Electrochemical Synthesis and Characterization of Zinc(II) Complexes with [(4-Methylphenyl)Sulfonyl]-1*H*-Amido-2-Phenyl-2-Oxazolines

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Received December 3rd, 2001.

Dedicated to Professor Joachim Strähle on the Occasion of his 65th Birthday

Abstract. A series of [(4-methylphenyl)sulfonyl]-1*H*-amido-2-phenyl-2-oxazoline ligands, HTs-ROz, has been synthesized by the reaction of substituted 2-(2-aminophenyl)oxazolines and *p*-toluensulfonyl chloride. The electrochemical oxidation of a sacrificial zinc anode in an acetonitrile solution of the corresponding ligand gave compounds of general formula $[Zn(Ts\text{-}ROz)_2]$. All complexes have been characterized by microanalysis, IR and ^1H NMR spectroscopy and single-crystal X-ray diffraction. In all cases, the metal atom is coordinated by the nitrogen atoms of two monoanionic ligands.

Keywords: Zinc; Electrochemical synthesis; Oxazolines; Sulfonamide complexes; Crystal structure

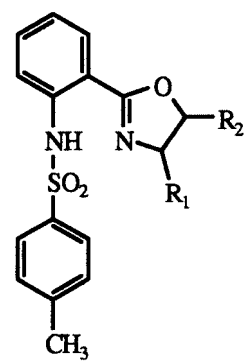
Elektrochemische Synthese und Charakterisierung von Zink(II)-Komplexen mit [(4-Methylphenyl)sulfonyl]-1*H*-amido-2-phenyl-2-oxazolinen

Inhaltsübersicht. Eine Serie von [(4-Methylphenyl)sulfonyl]-1*H*-amido-2-phenyl-2-oxazolin-Liganden HTs-ROz wurden durch Reaktion von substituierten 2-(2-Aminophenyl)oxazolinen mit p-Toluolsulfonylchlorid synthetisiert. Die elektrochemische Oxidation von Opfer-Zink-Anoden in Acetonitrillösungen der entsprechenden Liganden führt zu Verbindungen der Formel $[Zn(Ts\text{-}ROz)_2]$. Alle Komplexe wurden durch Mikroanalysen, IR- und ^1H-NMR-Spektren und durch Einkristall-Strukturanalysen charakterisiert. In allen Fällen sind die Metallatome durch die N-Atome zweier monoanionischer Liganden koordiniert.

1 Introduction

It is very well known that dialkylzinc compounds are used in the presence of chiral ligands for the asymmetric synthesis of alcohols from prochiral ketones [1]. It has been suggested that the actual zinc compound is derived from the interaction of the dialkylzinc and the chiral ligand. For this reason, an understanding of the enantiomeric excess produced in the reaction requires an understanding of the nature of such an intermediate. The work described in this paper involves the synthesis and elucidation of the molecular structures of some zinc complexes of nitrogen ligands. In particular, chiral amines bearing multiple nitrogen atoms, which are capable of chelating behaviour, have been found to be effective for this type of transformation.

Among the various types of such ligands, those containing oxazoline rings and a sulfonamide group as donor centres have been chosen for this study (See scheme 1).



Scheme 1

The reason for this choice is that oxazoline rings bearing chiral centres can be easily prepared and that a sulfonamide group can be deprotonated. In this way, the proligands can be transformed into bidentate mononionic ligand systems.

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  0044−2313/02/628/1210−1217 $ 20.00+.50/0 Z. Anorg. Allg. Chem. **2002**, *628*, 1210−1217

Table 1 Summary of crystal data and structure refinement.

Identification code	$[Zn(TsOz)_2]$	$[Zn(Ts\text{-}5MeOz)_2]$	$[Zn(Ts\text{-}4MeOz)_2]$	$[Zn\ (Ts\text{-}4EtOz)_2]$	$[Zn(Ts\text{-}4^iPrOz)_2]$
Empirical formula	$C_{32}H_{30}N_4O_6S_2Zn$	$C_{34}H_{34}N_4O_6S_2Zn$	$C_{34}H_{34}N_4O_6S_2Zn$	$C_{36}H_{38}N_4O_6S_2Zn$	$C_{38}H_{40}N_4O_6S_2Zn$
Formula weight	696.09	724.17	724.17	752.22	778.23
Temperature	293(2) K	293(2) K	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 A	0.71073 A	0.71073 Å	0.71073 Å	1.54184 Å
Crystal system, space group	triclinic, $P\bar{1}$ (#2)	orthorhombic, *P*naa (#56)	monoclinic, $P2_1/n$ (#14)	orthorhombic, *F*ddd (#70)	monoclinic, *C*2/c (#15)
Unit cell dimensions	a = 9.7607(1) Å	a = 12.8384(1) Å	a = 14.8100(3) Å	a = 21.8490(2) Å	a = 21.0493(3) Å
	b = 12.1370(1) Å	b = 13.5934(2) Å	b = 15.0892(3) Å	b = 23.0172(4) Å	b = 11.1935(12) Å
	c = 13.7243(2) Å	c = 18.9643(2) Å	c = 16.7306(4) Å	c = 29.1244(3) Å	c = 16.6097(10) Å
	α = 89.9111(7)°	α = 90°	α = 90°	α = 90°	α = 90°
	β = 86.1672(9)°	β = 90°	β = 105.9562(5)°	β = 90°	β = 100.917(6)°
	γ = 72.8279(8)°	γ = 90°	γ = 90°	γ = 90°	γ = 90°
Volume	1549.62(3) Å^3	3309.60(7) Å^3	3594.76(13) Å^3	14646.7(3) Å^3	3842.7(5) Å^3
Z, Calculated density	2, 1.492 Mg/m^3	4, 1.453 Mg/m^3	4, 1.338 Mg/m^3	16, 1.364 Mg/m^3	4, 1.345 Mg/m^3
Absorption coefficient	0.979 mm^{-1}	0.920 mm^{-1}	0.847 mm^{-1}	0.834 mm^{-1}	2.310 mm^{-1}
F(000)	720	1504	1504	6272	1624
Crystal size	0.40 × 0.25 × 0.15 mm	0.6 × 0.1 × 0.05 mm	0.45 × 0.35 × 0.20 mm	0.50 × 0.35 × 0.25 mm	0.25 × 0.15 × 0.10 mm
θ range for data collection	1.49 to 28.29°	1.84 to 28.36°	1.63 to 28.30°	1.46 to 28.20°	4.28 to 75.90°
Limiting indices	−9≤h≤13	−15≤h≤17	−18≤h≤19	−28≤h≤28	−26≤h≤26
	−15≤k≤16	−15≤k≤18	−20≤k≤19	−30≤k≤11	−14≤k≤14
	−18≤l≤15	−25≤l≤18	−21≤l≤22	−38≤l≤38	0≤l≤20
Reflections collected / unique	10757 / 7405	22446 / 4114	24851 / 8894	25960 / 4508	8089 / 4002
	[R(int) = 0.0162]	[R(int) = 0.0638]	[R(int) = 0.0264]	[R(int) = 0.0331]	[R(int) = 0.0411]
Completeness to θ Max.	96.1 %	99.3 %	99.5 %	99.8 %	100.0 %
Data / restraints / parameters	7405 / 0 / 406	4114 / 0 / 215	8894 / 0 / 424	4508 / 0 / 224	4002 / 0 / 231
Goodness-of-fit on F^2	1.027	1.097	1.069	1.100	1.013
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0330	R_1 = 0.0588	R_1 = 0.0431	R_1 = 0.0392	R_1 = 0.0422
	wR_2 = 0.0875	wR_2 = 0.1087	wR_2 = 0.0967	wR_2 = 0.1212	wR_2 = 0.1076
R indices (all data)	R_1 = 0.0425	R_1 = 0.1088	R_1 = 0.0661	R_1 = 0.0526	R_1 = 0.0914
	wR_2 = 0.0939	wR_2 = 0.1266	wR_2 = 0.1071	wR_2 = 0.1318	wR_2 = 0.1298
Largest diff. Peak and hole	0.406 and −0.480 e·A^{-3}	0.312 and −0.326 e·A^{-3}	0.303 and −0.284 e·Å^{-3}	1.008 and −0.347 e·A^{-3}	0.498 and −0.303 e·Å^{-3}

