)]. LSIMS (*m*/*z*): 743 [Zn(Ts3mepy)$_2$bipy]$^+$; 481 [Zn(Ts3mepy)bipy]$^+$; 263 (Ts3mepy)$^+$. Air-sensitive crystals were obtained from the liquor and these were used for X-ray studies at low temperature.

*2.2.2. [Zn(Ts3mepy)$_2$phen] (**2**)*

A similar experiment to that described above (12 V, 10 mA, 1.5 h) with the same sulfonamide ligand (0.15 g, 0.56 mmol) and 1,10-phenanthroline (0.05 g, 0.28 mmol) in acetonitrile (50 cm^3) led to the dissolution of 19.0 mg of zinc, $E_f = 0.52$ mol F^{-1}. *Anal. Calc.* for $C_{38}H_{34}N_6O_4S_2Zn$: C, 59.4; H, 4.5; N, 10.9; S, 8.3%. Found: C, 58.5; H, 4.7; N, 10.7; S, 8.1%. IR (KBr, cm^{-1}): 3062(m), 2920(w), 1601(m), 1540(w), 1519(w), 1418(s), 1333(m), 1243(m), 1114(m), 1085(m), 1002(m), 845(w), 728(w), 664(m), 588(m), 545(w), 420(w). ^{1}H NMR ($CDCl_3$, ppm): δ 9.19–6.60 (m, 22H), 2.14 [s, 6H, *p*-Me(Tos)], 1.98 [s, 6H, Me(py)]. LSIMS (*m*/*z*): 767 [Zn(Ts3mepy)$_2$phen]$^+$; 505 [Zn(Ts3mepy)phen]$^+$; 263 (Ts3mepy)$^+$. Suitable crystals for X-ray studies were obtained by crystallisation of the initial product from acetonitrile/methanol.

*2.2.3. [Zn(Ts6mepy)$_2$bipy] (**3**)*

Electrolysis of a solution of the ligand (0.15 g, 0.56 mmol) and 2,2′-bipyridine (0.04 g, 0.28 mmol) in acetonitrile (50 cm^3) at 11 V and 10 mA for 1.5 h dissolved 20.1 mg of zinc, $E_f = 0.55$ mol F^{-1}. *Anal. Calc.* for $C_{36}H_{34}N_6O_4S_2Zn$: C, 58.2; H, 4.6; N, 11.3; S, 8.6%. Found: C, 59.1; H, 4.7; N, 11.8; S, 8.7%. IR (KBr, cm^{-1}): 3067(w), 2921(w), 1591(s), 1456 (s), 1324(s), 1276(w), 1140(s), 1099(m), 1019(w), 1012(w), 858(m), 766(m), 736(w), 664(m), 581(m), 552(m), 415(w). ^{1}H NMR ($CDCl_3$, ppm): δ 9.7–6.4 (m, 22H), 2.2 [s, 6H, Me(py)], 2.1 [s, 6H, *p*-Me(Tos)]. LSIMS (*m*/*z*): 743 [Zn(Ts6mepy)$_2$bipy]$^+$; 481 [Zn(Ts6mepy)bipy]$^+$; 263 (Ts6mepy)$^+$.

*2.2.4. [Zn(Ts6mepy)$_2$phen] (**4**)*

A solution of the ligand (0.15 g, 0.56 mmol) and 1,10-phenanthroline (0.05 g, 0.28 mmol) in acetonitrile (50 cm^3) was electrolysed at 15 V and 10 mA during 1.5 h; 17.9 mg of zinc metal was dissolved from the anode, $E_f = 0.49$ mol F^{-1}. *Anal. Calc.* for $C_{38}H_{34}N_6O_4S_2Zn$: C, 59.4; H, 4.5; N, 10.9; S, 8.3%. Found: C, 58.7; H, 4.8; N, 10.9; S, 8.1%. IR (KBr, cm^{-1}): 3063(w), 2922(w), 1590(m), 1576(w), 1517(w), 1456(s), 1322(m), 1275(m), 1138(m), 1099(m), 1004(vw), 858(m), 786(m), 727(m), 667(m), 581(m), 553(w), 419(w). ^{1}H NMR ($CDCl_3$, ppm): δ 9.7–6.4 (m, 22H), 2.2 [s, 6H, Me(py)], 2.1 [s, 6H, *p*-Me(Tos)]. LSIMS (*m*/*z*): 767 [Zn(Ts6mepy)$_2$phen]$^+$; 505 [Zn(Ts6mepy)phen]$^+$; 263 (Ts6mepy)$^+$. Suitable crystals for X-ray studies were obtained by air concentration of the resulting solution.

*2.2.5. [Zn(Ms6mepy)$_2$bipy] (**5**)*

Electrolysis of a solution of the ligand (0.165 g, 0.565 mmol) and 2,2′-bipyridine (0.04 g, 0.28 mmol) in acetonitrile (50 cm^3) at 12 V and 10 mA for 1.5 h dissolved 16.8 mg of zinc, $E_f = 0.46$ mol F^{-1}. *Anal. Calc.* for $C_{40}H_{42}N_6O_4S_2Zn$: C, 59.9; H, 5.3; N, 10.5; S, 8.0%. Found: C, 59.3; H, 5.4; N, 10.4; S, 7.6%. IR (KBr, cm^{-1}): 2966(w), 2932(w), 1588(s), 1453(s), 1404(w), 1311(s), 1289(w), 1134(s), 1076(m), 1023(w), 967 (w), 867(m), 850(w), 780(m), 734(m), 655(m), 589(w), 535(w),

416(w). ^{1}H NMR ($CDCl_3$, ppm): δ 9.4–6.4 (m, 18H), 2.3 [s, 6H, Me(py)], 2.2 [s, 6H, *p*-Me(Tos)], 2.1 [s, 12H, *o*-Me(Tos)]. LSIMS (*m*/*z*): 798 $[Zn(Ms6mepy)_2bipy]^+$; 509 $[Zn(Ms6mepy)bipy]^+$; 291 $(Ms6mepy)^+$. Suitable crystals for X-ray studies were obtained by air concentration of the resulting solution.

