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(2,2′-Bipyridine-κ^2N)bis[*N*-(2-pyridyl-κN)-*p*-toluenesulfonamido-κN]zinc(II)

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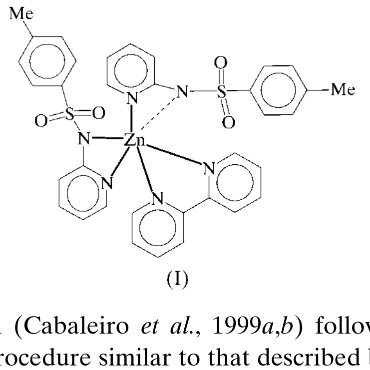
The structure of the title compound, $[Zn(C_{12}H_{11}N_2O_2S)_2(C_{10}H_8N_2)]$, consists of monomeric molecules in which the central $ZnN_2N'N''$ unit has a distorted tetrahedral geometry, with bond lengths ranging from 2.020 (3) to 2.109 (3) Å. The anionic ligands are potential bidentate donors and thus there are two secondary Zn—N interactions. The shorter of these is 2.317 (3) Å and completes at the Zn atom an irregular five-coordinated geometry, which can be described as a square pyramid showing 30% distortion towards the trigonal bipyramid; the other Zn—N contact is much longer at 2.549 (3) Å.

Comment

The coordination chemistry of sulfonamide ligands has been the subject of some recent investigation (Otter *et al.*, 1998, and references therein). The electron-withdrawing nature of the sulfonyl group causes important changes both in the neutral ligand and in its complexes. Free ligands, such as tosylsulfonylimino-1*H*-pyridine, are expected to exist as sulfonamides; however, crystallographic and spectroscopic data show that the most stable form bears the acidic hydrogen at the pyridine nitrogen (Cabaleiro *et al.*, 1999*a*). Therefore, its metal complexes could be easily obtained by its electrochemical deprotonation (Cabaleiro *et al.*, 1999*a*,*b*) following an electrochemical procedure similar to that described by Oldham & Tuck (1982).



(I)

The title compound, (I), was obtained (see *Experimental*) by electrolysis of a solution of [(4-methylphenyl)sulfonyl]-imino-1*H*-pyridine and 2,2′-bipyridine in a mixture of acetonitrile and dichloromethane, using a zinc plate as the anode. The value of the electrochemical efficiency, defined as the amount of zinc dissolved per number of Faradays, was close to 0.5 mol F^{-1}. This fact and the formation of hydrogen gas at the cathode are compatible with a reaction mechanism involving the anodic oxidation to zinc(II) and the deprotonation of the ligand at the cathode.

The molecule consists of monomeric units where the Zn atom is coordinated to two anionic ligands and to one neutral bipyridine ligand resulting in a highly distorted tetrahedral environment, ZnN_4; the disposition of the anionic ligands around the metal corresponds approximately to non-crystallographic twofold point symmetry. The distortion is, in part, due to the small bite of the 2,2′-bipyridine, N31—Zn—N32 77.86 (10)°, which also leads to non-ideal values for the other N—Zn—N angles, 99.32 (10)–134.82 (10)°. The Zn—N bond lengths, between 2.020 (3) and 2.109 (3) Å, are slightly longer than in other tetracoordinated complexes with tosylamide ligands such as bis{*N*-[(2-pyrrolyl)methylene]-*N*′-tosylbenzene-1,2-diaminato}zinc(II) with values between 1.962 (3) and 2.049 (4) Å (Romero *et al.*, 1997). Nevertheless, the Zn—N_{bipy} bond distances, 2.106 (3) and 2.110 (3) Å, are similar to those observed in other complexes containing tetrahedral zinc and bipyridine, *e.g.* $[Zn(S\text{-}2,4,6\text{-}{}^iPr_3C_6H_2)_2bipy]$ (Corwin & Koch, 1988) or 2,2′-bipyridinebis(benzothiazole-2-thionato)-zinc(II) (Castro *et al.*, 1993).