2 Results and Discussion

The analytical results show that the electrochemical procedure described (*vide infra*) is an effective method for the synthesis of zinc complexes with [(4-methylphenyl)sulfonyl]-1*H*-amido-2-phenyl-2-oxazoline ligands and represents a simple alternative to other standard chemical procedures. The compounds are of the general formula $[Zn(Ts\text{-}ROz)_2]$ where $Ts\text{-}ROz^-$ represents the anion of the corresponding ligand. The electrochemical efficiency value, E_f, defined as the amount of metal dissolved per Faraday of charge, was always close to 0.5 mol·F^{-1}. This fact, along with the evolution of hydrogen at the cathode, is consistent with the following reaction mechanism:

Cathode: 2 HTs-ROz + 2e$^-$ → 2 Ts-ROz$^-$ + H_2

Anode : Zn + 2 Ts-ROz$^-$ → $[Zn(Ts\text{-}ROz)_2]$ + 2e$^-$

2.1 X-ray Structural Studies

Table 1 lists crystal data, experimental details, refinement results and details of structure determination.

Description of the structure of [Zn(TsOz)$_2$] **(1)**

The molecular structure of compound 1 is shown in Fig. **1** together with the labelling scheme used. Selected bond lengths and angles, along with estimated deviations, are summarised in Table 2.

Table 2 Selected bond distances/Å and angles/° for $[Zn(TsOz)_2]$.

Zn-N(21)	1.9854(15)	Zn-N(22)	2.0001(15)
Zn-N(12)	2.0016(14)	Zn-N(11)	2.0263(16)
Zn-O(21)	2.6801(14)	S-O(11)	1.4419(15)
S-O(12)	1.4431(15)	S(1)-N(12)	1.6021(15)
S(1)-C(110)	1.7753(19)	N(11)-C(13)	1.281(2)
N(11)-C(11)	1.478(2)	N(12)-C(19)	1.408(2)
O(13)-C(13)	1.351(2)	O(13)-C(12)	1.458(3)
N(21)-Zn-N(22)	91.98(6)	N(21)-Zn-N(12)	123.28(6)
N(22)-Zn-N(12)	123.35(6)	N(21)-Zn-N(11)	106.50(6)
N(11)-Zn-N(22)	122.74(7)	N(12)-Zn-N(11)	90.63(6)
N(21)-Zn-O(21)	148.67(6)	N(22)-Zn-O(21)	59.85(5)
N(12)-Zn-O(21)	86.13(5)	N(11)-Zn-O(21)	81.30(6)
O(11)-S(1)-O(12)	116.44(10)	O(11)-S(1)-N(12)	105.68(8)

The compound consists of discrete molecules without significant interactions between one another. The zinc atom is coordinated to two monoanionic bidentate chelating ligands, which are bonded to the metal atom through their sulfonyl and oxazoline nitrogen atoms. Although electron density data does not normally provide sufficient evidence to decide if the coordination of the oxazoline ring is through the nitrogen or the oxygen atom, the fact that the C=N double bond is shorter than the C−O bond leads us to conclude that the metal is coordinated through the nitrogen atom of the oxazoline ring.

The coordination sphere around the zinc atom can be described as slightly distorted tetrahedral with a dihedral angle between chelate rings of 81.91(6)°, which is not far

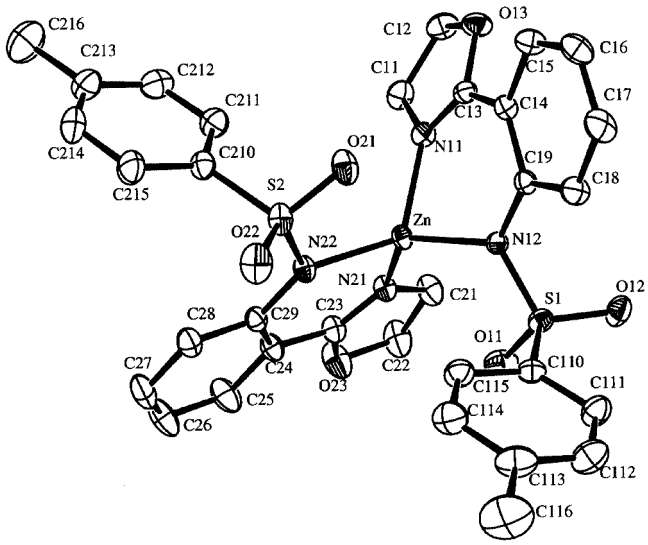


Fig. 1 The molecular structure of $[Zn(TsOz)_2]$.