2.2.6. [Zn(Ms6mepy)$_2$phen] (**6**)

A solution of the ligand (0.165 g, 0.56 mmol) and 1,10-phenanthroline (0.05 g, 0.28 mmol) in acetonitrile (50 cm^3) was electrolysed at 8 V and 10 mA during 1.5 h; 17.5 mg of zinc metal was dissolved from the anode, $E_f = 0.48$ mol F^{-1}. *Anal. Calc.* for $C_{42}H_{42}N_6O_4S_2Zn$: C, 61.1; H, 5.1; N, 10.2; S, 7.7%. Found: C, 59.9; H, 5.3; N, 10.6; S, 7.2%. IR (KBr, cm^{-1}): 3055(w), 2934(w), 1592(s), 1520(m), 1456(s), 1418(w), 1326(s), 1287(w), 1132(s), 1085(m), 1004(vw), 966(w), 848(s), 781(m), 727(m), 654(m), 589(m), 532(m), 422(w). ^{1}H NMR ($CDCl_3$, ppm): δ 9.6–6.4 (m, 18H), 2.3 [s, 6H, Me(py)], 2.1 [s, 6H, *p*-Me(Tos)], 2.0 [s, 12H, *o*-Me(Tos)]. LSIMS (*m*/*z*): 825 $[Zn(Ms6mepy)_2phen]^+$; 533 $[Zn(Ms6mepy)phen]^+$; 291 $[Ms6mepy]^+$. Suitable crystals for X-ray studies were obtained by crystallisation of the initial product from acetonitrile.

2.3. Physical measurements

Elemental analyses were performed using a Carlo–Erba EA 1108 microanalyser. IR spectra were recorded in KBr mulls using a Bruker Vector-22 spectrophotometer. LSI mass spectra were recorded using a Micromass VG Autospec M instrument. The ^{1}H NMR spectra were recorded using a Bruker ARX-400 MHz spectrometer with $CDCl_3$ as solvent.

2.4. Crystal structure determination

The data collections were taken on a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation. In the case of $[Zn(Ts3mepy)_2bipy]$ the data collection was made at 173 K since the crystalline product decomposed at room temperature, probably due the evaporation of the CH_3CN present in the network. Absorption corrections were carried out using SADABS [14]. All the structures were solved by direct methods and refined by full-matrix least-squares based on F^2 [15]. All non-hydrogen atoms were refined with anisotropic displacement parameters. For all the complexes, hydrogen atoms were also included in idealised positions and refined with isotropic displacement. In the case of HTs3mepy, hydrogen atoms were located on a difference electron density map and refined with isotropic displacement parameters, except those of the methyl groups, which were included in idealised positions and refined with isotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from *International Tables for X-ray Crystallography* [16]. For the compounds $[Zn(Ts3mepy)_2phen]$, $[Zn(Ts6mepy)_2phen]$ and $[Zn(Ms6mepy)_2bipy]$ the SQUEEZE program [17] was used to correct the reflection data for the diffuse scattering due to disordered solvent. The crystal parameters and other experimental details of data collection and refinement are summarised in Table 1.

3. Results and discussion

The analytical results show that the electrochemical procedure described above is an effective method for the synthesis of zinc complexes with these sulfonamide ligands. The method represents a simple alternative to other standard chemical procedures. The compounds are of general formula $[ZnL_2L']$, where L represents the anion of the corresponding sulfonamide ligand and L′ the co ligand, i.e. 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen). The electrochemical efficiency value, E_f, defined as the amount of metal dissolved per Faraday of charge, was close to 0.5 mol F^{-1} in all cases. This fact, along with the evolution of hydrogen at the cathode, is compatible with the following reaction mechanisms:

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

Anode: $Zn + 2L^- \rightarrow [ZnL_2] + 2e^-$

or

$Zn + 2L^- + L' \rightarrow [ZnL_2L'] + 2e^-$

3.1. Crystal structure of HTs3mepy

The molecular structure of HTs3mepy is shown in Fig. 1 together with the atomic numbering scheme. Selected bond lengths, angles and hydrogen bond parameters are given in Table 2.

A relevant feature of this structure is the presence of a hydrogen atom on the *N*-pyridine ring, indicating that the free ligand exists as the imido tautomer (I) rather than the amido tautomer (II) (see Scheme 5). This situation is similar to that found in other *N*-2-pyridinylbenzenesulfonamide derivatives described previously [8,10].

Both the phenyl and the pyridine rings are almost planar. The sulfur atom is out of the best plane of the benzene ring by 0.043(4) Å and the imine nitrogen atom is out of the pyridine ring plane by 0.0314(5) Å. The interplanar angle, 79.2(1)°, is slightly lower than those found in other sulfonamides.

It is worth noting that the molecules of [(4-methylphenyl)sulfonyl]imino-1*H*-3-methyl-2-pyridine are associated by intermolecular hydrogen bonds. The hydrogen

Table 1
Summary of crystal data and structure refinement

Compound	HTs3mepy	[Zn(Ts3mepy)$_2$bipy]	[Zn(Ts3mepy)$_2$phen]
Empirical formula	$C_{13}H_{14}N_2O_2S$	$C_{38}H_{37}N_7O_4S_2Zn$	$C_{38}H_{34}N_6O_4S_2Zn$
Formula weight	262.32	785.24	768.20
Temperature (K)	293(2)	173(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	orthorhombic	triclinic
Space group	$P\bar{1}$	$Pna2_1$	$P\bar{1}$
Unit cell dimensions			
a (Å)	7.200(2)	11.3562(8)	12.448(2)
b (Å)	8.316(2)	18.831(2)	12.647(2)
c (Å)	11.199(3)	16.973(2)	14.504(2)
α (°)	99.131(4)	90	103.860(2)
β (°)	99.651(5)	90	106.459(2)
γ (°)	95.164(5)	90	97.121(2)
Volume (Å^3)	648.0(3)	3629.7(4)	2080.4(3)
Z	2	4	2
D_{calc} (Mg m^{-3})	1.344	1.437	1.226
Absorption coefficient (mm^{-1})	0.245	0.843	0.734
$F(0\,0\,0)$	276	1632	796
Crystal size (mm)	0.14 × 0.20 × 0.25	0.29 × 0.18 × 0.16	0.13 × 0.20 × 0.37
θ Range for data collection (°)	1.87–28.11	1.62–28.03	1.53–28.03
Index ranges	$-8 \leqslant h \leqslant 9$	$-14 \leqslant h \leqslant 14$	$-14 \leqslant h \leqslant 16$
	$-9 \leqslant k \leqslant 10$	$-24 \leqslant k \leqslant 20$	$-16 \leqslant k \leqslant 16$
	$-11 \leqslant l \leqslant 14$	$-15 \leqslant l \leqslant 22$	$-19 \leqslant l \leqslant 8$
Reflections collected	3939	21 489	12 247
Independent reflections	2737 [$R_{int} = 0.0366$]	6532 [$R_{int} = 0.0772$]	8517 [$R_{int} = 0.0299$]
Completeness to theta max.	86.6%	98.8%	84.6%
Max. and min. transmission	1.0000 and 0.5162	1.0000 and 0.7740	1.0000 and 0.8230
Data/restraints/parameters	2737/0/197	6532/1/474	8517/0/464
Goodness-of-fit on F^2	0.907	0.868	0.736
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0636$	$R_1 = 0.0477$	$R_1 = 0.0402$
	$wR_2 = 0.1437$	$wR_2 = 0.0583$	$wR_2 = 0.0706$
R indices (all data)	$R_1 = 0.1013$	$R_1 = 0.0959$	$R_1 = 0.0903$
	$wR_2 = 0.1572$	$wR_2 = 0.0662$	$wR_2 = 0.0777$
Absolute structure parameter [18]		−0.011(11)	
Largest difference peak and hole (e Å^{-3})	0.442 and −0.534	0.768 and −0.704	0.251 and −0.270