The Zn—N_{py} bond lengths, 2.020 (3) and 2.082 (3) Å, are as expected for tetrahedral pyridine complexes of zinc(II) (Steffen & Palenik, 1977; Xiong *et al.*, 1997; Xu *et al.*, 1998) but they are also consistent with values for pentacoordinated zinc(II), *e.g.* the cation [μ^2-(4-nitrophenyl)phosphato-*O*,*O*′]-bis[tris(2-pyridylmethyl)amine-*N*,*N*′,*N*″]zinc(II) showed values in the range 2.034–2.082 Å (Adams *et al.*, 1995).

In the title compound, further Zn—N contacts are provided by the second N atoms of the potentially bidentate amide ligands. One such nitrogen, N22, is located 2.317 (3) Å from the Zn atom, whereas N12 is appreciably more distant at 2.549 (3) Å. We consider the latter as a contact rather than a bond. However, the former is close to the sum of the covalent radii (0.19 Å larger), and could thus be considered as a bond. Similar Zn—N distances of 2.330 (6), 2.362 (4), 2.345 (3) or 2.437 (3) Å have been found in various pentacoordinated zinc complexes with N-donors (Alcock *et al.*, 1988; Shionoya *et al.*, 1994; Bhattacharyya *et al.*, 1996; Meyer & Rutsch, 1998), and have also been interpreted as corresponding to bonds. Accordingly, the coordination polyhedron in the title compound could be described as a square pyramid showing 30% distortion towards a trigonal bipyramid ($\tau = 0.3$; Addison *et al.*, 1984). The N—Zn—N angle of the four-membered chelate ring is 60.44 (10)°, slightly smaller than those found in other four-membered chelate rings, 63.58 and 63.21° (Engelhardt *et al.*, 1991).

Both tosyl ligands are similar, but with different dihedral angles between the pyridine and benzene rings, 79.30 (11) and

89.86 (12)°, the former corresponding to the bidentate ligand. This angle is smaller than that in the free ligand [83.7 (3) and 87.6 (1)°; Cabaleiro *et al.*, 1999*a*], probably due to the coordination.

Although the H atoms have been included in their idealized positions, some of them are situated close to sulfonyl O atoms, providing evidence for C—H···O hydrogen bonds (Taylor & Kennard, 1982) (Table 2). The intramolecular interactions might be due to geometrical constraints, but intermolecular ones may be assumed to play a significant role in the packing arrangement.

In the bipyridyl ligand, the pyridine rings are essentially coplanar, with a dihedral angle of 6.9 (2)°.

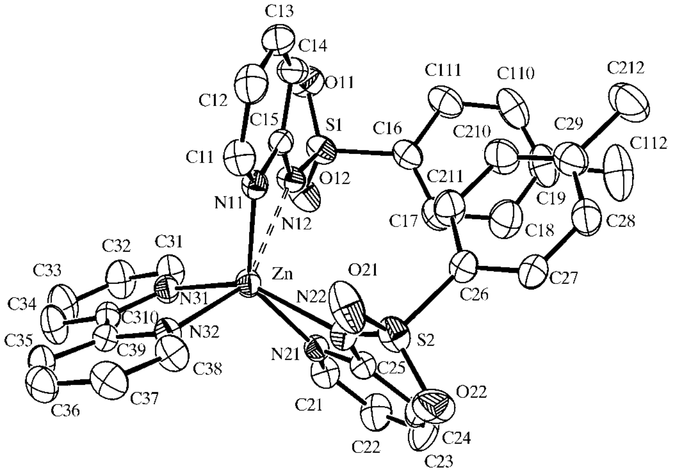


Figure 1
The title molecule, including the atomic numbering scheme, drawn using *ORTEP*-3 (Farrugia, 1998). H atoms are represented as circles of arbitrary radius, other atoms as displacement ellipsoids drawn at the 30% probability level.

Experimental

The electrochemical oxidation of a zinc anode in an acetonitrile/-dichloromethane solution (25 + 25 ml) containing the free ligand H*L* (198.7 mg, 0.8 mmol), 2,2′-bipyridine (62.5 mg, 0.4 mmol) and tetramethylammonium perchlorate (*ca* 10 mg) for 2 h at 12.5 V and 10 mA, resulted in a loss of 28.5 mg of zinc from the anode and the formation of a colourless solution, which after concentration gave a well crystallized solid. This solid was identified as $[Zn(C_{12}H_{11}N_2O_2S)_2(C_{10}H_8N_2)]$. Found: H 4.5, C 56.8, N 12.1, S 9.0%; calculated for $C_{34}H_{30}N_6O_4S_2Zn$: H 4.2, C 57.0, N 11.7, S 8.9%.