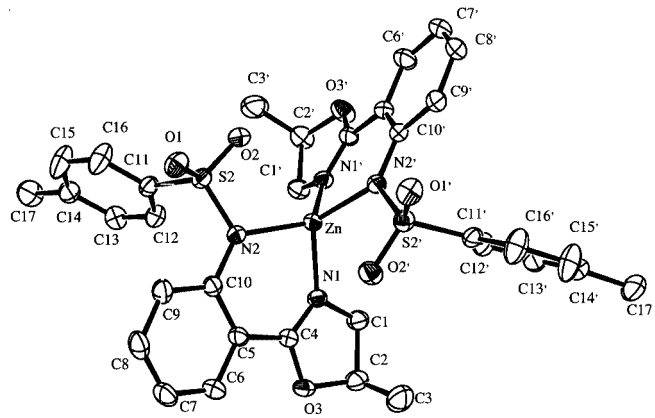


Fig. 2 The molecular structure of $[Zn(Ts\text{-}5MeOz)_2]$.

Table 3 Selected bond distances/Å and angles/° for $[Zn(Ts5\text{-}MeOz)_2]$.

Zn-N(1)	1.988(3)	Zn-N(1′)	1.988(3)
Zn-N(2)	2.011(2)	Zn-N(2′)	2.011(2)
Zn-O(2)	2.759(2)	Zn-O(2′)	2.759(2)
S(2)-O(1)	1.435(2)	S(2)-O(2)	1.453(3)
S(2)-N(29	1.608(3)	S(2)-C(11)	1.771(3)
N(1)-C(4)	1.279(4)	N(1)-C(1)	1.468(4)
N(2)-C(10)	1.402(4)	N(2)-S(2)	1.608(3)
O(3)-C(4)	1.343(4)	O(3)-C(2)	1.472(5)
N(1)-Zn-N(1′)	105.66(15)	N(1)-Zn-N(2)	91.12(10)
N(1′)-Zn-N(2)	121.47(10)	N(1)-Zn-N(2′)	121.47(10)
N(1′)-Zn-N(2′)	91.12(10)	N(2)-Zn-N(2′)	126.74(15)
N(1)-Zn-O(2)	142.21(9)	N(1′)-Zn-O(2)	76.88(9)
N(2)-Zn-O(2)	58.65(9)	N(2′)-Zn-O(2)	95.87(9)
N(1)-Zn-O(2′)	76.88(9)	N(1′)-Zn-O(2′)	142.21(9)
N(2)-Zn-O(2′)	95.87(9)	N(2′)-Zn-O(2′)	58.65(9)

Symmetry transformations used to generate equivalent atoms: (′)= x, .5−y, .5−z

from the theoretical value. The main source of the distortion is the small bite angle of these chelate rings, which is close to 90°. This situation makes the other angles around the metal larger than the theoretical value, with the biggest angle being 123.35(6)° for N(amide)−Zn−N(amide). A weak contact between the zinc atom and the O(21) atom of the sulfonyl group is also observed, with the bond distance Zn−O(21) being 2.6801(14) Å. This weak interaction makes the N(11)−Zn−N(22) bond angle, 122.74(7)°, slightly longer than one would expect for a regular tetrahedron. If this interaction is taken into account, the metal atom would be in a $[ZnN_4O]$ five-coordinate environment with a τ value [2] of 0.42 [$\tau = (\beta - \alpha)/60$, where β and α are the bond angles N(21)−Zn−O(21) and N(22)−Zn−N(12), respectively]. This situation suggests that the complex can be described as being 58 % along the distortion pathway between a trigonal bipyramid ($\tau = 1$) and a square pyramid ($\tau = 0$).

The two Zn−N(oxazoline) bond distances are slightly different from each other and have values of 1.9854(15) and 2.0263(16) Å. The difference is probably due to steric effects and, despite this fact, the values are very similar to those found in other zinc complexes with ligands containing oxazoline rings; for instance 2.031(4) Å in {dichloro-bis[5-(2-methylallyl)-2-phenyl-1,3-oxazole-N]}zinc(II) [3] or 2.066(3) Å in {dichloro-[2-(2′-(diphenylphosphino) phenyl)]-4,5-dihydro-4-phenyloxazole}zinc(II) [4]. The Zn−N(amide) bond distances, 2.0001(15) and 2.0016(14) Å (average 2.0008 Å), are longer than those found in other complexes containing an amide nitrogen and a zinc atom in a tetrahedral environment; for instance 1.942(8) Å in {[*N,N′*-bis(butanesulfonamide)-1,2-diaminocyclohexane]-(2,2′-bipyridyl)}zinc(II) [5], or 1.962(3) Å in bis{*N*-[(2-pyrrolyl)methylene]-*N′*-tosylbenzene-1,2-diaminato}zinc(II) [6]. This increase in the bond lengths could be a consequence of the increase in the coordination number due the presence of the oxygen atom in the coordination sphere of the metal.

Description of the structure of [Zn(Ts-5MeOz)$_2$] **(2)**

The molecular structure of compound **2** is shown in Fig. 2. Selected bond distances and angles are summarised in Table 3. The substitution of a methyl group for a β-hydrogen atom in the oxazoline ring causes only minor changes in the structure of the compound. This complex also exists as a monomer that does not experience significant contacts with neighbouring molecules. The coordination polyhedron around the metal is best described as a tetrahedron, with small chelate angles of 91.12(10)° and values of the N(amide)−Zn−N(amide) angle of 126.74(15)°.