Compound	[Zn(Ts6mepy)$_2$phen]	[Zn(Ms6me)$_2$bipy]	[Zn(Ms6mepy)$_2$phen]
Empirical formula	$C_{38}H_{34}N_6O_4S_2Zn$	$C_{40}H_{42}N_6O_4S_2Zn$	$C_{42}H_{42}N_6O_4S_2Zn$
Formula weight	768.20	800.29	824.31
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$Pbca$	$P2_1/c$
Unit cell dimensions			
a (Å)	10.244(2)	18.014(2)	17.485(2)
b (Å)	11.839(3)	18.296(2)	11.6697(9)
c (Å)	17.154(4)	25.313(3)	19.675(2)
α (°)	99.591(4)	90	90
β (°)	95.962(4)	90	103.188(2)
γ (°)	103.358(5)	90	90
Volume (Å^3)	1973.6(7)	8342.9(17)	3908.7(5)
Z	2	8	4
D_{calc} (Mg m^{-3})	1.293	1.274	1.401
Absorption coefficient (mm^{-1})	0.773	0.734	0.786
$F(0\,0\,0)$	796	3344	1720
Crystal size (mm)	0.05 × 0.14 × 0.27	0.19 × 0.34 × 0.38	0.35 × 0.22 × 0.16
θ Range for data collection (°)	1.80–28.04	1.61–28.08	2.04–25.00
Index ranges	$-13 \leqslant h \leqslant 11$	$-20 \leqslant h \leqslant 23$	$-20 \leqslant h \leqslant 19$
	$-15 \leqslant k \leqslant 15$	$-24 \leqslant k \leqslant 24$	$-12 \leqslant k \leqslant 13$
	$-22 \leqslant l \leqslant 22$	$-33 \leqslant l \leqslant 26$	$-23 \leqslant l \leqslant 22$
Reflections collected	10 592	39 451	17 796

Table 1 (*Continued*)

Independent reflections	7445 [$R_{int} = 0.0677$]	9751 [$R_{int} = 0.1278$]	6592 [$R_{int} = 0.0472$]
Completeness to theta max.	77.7%	88.7%	90.9%
Max. and min. transmission	1.0000 and 0.6818	1.0000 and 0.4802	1.0000 and 0.6409
Data/restraints/parameters	7445/0/464	9751/0/486	6592/0/504
Goodness-of-fit on F^2	0.751	0.876	0.803
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0664$ $wR_2 = 0.1205$	$R_1 = 0.1134$ $wR_2 = 0.2619$	$R_1 = 0.0384$ $wR_2 = 0.0640$
R indices (all data)	$R_1 = 0.1795$ $wR_2 = 0.1439$	$R_1 = 0.2722$ $wR_2 = 0.3086$	$R_1 = 0.0951$ $wR_2 = 0.0721$
Largest difference peak and hole (e Å^{-3})	0.521 and −0.359	3.729 and −0.687	0.296 and −0.251

bonds are established between the pyridine nitrogen atom and two sulfonamide oxygen atoms, one from the same molecule, giving an intramolecular contact, and the other from a neighbouring molecule, which is involved in an intermolecular contact. The sulfonamide nitrogen atom is not implicated in these hydrogen bonds. This arrangement contrasts with the hydrogen network found in HTspy and HTs6mepy, where the hydrogen bonds involve the N_{py} and the $N_{sulfonamide}$ atoms. It appears that, for steric reasons, the presence of the methyl group in position 3 of the pyridine ring precludes the use of the $N_{sulfonamide}$ atom in the case of HTs3mepy. This behaviour will be described again in the ligational mode of HTs3mepy (vide infra).

3.2. Molecular structures of [Zn(Ts3mepy)$_2$bipy] (1) and [Zn(Ts3mepy)$_2$phen] (2)

The molecular structures of **1** and **2** are shown in Figs. 2 and 3, respectively, together with the labelling scheme used. Compound **1** crystallises with a molecule of acetonitrile, which has been omitted for clarity. Selected bond lengths and angles, with the estimated deviations, are summarised in Table 3.

Both compounds consist of discrete molecules, with the zinc atom coordinated to two (N_{py},O) didentate sulfonamide ligands and an (N,N) didentate 2,2′-bipyridine or 1,10-phenanthroline. The sulfonamide nitrogen atom of the ligand is not bonded to the metal. This behaviour contrasts with that found in [Zn(Tspy)$_2$bipy] [6], where the pyridine ring is unsubstituted. In this case, one ligand behaves as an N_{py} monodentate system and the other as an (N_{py},$N_{sulfonamide}$) didentate ligand. It is feasible that in the case of the HTs3mepy ligand, for steric reasons, the presence of the methyl group precludes the use of the sulfonamide nitrogen as a donor atom.