Crystal data

$[Zn(C_{12}H_{11}N_2O_2S)_2(C_{10}H_8N_2)]$	$D_x = 1.421$ Mg m^{-3}
$M_r = 716.13$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 10.8157$ (7) Å	$\theta = 19.1$–$45.2°$
$b = 21.6466$ (6) Å	$\mu = 2.576$ mm^{-1}
$c = 14.354$ (2) Å	$T = 293$ (2) K
$\beta = 95.114$ (8)°	Block, colourless
$V = 3347.3$ (5) Å^3	0.30 × 0.20 × 0.15 mm
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.040$
ω–θ scans	$\theta_{max} = 75.93°$
Absorption correction: ψ scan (North *et al.*, 1968) and *PLATON* (Spek, 1998)	$h = 0 \rightarrow 13$
$T_{min} = 0.610$, $T_{max} = 0.679$	$k = -27 \rightarrow 0$
7357 measured reflections	$l = -18 \rightarrow 17$
6986 independent reflections	3 standard reflections every 200 reflections frequency: 60 min intensity decay: none
4479 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2 + 0.9056P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.137$	$\Delta\rho_{max} = 0.483$ e Å^{-3}
$S = 1.018$	$\Delta\rho_{min} = -0.380$ e Å^{-3}
6986 reflections	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
427 parameters	Extinction coefficient: 0.00124 (11)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Zn—N11	2.020 (3)	Zn—N12	2.549 (3)
Zn—N21	2.082 (3)	S1—N12	1.576 (3)
Zn—N31	2.106 (3)	S1—C16	1.775 (4)
Zn—N32	2.109 (3)	S2—N22	1.581 (3)
Zn—N22	2.317 (3)	S2—C26	1.763 (3)
N11—Zn—N21	134.82 (10)	N31—Zn—N22	152.52 (10)
N11—Zn—N31	111.56 (10)	N32—Zn—N22	94.46 (10)
N21—Zn—N31	99.32 (10)	N11—Zn—N12	57.09 (9)
N11—Zn—N32	101.51 (10)	N21—Zn—N12	92.43 (9)
N21—Zn—N32	117.07 (10)	N31—Zn—N12	89.52 (10)
N31—Zn—N32	77.86 (10)	N32—Zn—N12	149.25 (9)
N11—Zn—N22	95.78 (10)	N22—Zn—N12	108.51 (9)
N21—Zn—N22	60.44 (10)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···O21^{i}	0.93	2.42	3.281 (4)	154
C13—H13···O12^{ii}	0.93	2.41	3.257 (5)	152
C14—H14···O11	0.93	2.38	2.970 (5)	121
C111—H111···O11	0.93	2.54	2.908 (6)	104
C24—H24···O22	0.93	2.42	3.005 (5)	121
C27—H27···O11^{iii}	0.93	2.57	3.216 (4)	127
C27—H27···O22	0.93	2.63	2.941 (5)	100
C28—H28···O11^{iii}	0.93	2.73	3.301 (5)	120
C31—H31···O12	0.93	2.46	3.377 (5)	171
C32—H32···O22^{iv}	0.93	2.42	3.087 (5)	129
C35—H35···O12^{v}	0.93	2.56	3.316 (4)	139
C38—H38···O21	0.93	2.44	3.348 (5)	164

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $\frac{5}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$.

H atoms were refined using a riding model (*HFIX* 43 for aromatic H) and rigid methyl groups (*HFIX* 137).

Data collection: *CAD*-4-*EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *HELENA* (Spek, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1998); software used to prepare material for publication: *SHELXL*97.

Intensity measurements were performed at the Unidade de Raios X (monocristal), Universidade de Santiago de Compostela. All crystallographic calculations were performed at the web site http://angus.uvigo.es. This study was carried out with financial support by the Xunta de Galicia (XUGA 20302B97).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1373). Services for accessing these data are described at the back of the journal.

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