However, the compound is now centrosymmetric and crystallizes in an orthorhombic space group. This is a consequence of a twist in one of the sulfonyl groups through the S−N bond. This twist has the effect of moving the oxygen atoms of the SO_2 away from one another, meaning that they are now related by symmetry. The zinc atom

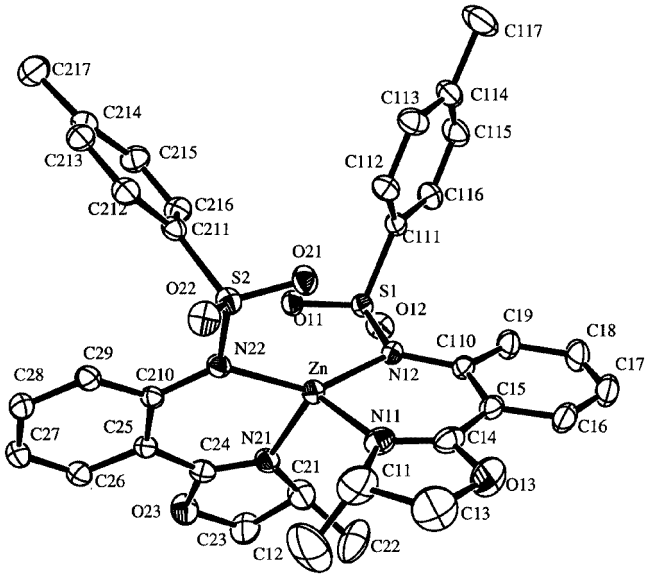


Fig. 3 The molecular structure of $[Zn(Ts\text{-}4MeOz)_2]$.

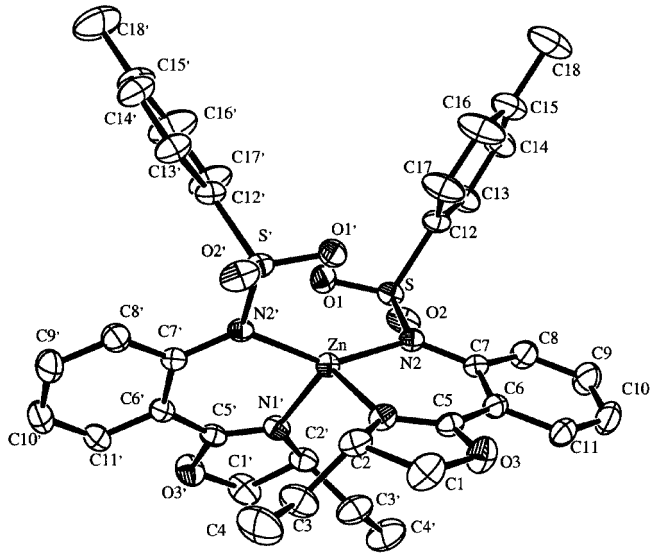


Fig. 4 The molecular structure of $[Zn(Ts\text{-}4EtOz)_2]$.

is coordinated by two amide nitrogens and two nitrogen atoms from two oxazoline rings. This gives a distorted tetrahedral environment, although once again a bonding interaction between O(2) and the zinc atom can be envisaged [Zn−O(2) = 2.759(2) Å]. If this interaction is taken into account, the coordination polyhedron around the metal can be described as a distorted trigonal prism. In this case, each triangular face of the prism would be formed by the N(oxazoline) and the N(amide) atoms, both of which belong to the same ligand, and one oxygen atom from the other ligand. The dihedral angle between these two triangular faces is 18.13(10)° with the zinc atom situated at a distance 1.2856(16) Å from each plane.

The crystals of this compound contain complexes [Zn(R)(R)] and [Zn(S)(S)]. Figure 2 shows the [Zn(S)(S)] form of the complex.

Description of the structures of [Zn(Ts-4MeOz)$_2$] **(3)**, *[Zn(Ts-4EtOz)$_2$]* **(4)** *and [Zn(Ts-4^{i}PrOz)$_2$]* **(5)**

The molecular structures of these complexes are shown in Figs. 3, 4 and 5, respectively. Selected bond distances and angles are given in Tables 4 to 6.

These compounds are monomeric and the ligands show a coordination behaviour similar to that described above, with a distorted tetrahedral environment around the metal atom. However, the replacement of an α-hydrogen atom by different R groups in the oxazoline ring causes some changes in the structures of the complexes. For example, the presence of these substituents causes steric restrictions in the complex that force the ligand to adopt configuration A (according to the *Fujisawa's* definition [7]). This configuration should be compared with configuration B, which is adopted by the free ligand [8]. As can be seen in Scheme 2, the main difference between the two configurations is the

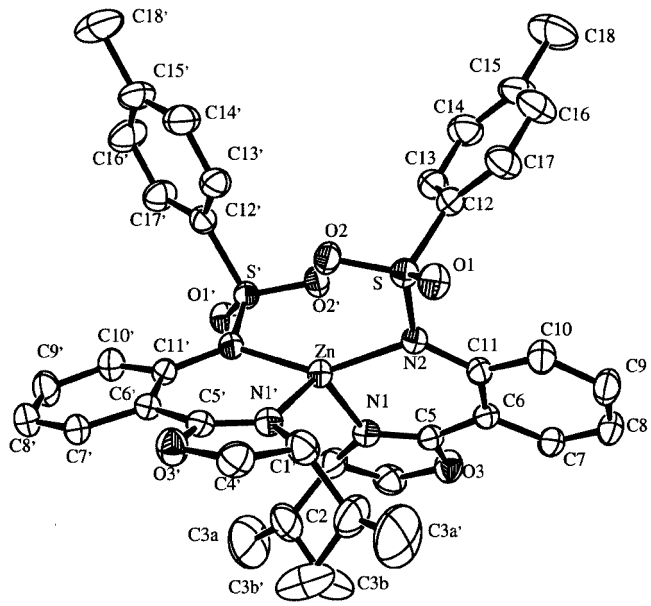


Fig. 5 The molecular structure of $[Zn(Ts\text{-}4^iPrOz)_2]$.

relative position of the groups directly attached to the sulfur atom in the sulfonamide group.

The influence of the nature of the substituent in the oxazoline ring is also reflected in the relative positions adopted by the *p*-toluene rings of the sulfonamide groups in the structures of the complexes containing substituents. For example, the angle formed by the carbon atoms bonded to the sulfur and the metal changes from 114.04° and 158.63° for **1** and **2** to 79.70°, 83.41°, 81.48° for compounds **3**, **4** and **5**, respectively. This increases the distance between the α-carbon of the oxazoline ring and the *p*-toluene ring carbon atom bonded to sulfur in the complexes containing a substituent (in the range 5.602−5.861 Å) in comparison to

Table 4 Selected bond distances/Å and angles/° for [Zn(Ts4-MeOz)$_2$].