The environment around the metal can be described in both cases as a slightly distorted octahedron, but some differences are found between the two complexes. In [Zn(Ts3mepy)$_2$bipy] (**1**) the pyridine nitrogen atoms of the sulfonamide ligands are in *trans* positions and the

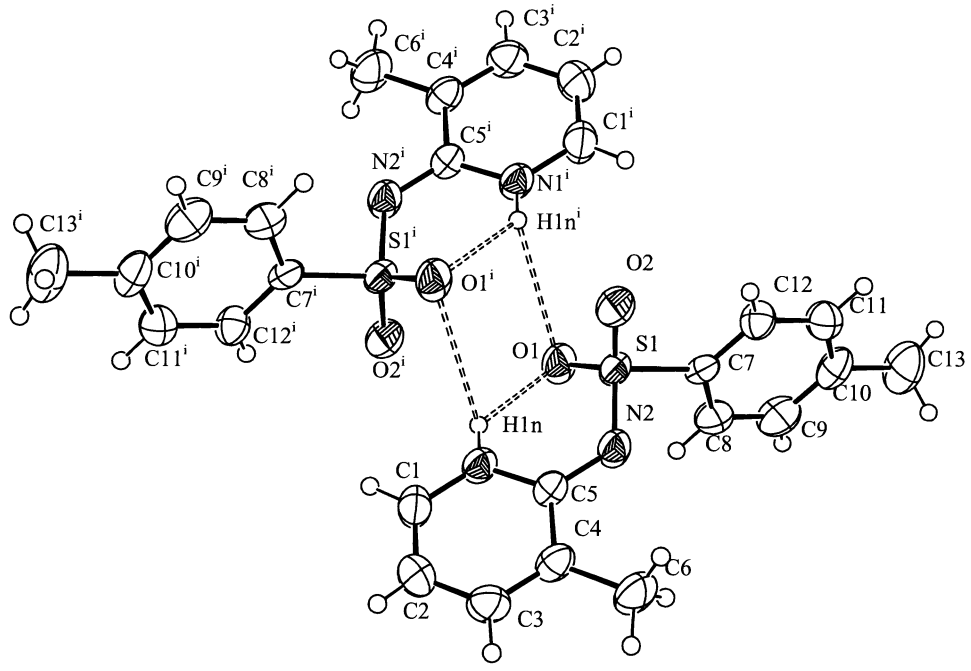


Fig. 1. Molecular structure of HTs3Mepy.

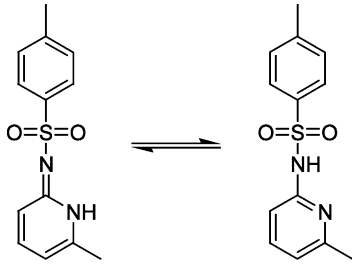
Table 2
Selected bond lengths (Å) and angles (°) for HTs3mepy

Bond lengths			
S(1)–O(2)	1.442(2)	S(1)–O(1)	1.448(2)
S(1)–N(2)	1.582(3)	S(1)–C(7)	1.761(3)
N(1)–C(1)	1.360(4)	N(1)–C(5)	1.361(4)
N(1)–H(1N)	0.84(3)	N(2)–C(5)	1.335(4)
Bond angles			
O(2)–S(1)–O(1)	114.69(15)	O(2)–S(1)–N(2)	111.30(15)
O(1)–S(1)–N(2)	112.63(13)	O(2)–S(1)–C(7)	107.08(14)
O(1)–S(1)–C(7)	107.92(14)	N(2)–S(1)–C(7)	102.25(13)
C(1)–N(1)–C(5)	124.0(3)	C(1)–N(1)–H(1N)	120.4(19)
C(5)–N(1)–H(1N)	115.5(19)	C(5)–N(2)–S(1)	124.0(2)

Hydrogen bonds for HTs3mepy [Å and °]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(1)–H(1n)···O(1)	0.84(3)	2.15(3)	2.805(4)	135(3)
N(1)–H(1n)···O(2)^{i}	0.84(3)	2.39(3)	3.042(4	135(3)
C(3)–H(3)···O(1)^{ii}	0.90(3)	2.54(3)	3.361(4)	151(2)
C(12)–H(12)···O(2)	0.81(3)	2.51(3)	2.892(4)	110(3)

Symmetry transformations used to generate equivalent atoms: $^{i}1-x, 2-y, 1-z$; $^{ii}x, y-1, z$.



I II

Scheme 5.

oxygen atoms are in *cis* positions with respect to each other. However, in [Zn(Ts3mepy)$_2$phen] (**2**) the oxygen atoms are in *trans* positions and the pyridine nitrogen atoms of the sulfonamide ligand in *cis* positions. This latter disposition is stabilised by a π,π-stacking interaction between the toluene group of one of the ligands and the central benzene ring of the 1,10-phenanthroline molecule, with the distances between the centroids being 3.7755(3) Å and the dihedral angle between the rings only 2.24(11)°. Some short distances are given in Table 4.

In [Zn(Ts3mepy)$_2$bipy] (**1**) the zinc atom is almost coplanar—with a maximum deviation of 0.057(2) Å—with the best plane defined by the two oxygen atoms and the bipyridine nitrogen atoms. The dihedral angle between the bipyridine ligand and this plane is 6.5(1)°. The pyridine ring of each anionic ligand is almost perpendicular to this plane [dihedral angle of 85.4(1)° and 89.9(1)°] and the pyridines are slightly twisted with respect to each other [dihedral angle of 17.5(2)°]. The dihedral angle between the rings in each ligand are 54.2(2)° and 74.9(1)°, far from the values usually found for the free ligand (close to 90°).

In [Zn(Ts3mepy)$_2$phen] (**2**) the zinc(II) atom lies at a distance of 0.047(1) Å from the best calculated plane formed by the four nitrogen atoms. The dihedral angle formed by the 1,10-phenanthroline and this plane is 14.91(6)°. The pyridine ring of the anionic ligand implicated in the π,π-stacking interaction is almost perpendicular to the aforementioned plane [dihedral angle of 79.28(7)°]. The other pyridine ring forms a dihedral angle close to 45° [49.98(9)°], probably due to the freedom to adopt this disposition, which is only restricted by chelation and not by a π,π-stacking interaction.

For the complexes discussed above, bond angles around the Zn(II) centre are close to the theoretical values, with the only exception being the bond corresponding to the chelate rings of the coligands [76.16(13)° and 76.74(8)°] [6,19,20]. The Zn–N and Zn–O bond lengths are similar to those found in other octahedral Zn(II) complexes with similar ligands [6,21,22] and do not warrant further comment.

3.3. Crystal structure of [Zn(Ts6mepy)$_2$phen] (*4*)

The molecular structure of **4** is shown in Fig. 4 together with the labelling scheme used. Selected bond lengths and angles, with the estimated deviations, are summarised in Table 5.

The compound consists of monomeric units with the six-coordinated zinc atoms associated with two (*N*,*N*) didentate anionic ligands and an (*N*,*N*) 1,10-phenanthroline molecule. This behaviour is similar to that found in the case of [Zn(Tspy)$_2$bipy] [6].