Zn-N(11)	2.000(2)	Zn-N(12)	2.0019(18)
Zn-N(21)	2.0084(19)	Zn-N(22)	2.0109(18)
Zn-O(11)	2.6319(16)	Zn-O(21)	2.6768(17)
S(2)-O(22)	1.4415(17)	S(2)-O(21)	1.4416(17)
S(2)-N(22)	1.5999(18)	S(2)-C(211)	1.772(2)
S(1)-O(12)	1.4367(17)	S(1)-O(11)	1.4429(16)
S(1)-N(12)	1.6062(18)	S(1)-C(111)	1.772(2)
N(11)-Zn-N(12)	91.05(8)	N(11)-Zn-N(21)	111.68(9)
N(12)-Zn-N(21)	106.90(8)	N(11)-Zn-N(22)	112.38(8)
N(12)-Zn-N(22)	142.96(7)	N(21)-Zn-N(22)	91.13(7)
N(11)-Zn-O(11)	150.36(7)	N(12)-Zn-O(11)	60.39(6)
N(21)-Zn-O(11)	86.12(7)	N(22)-Zn-O(11)	89.81(6)
N(11)-Zn-O(21)	88.10(8)	N(12)-Zn-O(21)	94.93(6)
N(21)-Zn-O(21)	149.71(7)	N(22)-Zn-O(21)	59.43(6)
O(11)-Zn-O(21)	86.78(5)		

Table 5 Selected bond distances/Å and angles/° for [Zn(Ts4-EtOz)$_2$].

Zn-N(2′)	2.0069(17)	Zn-N(2)	2.0069(17)
Zn-N(1′)	2.0229(18)	Zn-N(1)	2.0229(18)
Zn-O(1′)	2.6291(16)	Zn-O(1)	2.6291(16)
S-O(2)	1.4338(18)	S-O(1)	1.4495(18)
S-N(2)	1.6100(16)	S-C(12)	1.775(2)
N(1)-C(5)	1.282(3)	N(1)-C(2)	1.483(3)
O(3)-C(5)	1.349(2)	O(3)-C(1)	1.439(4)
N(2)-C(7)	1.407(3)		
N(2′)-Zn-N(2)	145.81(10)	N(2′)-Zn-N(1′)	91.28(7)
N(2)-Zn-N(1′)	107.88(7)	N(2′)-Zn-N(1)	107.88(7)
N(2)-Zn-N(1)	91.28(7)	N(1′)-Zn-N(1)	111.87(11)
N(2′)-Zn-O(1′)	60.61(6)	N(2)-Zn-O(1′)	92.97(7)
N(1′)-Zn-O(1′)	150.02(6)	N(1)-Zn-O(1′)	88.30(7)
N(2′)-Zn-O(1)	92.97(7)	N(2)-Zn-O(1)	60.61(6)
N(1′)-Zn-O(1)	88.30(7)	N(1)-Zn-O(1)	150.02(6)
O(1′)-Zn-O(1)	83.39(9)		

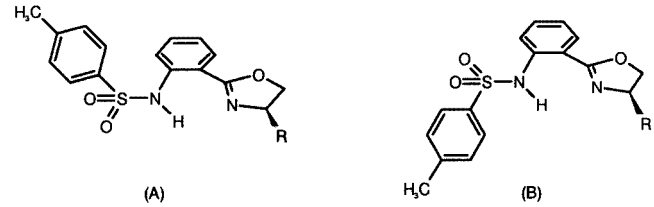
Symmetry transformations used to generate equivalent atoms: (′) x, 1.5−y, 1.5−z

Table 6 Selected bond distances/Å and angles/° for [Zn(Ts4-^{i}PrOz)$_2$].

Zn-N(2)	2.008(2)	Zn-N(2′)	2.008(2)
Zn-N(1)	2.015(3)	Zn-N(1′)	2.015(3)
Zn-O(2)	2.660(2)	Zn-O(2′)	2.660(2)
S-O(1)	1.443(2)	S-O(2)	1.449(2)
S-N(2)	1.597(3)	S-C(12)	1.765(3)
N(2)-Zn-N(2′)	145.96(15)	N(2)-Zn-N(1)	91.23(10)
N(2′)-Zn-N(1)	106.25(10)	N(2)-Zn-N(1′)	106.25(10)
N(2′)-Zn-N(1′)	91.23(10)	N(1)-Zn-N(1′)	118.05(16)
N(2)-Zn-O(2)	59.67(8)	N(2′)-Zn-O(2)	93.67(9)
N(1)-Zn-O(2)	147.58(9)	N(1′)-Zn-O(2)	86.06(9)
N(2)-Zn-O(2′)	93.67(9)	N(2′)-Zn-O(2′)	59.67(8)
N(1)-Zn-O(2′)	86.06(9)	N(1′)-Zn-O(2′)	147.58(9)

Symmetry transformations used to generate equivalent atoms: (′) −x, y, .5−z

the corresponding distances in the complexes without a substituent (in the range 4.563−5.151 Å). This fact surely reflects a tendency to reduce the interaction between the substituent on the oxazoline ring and the *p*-toluene ring. In this respect, the value of the N(amide)-Zn-N(amide) bond angle increases up to 150.36(7), 145.81(10) and 145.96(15) for complexes 3, 4 and 5, respectively, and, consequently, the extent of distortion of the geometry around the metal increases.



Scheme 2

In these compounds the distances between the zinc atom and one oxygen atom from the sulfonyl group are in the range 2.6291(16)−2.6768(17) Å. This fact can be interpreted in terms of a weak interaction between the two atoms, as discussed in the cases of compounds **1** and **2**.

The crystals of compounds **3** and **5** contain [Zn(R)(R)] and [Zn(S)(S)] forms and the solved were [Zn(S)(S)] and [Zn(R)(R)], respectively. Crystals of compound **4** contain only the [Zn(S)(S)] form.