The coordination polyhedron around the Zn(II) atom can be described as intermediate between an octahedron and a trigonal prism in geometry, with the sulfonamide nitrogen atoms in *trans* positions and the pyridine nitrogen atoms in *cis* positions with respect to each other. The value of the angles ϕ are −35.3(2)°, −36.7(2)° and −34.0(2)° [23] and these reflect the high degree of distortion towards a trigonal prism (see Scheme 6).

The disposition of the anionic ligands around the metal corresponds to a non-crystallographic twofold point symmetry. The pyridine rings are arranged almost perpendicular to the plane formed by the pyridine

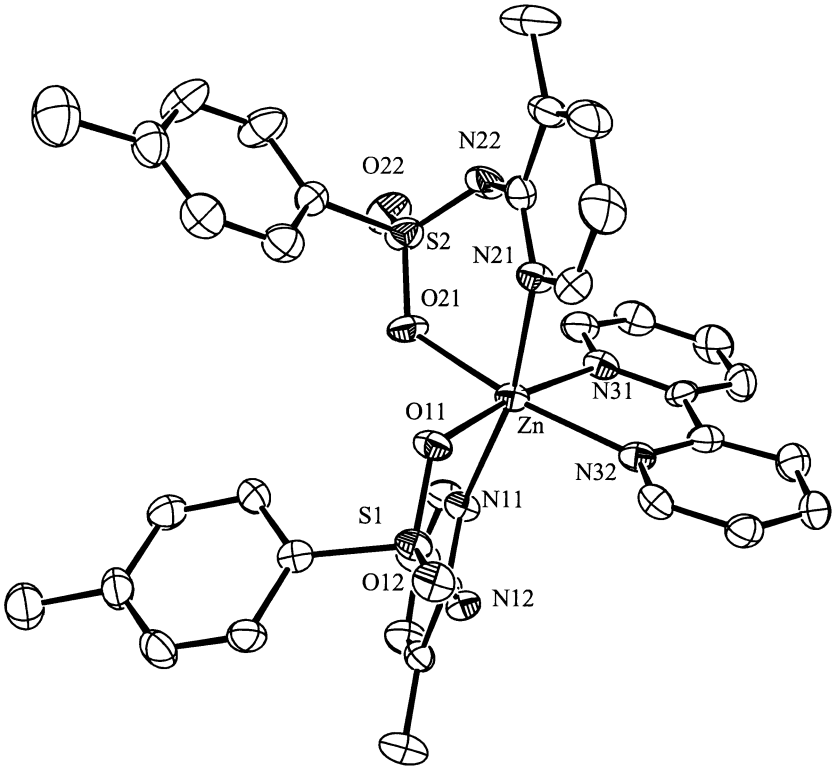


Fig. 2. Molecular structure of [Zn(Ts3mepy)$_2$bipy] (**1**).

nitrogen atoms and the phenanthroline nitrogen atoms [dihedral angles of 76.8(2)° and 88.6(2)°].

In one of the ligands the Zn–N_{py} bond distance is shorter than the Zn–$N_{sulfonamide}$ distance but the situation is reversed for the other ligand. The N–Zn–N angles are smaller than the theoretical values expected for an octahedron.

3.4. Crystal structure of [Zn(Ms6mepy)$_2$bipy] (5)

Unfortunately the crystal data for [Zn(Ms6mepy)$_2$bipy] (**5**) are rather poor. However, the refinement gives the final map shown in Fig. 5 and the final R_1 converged to 11.3%. Several attempts to obtain a better quality monocrystal were unsuccessful. Selected bond

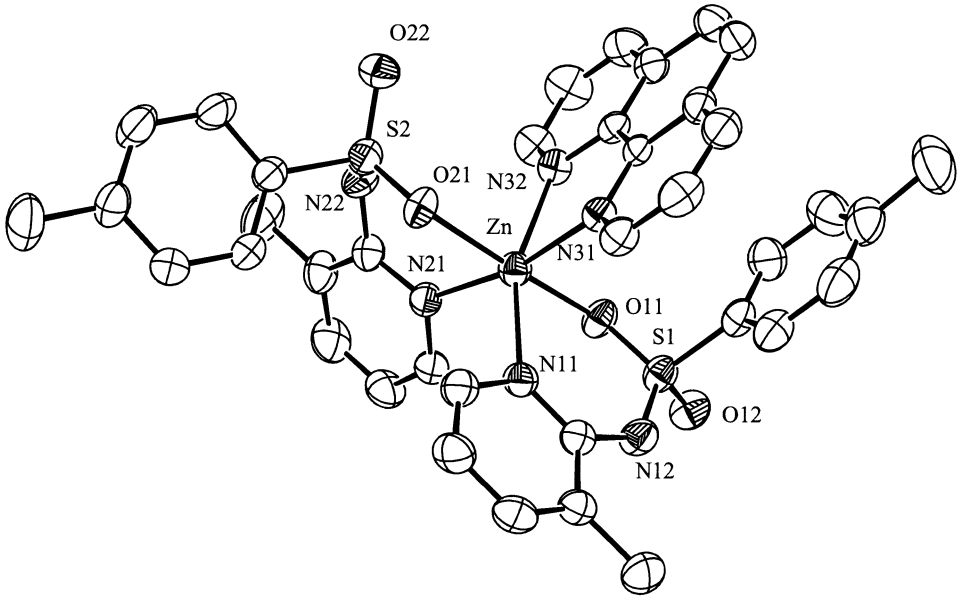


Fig. 3. Molecular structure of [Zn(Ts3mepy)$_2$phen] (**2**).

Table 3
Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

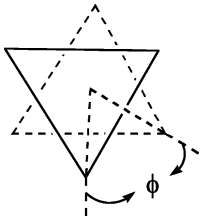
	[Zn(Ts3mepy)$_2$bipy] (**1**)	[Zn(Ts3mepy)$_2$phen] (**2**)
Bond lengths		
Zn–N(11)	2.154(3)	2.138(2)
Zn–N(21)	2.161(3)	2.121(2)
Zn–O(11)	2.140(3)	2.1328(19)
Zn–O(21)	2.102(2)	2.1548(18)
Zn–N(31)	2.186(3)	2.211(2)
Zn–N(32)	2.163(3)	2.145(2)
Bond angles		
O(21)–Zn–O(11)	93.23(10)	172.37(7)
O(11)–Zn–N(11)	86.38(12)	85.63(8)
O(11)–Zn–N(21)	85.99(12)	91.49(8)
N(11)–Zn–N(32)	97.44(12)	158.71(8)
O(21)–Zn–N(31)	94.61(12)	86.03(7)
N(11)–Zn–N(31)	92.22(13)	89.31(8)
N(31)–Zn–N(32)	76.16(13)	76.74(8)
O(21)–Zn–N(11)	85.66(11)	101.13(8)
O(21)–Zn–N(21)	85.72(12)	84.13(8)
O(11)–Zn–N(32)	96.11(11)	80.49(8)
N(21)–Zn–N(32)	92.38(13)	98.57(9)
N(21)–Zn–N(31)	96.58(13)	168.78(9)
N(11)–Zn–N(21)	168.15(13)	97.85(9)
O(11)–Zn–N(31)	171.91(12)	97.68(8)
O(21)–Zn–N(32)	170.32(12)	93.95(8)

Table 4
Some short contacts between rings for [Zn(Ts3mepy)$_2$bipy] (**1**)

C17–N31	3.429(4)	C17–C311	3.532(4)
C18–C31	3.466(4)	C18–C32	3.688(4)
C18–C311	3.764(4)	C19–C32	3.607(5)
C19–C33	3.486(4)	C19–C34	3.689(4)
C110–C35	3.688(5)	C110–C34	3.511(5)
C110–C33	3.660(5)	C111–C34	3.642(5)
C111–C35	3.636(5)	C111–C36	3.782(5)
C112–C312	3.557(4)	C112–C311	3.543(4)

Table 5
Selected bond lengths (Å) and angles (°) for [Zn(Ts6mepy)$_2$phen] (**4**), [Zn(Ms6mepy)$_2$bipy] (**5**) and [Zn(Ms6mepy)$_2$phen] (**6**)

	4	**5**	**6**
Bond lengths			
Zn–N(11)	2.267(5)	2.578(7)	2.238(3)
Zn–N(12)	2.117(5)	2.037(6)	2.137(1)
Zn–N(21)	2.132(5)	2.673(7)	2.145(2)
Zn–N(22)	2.242(5)	2.033(6)	2.245(3)
Zn–N(31)	2.083(6)	2.074(8)	2.144(5)
Zn–N(32)	2.170(6)	2.093(7)	2.137(2)
Bond angles			
N(31)–Zn–N(12)	101.0(2)	108.5(2)	103.03(9)
N(31)–Zn–N(21)	101.3(2)	159.0(2)	95.69(9)
N(31)–Zn–N(32)	77.5(2)	78.0(3)	77.25(9)
N(21)–Zn–N(32)	151.9(2)	89.9(2)	158.29(9)
N(12)–Zn–N(22)	159.4(2)	129.5(3)	156.23(9)
N(32)–Zn–N(22)	91.0(2)	108.6(2)	98.76(9)
N(11)–Zn–N(12)	61.5(2)	56.9(2)	61.57(9)
N(32)–Zn–N(11)	89.9(2)	157.9(2)	98.24(9)
N(12)–Zn–N(21)	108.5(2)	91.5(2)	102.54(9)
N(12)–Zn–N(32)	99.2(2)	108.2(3)	99.07(9)
N(31)–Zn–N(22)	98.70(19)	112.0(2)	96.14(8)
N(21)–Zn–N(22)	61.3(2)	55.6(2)	61.19(8)
N(31)–Zn–N(11)	156.9(2)	91.0(2)	163.42(9)
N(21)–Zn–N(11)	98.84(19)	105.8(2)	93.89(8)
N(22)–Zn–N(11)	100.8(2)	93.2(2)	100.33(9)



Scheme 6.

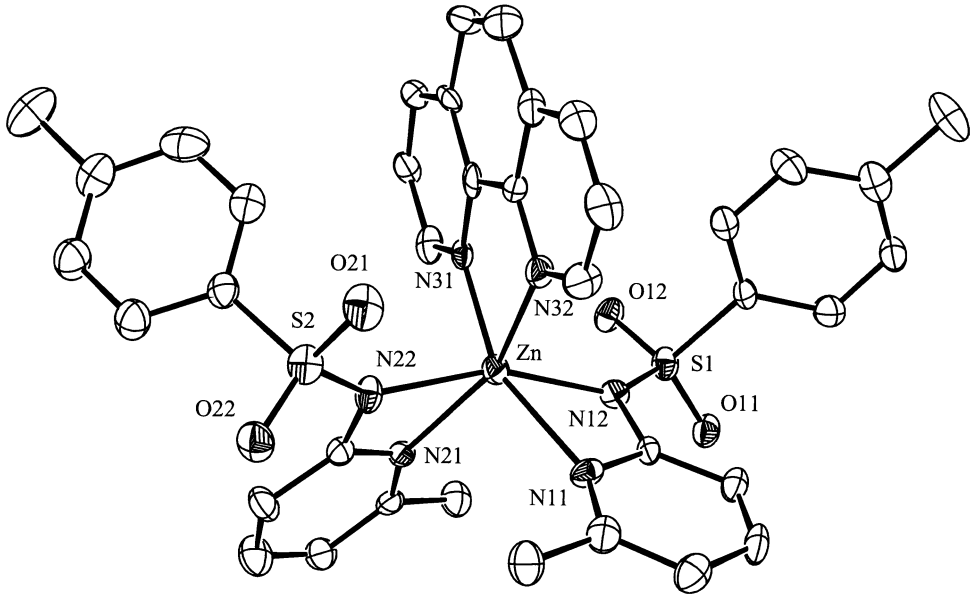


Fig. 4. Molecular structure of [Zn(Ts6mepy)$_2$phen] (**4**).

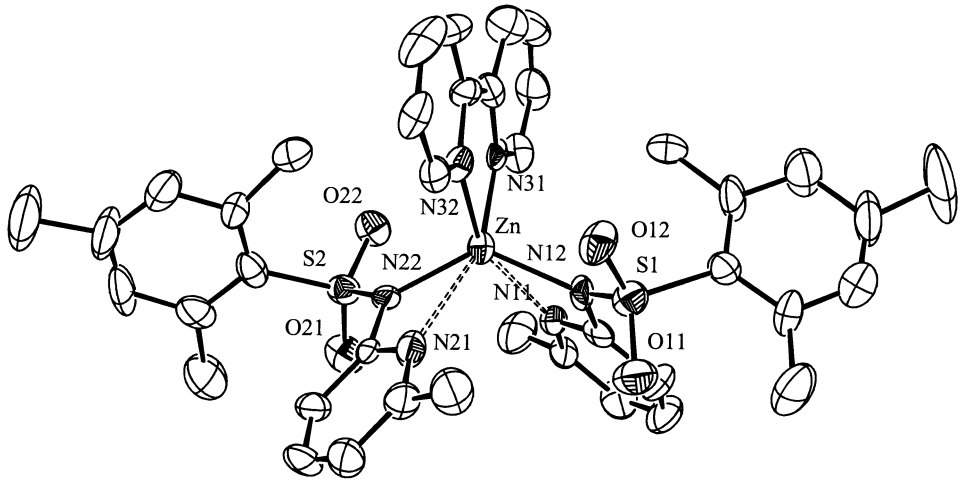


Fig. 5. Molecular structure of [Zn(Ms6mepy)$_2$bipy] (**5**).

lengths and angles, with the estimated deviations, are summarised in Table 5.