2.2 Spectroscopic studies

The IR spectra of the complexes do not show a band due to ν(N−H), thus confirming that the hydrogen atom of the amide group is lost during the electrolysis. The IR spectra of the complexes exhibit a strong band in the 1625−1620 cm^{-1} range, attributed to ν(C=N), which is shifted to slightly lower frequency on going from the free ligand to the complex. Bands at 1130−1180 cm^{-1} and 1315−1320 cm^{-1} can be assigned to the symmetric and asymmetric ν(S=O) vibrations, respectively. The ^{1}H NMR spectra of the complexes show signals for all hydrogen atoms of the ligand with the exception of the NH proton. In the spectra of the free ligand this signal appears at about 12.5−13.1 ppm. This provides further evidence that the ligands are deprotonated in the complexes and coordinate in their anionic form. Aromatic resonances at 8.0−6.6 ppm, a singlet at 2.2 ppm for the $-CH_3$ protons of the *p*-toluensulfonic group, and a multiplet at 5.0−3.2 ppm for the hydrogen atoms of the oxazoline ring appear in the spectra of all compounds. These signals all appear at practically the same chemical shift as the corresponding signals in the free ligand. The complexes also exhibit signals at around of 0.8−1.5 ppm due to the substituent on the oxazoline ring groups.

The FAB mass spectra of all compounds show the molecular ion with appropriate isotope distributions. In many cases, ions formed by loss of one ligand from the initial complex are also observed, as well as a peak attributed to the free ligand.

All these data are in accordance with the structures described above for the complexes.

3 Experimental

Anthranilonitrile, *p*-toluenesulfonyl chloride and amino alcohols were all commercial products and were used as supplied. Acetonitrile, chlorobenzene, dichloromethane and other solvents were dried by standard methods [9]. Zinc (Aldrich) was used in plate form (*ca.* 2 × 2 cm).

Ligands were synthesised under argon using slight modifications of the standard literature procedure [10] (see Scheme 3). Details are given for a representative example.

*[(4-methylphenyl)sulfonyl]-1*H*-amido-(2-phenyl-2-oxazoline)] (HTs-Oz)*

2-(2-oxazoline)aniline was prepared by reaction of anthranilonitrile (3 g, 25 mmol) and 2-aminoethanol (5.0 mL, 82 mmol), in chlorobenzene (40 mL), using $ZnCl_2$ (0.5 g, 3.7 mmol) as a catalyst. The mixture was refluxed under argon during 36 h to give a red solution. The solvent was removed and the red crude product was dissolved in dichloromethane. The organic solution was washed with water, dried over anhydrous Na_2SO_4 and the solvent removed under vacuum. The resulting solid was purified by chromatography on silica gel using hexane/ethyl acetate (19:1) as eluent to obtain the pure amine (2.8 g, 68 %). A dichloromethane solution of this amine (1 g, 6.2 mmol) was treated with *p*-toluenesulfonyl chloride (1.6 g, 8.4 mmol) in aqueous KOH (0.5 g, 8.9 mmol) and the mixture was stirred for 24 h. The organic layer was separated, dried and concentrated to dryness to give a crude product, which was purified by chromatography on silica gel using hexane/ethyl acetate (4:1) as eluent. The ligand was obtained as a colourless solid (1.8 g, 92 %). Anal. Calcd. for $C_{16}H_{16}N_2O_3S$: C, 60.7; H, 5.1; N, 8.9; S, 10.1. Found: C, 60.4; H, 5.2; N, 9.0; S, 10.1 %.

IR (KBr, cm^{-1}): 2969 (m), 1625 (s), 1560 (s), 1313 (s), 1241 (m), 1132 (s). ^1H NMR (CDCl3): 13.1 ppm (s, 1H, NH), 8.6−7.6 ppm (m, 8H, phenyl), 5.2−4.8 ppm (m, 4H, $-CH_2$), 3.1 ppm (s, 3H, $-CH_3$). EI MS: (*m/z*): 316 (100 %, M^+); 161 (7 %, $M^+ - \{O_2S\text{-tolyl}\}$).

Analytical data for the other ligands

[(4-Methylphenyl)sulfonyl]-1H-imino-(2-phenyl-5-methyl-2-oxazoline), (HTs-5MeOz). Found: C, 62.1; H, 5.6; N, 8.5; S, 9.6. Calcd. for $C_{17}H_{18}N_2O_3S$: C, 61.8; H, 5.5; N, 8.5; S, 9.7 %.

IR (KBr, cm^{-1}): 2970(m), 1620(s), 1558(m), 1315(s), 1242(m), 1135(s). ^1H-NMR ($CDCl_3$): 12.4 ppm (s, 1H, NH), 7.9−6.9 ppm (m, 8H, phenyl), 4.4 ppm (m, H, −CH), 3.8 ppm (m, 2H, $-CH_2$), 2.3 ppm (s, 3H, $-CH_3$ tolyl), 1.3 ppm (s, 3H, $-CH_3$). EI MS: *m/z*: 330 (100 %, M^+); 175 (11 %, $M^+ - \{O_2S\text{-tolyl}\}$).

[(4-Methylphenyl)sulfonyl]-1H-imino-(2-phenyl-4-methyl-2-oxazoline), (HTs-4MeOz). Found: C, 61.7; H, 5.6; N, 8.5; S, 9.8. Calcd. for $C_{17}H_{18}N_2O_3S$: C, 61.8; H, 5.5; N, 8.5; S, 9.7 %.

IR (KBr, cm^{-1}): 2977(m), 1634(s), 1506(m), 1340(s), 1261(m), 1161(s). ^1H-NMR ($CDCl_3$): 12.2 ppm (s, 1H, NH), 7.6−6.9 ppm (m, 8H, phenyl), 4.4 ppm (m, 2H, $-CH_2$), 3.8 ppm (m, 1H, −CH), 2.3 ppm (s, 3H, $-CH_3$ tolyl), 1.3 ppm (s, 3H, $-CH_3$). EI MS: *m/z*: 330 (100 %, M^+); 175 (11 %, $M^+ - \{O_2S\text{-tolyl}\}$)

[(4-Methylphenyl)sulfonyl]-1H-imino-(2-phenyl-4-ethyl-2-oxazoline) (HTs-4EtOz). Found: C, 62.9; H, 5.2; N, 8.0; S, 10.1. Calcd. for $C_{18}H_{20}N_2O_3S$: C, 62.8; H, 5.9; N, 8.1; S, 9.3 %.

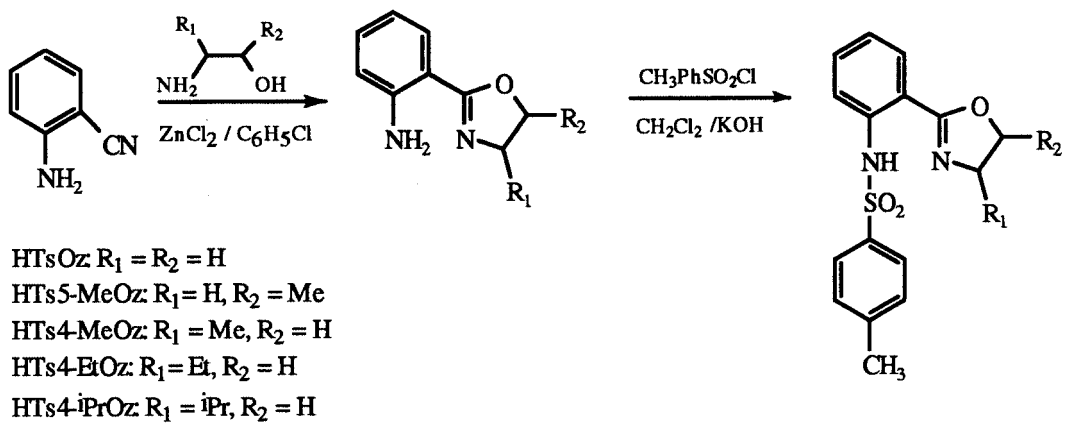
IR (KBr, cm^{-1}): 2970(m), 1634(s), 1506(s), 1339(s), 1268(m), 1154(s). ^1H-NMR ($CDCl_3$): 12.4 ppm (s, 1H, NH), 7.8−6.9 ppm (m, 8H, phenyl), 4.4 ppm (m, H, −CH), 3.8 ppm (m, 2H, $-CH_2$), 2.3 ppm (s, 3H, $-CH_3$ tolyl), 1.7 ppm (m, 2H, $-CH_2$(Et)), 1.1 ppm (m, 3H, $-CH_3$(Et). EI MS: *m/z*: 344 (100 %, M^+); 189 (6 %, $M^+ - \{O_2S\text{-tolyl}\}$).

[(4-Methylphenyl)sulfonyl]-1H-imino-(2-phenyl-4-isopropyl-2-oxazoline) (HTs-4^{i}PrOz.). Found: C, 63.5; H, 6.0; N, 7.9; S, 9.2, Calc. for $C_{19}H_{22}N_2O_3S$: C, 63.7; H, 6.2; N, 7.8; S, 8.9 %.

IR (KBr, cm^{-1}): 2964(m), 1625(s), 1559(m), 1318(s), 1241(m), 1173(s). ^1H NMR ($CDCl_3$): 12.4 ppm (s, 1H, NH), 7.8−6.7 ppm (m, 8H, phenyl), 4.3 ppm (m, 2H, $-CH_2$), 3.9 ppm (m, 1H, −CH), 2.3 ppm (s, 3H, $-CH_3$ tolyl), 1.5 ppm [s, 1H, −CH(isopropyl)], 1.0 ppm [d, 3H, $-CH_3$ (isopropyl)], 0.9 ppm [d, 3H, $-CH_3$ (isopropyl)]. EI MS: *m/z*: 358 (68 %, M^+); 203 (5 %, $M^+ - \{O_2S\text{-tolyl}\}$).

Electrochemical synthesis

The electrochemical method used in the synthesis of the complexes was similar to that described by *Tuck* [11]. The anode consisted of zinc foil suspended from a platinum wire and the cathode was a platinum wire. The ligand was dissolved in acetonitrile and a small



HTsOz: $R_1 = R_2 = H$
HTs5-MeOz: $R_1 = H$, $R_2 = Me$
HTs4-MeOz: $R_1 = Me$, $R_2 = H$
HTs4-EtOz: $R_1 = Et$, $R_2 = H$
HTs4-^{i}PrOz: $R_1 = {}^iPr$, $R_2 = H$

Scheme 3

amount of tetramethylammonium perchlorate was added to the solution as an electrolyte carrier. Applied voltages of 10−15 V allowed sufficient current flow for smooth dissolution of the metal. Nitrogen was bubbled through the solution during electrolysis to provide an inert atmosphere and also to stir the reaction mixture. Under these conditions the cell can be summarised as $Zn_{(+)}$/ CH_3CN + HTs−ROz/$Pt_{(-)}$.

***[Zn(TsOz)$_2$]* (1)**

Electrochemical oxidation of a zinc anode in a solution of [(4-methylphenyl)sulfonyl]-1*H*-amido-(2-phenyl-2-oxazoline) (0.236 g, 0.75 mmol) in acetonitrile (50 mL) at 6 V and 10 mA for 2 h, caused 24.4 mg of zinc to be dissolved, E_f = 0.50 mol·F^{-1}. During the electrolysis hydrogen was evolved at the cathode and at the end of the experiment a crystalline solid was observed at the bottom of the vessel. The solid was collected by filtration, washed with acetonitrile and diethyl ether and dried under vacuum. Anal. Calcd. for $C_{32}H_{30}ZnN_4O_6S_2$: C, 55.2; H, 4.3; N, 8.1; S, 9.2. Found: C, 55.0; H, 4.9; N, 8.3; S, 8.9 %.

IR (KBr, cm^{-1}): 2978 (m), 1631 (s), 1561 (m), 1320 (s), 1240 (m), 1137 (s). ^{1}H NMR ($CDCl_3$): 8.0−6.6 ppm (m, 16H), 5.0−3.2 ppm (m, 8H), 2.2 ppm (s, 6H). FAB (*m/z*): 696 $[Zn(TsOz)_2]^+$; 379 $[Zn(TsOz)]^+$; 316 $[TsOz]^+$. Crystals suitable for X-ray studies were obtained by crystallisation from chloroform.

***[Zn(Ts-5MeOz)$_2$]* (2)**

An experiment similar to that described above (7.5 V, 10 mA, 2 h) with the ligand (0.235 g, 0.71 mmol) in acetonitrile (50 mL) led to the dissolution of 23.3 mg of zinc, E_f = 0.48 mol·F^{-1}. The solid was filtered off, washed with cool acetonitrile, diethyl ether and dried under vacuum (0.27 g, 86 %). Anal. Calcd. for $C_{34}H_{34}ZnN_4O_6S_2$: C, 56.4; H, 4.7; N, 7.7; S, 8.9. Found: C, 55.9; H, 4.7; N, 7.8; S, 8.9 %.