The compound is a monomer with Zn–$N_{sulfonamide}$ and Zn–N_{py} distances of 2.037(6) and 2.578(7) Å in the case of one ligand, and 2.033(6) and 2.673(7) Å for the other. Consequently, the metal atom can be considered as being coordinated to two $N_{sulfonamide}$ monodentate anionic ligands and to a bipyridine molecule in a tetrahedral environment. It is noteworthy that in the complexes [Zn(Tspy)$_2$bipy)] and [Zn(Ts6mepy)$_2$phen] the sulfonamide ligands act as ($N_{sulfonamide}$,N_{py}) didentate ligands. This difference can be attributed to the fact that such a didentate mode in [Zn(Me6mepy)$_2$bipy] would cause too many methyl groups to be packed in a small volume. If the interaction between the pyridine nitrogen and the metal atom is considered as a bonding contact, the coordination around the zinc atom can be described as a trigonal prism, with each triangular face of the prism formed by one of the nitrogen atoms of the bipyridine, a sulfonamide nitrogen of one of the anionic ligands and a pyridine nitrogen of the other. These planes are almost parallel [dihedral angle of 0.2(2)°] in spite of the small bite of the anionic ligands. The values of the angles ϕ are 22.9(3)°, 24.8(3)° and 24.3(3)° [23].

3.5. Molecular structure of [Zn(Ms6mepy)$_2$phen] (**6**)

The molecular structure of **6** is shown in Fig. 6 together with the labelling scheme used. Selected bond lengths and angles, with the estimated deviations, are summarised in Table 5.

Compound **6** consists of monomeric units with a six-coordinated zinc atom associated with two anionic ligands and a molecule of 1,10-phenanthroline.

The coordination polyhedron around the Zn(II) atom is best described as a very distorted octahedron. The sulfonamide nitrogen atoms are in a *trans* arrangement and the pyridine nitrogen atoms in a *cis* disposition with respect to each other. The distortion can be noted in the equatorial plane, which deviates significantly from planarity. In this system N(11) and N(31) are located 0.281(1) and 0.357(1) Å, respectively, below the plane and N(21) and N(32) are 0.293(1) and 0.345(1) Å, respectively, above the best plane. The Zn(II) atom is also 0.037(1) Å below the best plane. The pyridine rings are arranged in an almost perpendicular manner with respect to the equatorial plane [dihedral angle of 87.98(7)° and 89.38(7)°] and the phenanthroline plane deviates slightly from the equatorial plane [dihedral angle of 13.86(9)°]. As found in the case of [Zn(Ts6mepy)$_2$phen], the Zn–N_{py} bond distance is shorter than Zn–$N_{sulfonamide}$ in one ligand, but the situation is reversed in the other ligand.

The disposition of the two anionic ligands around the metal corresponds to a non-crystallographic twofold point symmetry with a significant π,π-stacking interaction—also found in [Zn(Ts3mepy)$_2$phen] (**2**)—which in this case takes place between the phenanthroline plane and the two mesityl groups of the sulfonamide ligands. The dihedral angles between the mesityl and phenanthroline planes are 3.9(1) and 0.2(1)°, respectively. Short distances between ring atoms are shown in Table 6.

It should be noted that in [Zn(Ms6mepy)$_2$bipy] (**5**) the sulfonamide ligands act in an $N_{sulfonamide}$ monodentate mode, but in [Zn(Ms6mepy)$_2$phen] (**6**) they act in an (N_{py},$N_{sulfonamide}$) didentate way. The difference in behaviour can be attributed to the existence of a π,π-stacking interaction in the case of [Zn(Ms6mepy)$_2$phen]. The bipyridine coligand does not allow intramolecular π,π-stacking interactions, but the phenanthroline moiety does due to the presence of a third aromatic ring.

3.6. Spectroscopic studies

The IR spectra of these complexes do not show a ν(N–H) band, which appears at 3248–3220 cm^{-1} in the sulfonamide ligand. This is indicative that the ligand is

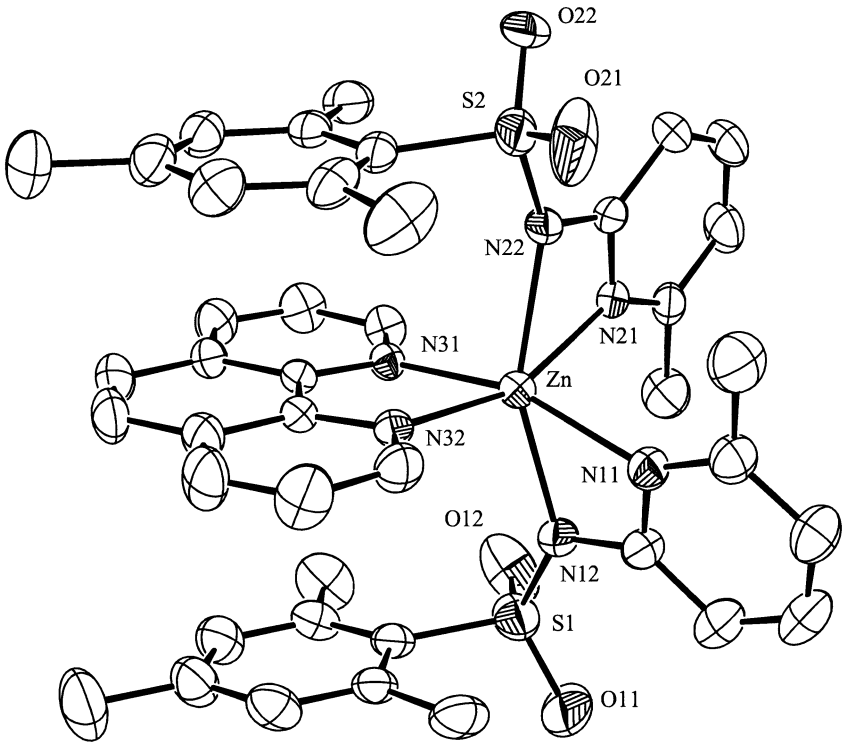


Fig. 6. Molecular structure of [Zn(Ms6mepy)$_2$phen] (**6**).

Table 6
Some short contacts between rings for [Zn(Ms6mepy)$_2$phen] (**6**)

C(110)–C(36)	3.766(5)	C(210)–C(36)	3.583(5)
C(112)–C(312)	3.695(4)	C(212)–C(312)	3.728(4)
C(19)–C(34)	3.842(4)	C(29)–C(34)	3.651(4)
C(18)–C(311)	3.611(4)	C(28)–C(311)	3.501(4)
C(111)–C(37)	3.678(5)	C(211)–C(37)	3.562(5)

in the anionic form in the complex. Bands in the region 1590–1616 cm^{-1}, attributable to ν(C=N), appear in the complexes in similar positions to those of the free ligands. In the derivatives of ligands Ts6mepy$^-$ and Ms6mepy$^-$, these bands are shifted to lower frequencies as a result of the coordination through the sulfonamide nitrogen atom. Table 7 collects the values of the main vibrations associated with the sulfonic group. As can be seen, when this group coordinates the metal atom through an oxygen atom, the value of $\Delta(\nu_{asym}-\nu_{sym})$ is higher than the value found in the case of coordination through the nitrogen atom. However, more work is needed to show that the value of $\Delta(\nu_{asym}-\nu_{sym})$ can be used to distinguish between both ways of coordination. The spectra also show bands in the aromatic region (1460–1415 cm^{-1}), which are characteristic of the ν(C=C) vibrations, and also a band at 2920–2940 cm^{-1}, which is attributable to ν(–CH$_3$). Bands at 1520, 850 and 725 cm^{-1} for 1,10-phenanthroline and 770 and 730 cm^{-1} for 2,2′-bipyridine confirm the presence of the coligands in the metal coordination sphere.

The ^{1}H NMR spectra show that the signal due to the –NH hydrogen atom, which in the free ligand appears around δ 12, is not present in the complexes. This provides good evidence that the ligand has been deprotonated. The aromatic resonances, including those of the coligands, appear between δ 9.5–6.4. In the region of δ 2.0–2.3 ppm appear all the methyl group signals that are shifted to higher field respect to their

Table 7
Selected IR bands associated with the sulfonic group in cm^{-1}

Compound	ν_{asym}(S=O)	ν_{sym}(S=O)	$\Delta(\nu_{asym}-\nu_{asym})$	ρ_wSO_2	ρ_tSO_2	Environment around the metal
[Zn(Ts3mepy)$_2$bipy]	1324	1117	207	590	546	[ZnN$_4$O$_2$]
[Zn(Ts3mepy)$_2$phen]	1333	1114	219	588	545	[ZnN$_4$O$_2$]
[Zn(Ts6mepy)$_2$phen]	1322	1138	184	581	553	[ZnN$_6$]
[Zn(Ms6mepy)$_2$bipy]	1311	1134	177	589	535	[ZnN$_4$]
[Zn(Ms6mepy)$_2$phen]	1326	1132	194	589	532	[ZnN$_6$]

Table 8
Summary of geometrical conclusions

Complex	Sulfonamide ligand behaviour	Coordination polyhedra	Environment around the metal	Other features
[Zn(Ts3mepy)$_2$bipy]	(N_{py},O) didentate	octahedral	[ZnN_4O_2]	
[Zn(Ts3mepy)$_2$phen]	(N_{py},O) didentate	octahedral	[ZnN_4O_2]	one π,π-stacking interaction
[Zn(Ts6mepy)$_2$phen]	(N_{py},$N_{sulfonamide}$) didentate	trigonal bipyramidal	[ZnN_6]	
[Zn(Ms6mepy)$_2$bipy]	($N_{sulfonamide}$) monodentate	tetrahedral	[ZnN_4]	two long N_{py}–Zn interactions
[Zn(Ms6mepy)$_2$phen]	(N_{py},$N_{sulfonamide}$) didentate	very distorted octahedral	[ZnN_6]	two π,π-stacking interactions

position in the free ligands. In the case of the methyl group from the picoline ring appears in the range δ 2.0–2.3 and is also observed a signal at about δ 2.1, assigned to the toluene methyl group of the complexes with Ts3mepy$^-$ and Ts6mepy$^-$ ligands. The Ms6mepy$^-$ complexes show two signals at about δ 2.2–2.0 due to the mesityl methyl groups.

In all cases, the LSIMS mass spectra show the molecular ion with the appropriate isotope distribution as well as the peak corresponding to the free ligand. In most cases, peaks corresponding to the ion formed by the loss of one ligand from the initial complex are also observed.

4. Conclusions

The work described here involved the electrochemical synthesis and the X-ray structure characterisation of several zinc mixed complexes derived from a series of pyridine sulfonamides. Table 8 summarises the main structural features of the compounds under investigation.

As can be seen, the ligands behave in an (N,O) didentate manner when a methyl group is located in position 3 of the pyridine ring. This behaviour has already been found in similar complexes with cadmium [10], and it can be explained as being the result of a steric effect. The presence of a substituent in position 3 forces the sulfonyl group towards the immediate vicinity of the metal and induces an (N,O) didentate behaviour.

However, when the substituent is in position 6, the ligand behaves either in an (N_{py},$N_{sulfonamide}$) didentate way or in an N_{py} monodentate mode depending on the nature of the coligand. When the coligand is bipyridine, the sulfonamide ligand binds the metal in a monodentate way. This trend could be the result of a steric effect produced by the methyl groups on the sulfonamide ring. However, when the coligand is phenanthroline, the presence of a π,π-stacking interaction stabilises the compound and allows the possibility of the sulfonamide ligand acting in an (N_{py},$N_{sulfonamide}$) didentate mode. It is particularly noteworthy that in the case of [M(Ms3mepy)$_2$phen] (M = Cu, Cd), the ligand behaves in an (N_{py},O) didentate way. In these cases, the steric effect produced by the methyl group in position 3 in the pyridine ring is more important than the stabilising effect of the π,π-stacking interaction.

5. Supplementary material

Crystallographic data have been deposited with the CCDC, (12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk)) and are available on request quoting the deposition numbers 197 497–197 502.

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