IR (KBr, cm^{-1}): 2966 (m), 1618 (s), 1560 (m), 1316 (m), 1238 (m), 1140 (s). ^{1}H NMR ($CDCl_3$): 8.0−6.6 ppm (m, 16H), 5.0−3.3 ppm (m, 6H), 1.5 ppm (s, 6H), 2.2 ppm (s, 6H). FAB (*m/z*): 724 $[Zn(Ts\text{-}5MeOz)_2]^+$; 393 $[Zn(Ts\text{-}5MeOz)]^+$; 329 $[Ts\text{-}5MeOz]^+$. Crystals suitable for X-ray studies were obtained by crystallisation from chloroform.

***[Zn(Ts-4MeOz)$_2$]* (3)**

Electrolysis of a solution of the ligand (0.251 g, 0.76 mmol) in acetonitrile (50 mL) at 6.5 V and 10 mA for 2 h dissolved 25.1 mg of zinc, E_f = 0.51 mol·F^{-1}. At the end of the electrolysis colourless crystals were present in the cell and these were filtered off, washed with cool acetonitrile, diethyl ether and dried under vacuum. Crystallisation from chloroform gave crystals identified as [Zn(Ts-4MeOz)$_2$]. Anal. Calcd. for $C_{34}H_{34}ZnN_4O_6S_2$: C, 56.4; H, 4.7; N, 7.7; S, 8.9. Found: C, 55.8; H, 4.5; N, 7.5; S, 8.5 %.

IR (KBr, cm^{-1}): 2967 (m), 1620 (s), 1560 (s), 1313 (s), 1239 (m), 1135 (s). ^{1}H NMR ($CDCl_3$): 8.0−6.6 ppm (m, 16H), 5.0−3.6 ppm (m, 6H), 1.5 ppm (s, 6H), 2.2 ppm (s, 6H). FAB (*m/z*): 724 $[Zn(Ts\text{-}4MeOz)_2]^+$; 393 $[Zn(Ts\text{-}4MeOz)]^+$; 329 $[Ts\text{-}4MeOz]^+$.

***[Zn(Ts-4EtOz)$_2$]* (4)**

A solution of ligand (0.283 g, 0.79 mmol) in acetonitrile (50 mL) was electrolysed at 8 V and 10 mA during 2 h; 25.9 mg of zinc was dissolved from the anode, E_f = 0.53 mol·F^{-1}. Colourless crystals, suitable for X-ray studies, were obtained directly from the cell. The solid was collected, washed with cool acetonitrile, diethyl ether and dried under vacuum. Anal. Calcd. for $C_{36}H_{38}ZnN_4O_6S_2$: C, 57.5; H, 5.1; N, 7.4; S, 8.5. Found: C, 57.3; H, 4.7; N, 7.5; S, 8.3 %.

IR (KBr, cm^{-1}): 2964 (m), 1615 (s), 1559 (m), 1318 (s), 1241 (m), 1135 (s). ^{1}H NMR ($CDCl_3$): 8.0−6.6 ppm (m, 16H), 5.0−3.3 ppm (m, 6H), 2.2 ppm (s, 6H), 1.5 ppm (m, 4H), 0.9 ppm (m, 6H). FAB (*m/z*): 751 $[Zn(Ts\text{-}4EtOz)_2]^+$; 408 $[Zn(Ts\text{-}4EtOz)]^+$; 343 $[Ts\text{-}4EtOz]^+$.

***[Zn(Ts-4^{i}PrOz)$_2$]* (5)**

A solution of {[(4-methylphenyl)sulfonyl]-1*H*-amido-(2-phenyl-4-isopropyl-2-oxazoline)} (0.159 g, 0.44 mmol) in acetonitrile (50 mL) was electrolysed at 10 mA during 1 h; 12.5 mg of zinc metal was dissolved from the anode, E_f = 0.51 mol·F^{-1}. Colourless crystals, suitable for X-ray studies, were obtained in the cell. The crystals were recovered by filtration, washed with acetonitrile, dried and characterised by elemental analysis. Anal. Calcd. for $C_{38}H_{40}ZnN_4O_6S_2$: C, 58.6; H, 5.2; N, 7.2; S, 8.2. Found: C, 58.1; H, 5.6; N, 7.2; S, 8.3 %.

IR (KBr, cm^{-1}): 2959 (m), 1621 (s), 1560 (m), 1304 (s), 1241 (m), 1139 (s). ^{1}H NMR ($CDCl_3$): 8.0−6.6 ppm (m, 16H), 5.0−3.6 ppm (m, 6H), 2.2 ppm (s, 6H), 1.5 ppm (m, 2H), 0.7 ppm (m, 12H). FAB (*m/z*): 779 $[Zn(Ts\text{-}4^iPrOz)_2]^+$; 422 $[Zn(Ts\text{-}4^iPrOz)]^+$; 357 $[Ts\text{-}4^iPrOz]^+$.

Physical measurement

Elemental analyses were obtained using a Carlo-Erba EA 1108 microanalyser. IR spectra were recorded on KBr mulls using a Bruker Vector-22 spectrophotometer. Mass spectra were recorded on a Kratos-MS-50T spectrophotometer connected to a DS90 data system. FAB Mass spectra were measured using 3-nitrobenzyl alcohol (3-NBA) as a matrix material. The ^{1}H NMR spectra were recorded on a Bruker ARX-400 MHz spectrometer using $CDCl_3$ as solvent.

Crystal structure determination

The data collection was carried out on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Cu-K_α radiation (λ = 1.54184 Å) for [Zn(Ts-4^{i}PrOz)$_2$], and on a Siemens Smart CCD area-detector diffractometer using graphite monocromated Mo-K_α radiation (λ = 0.71073 Å) in all other cases. All the structures were resolved by direct methods and refined by a full-matrix least-squares based on F^2 [12]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from the International Tables for X-ray Crystallography [13]. For the compound [Zn(Ts-4MeOz)$_2$] (**3**) the Squeeze program [14] was used to correct the reflection data for the diffuse scattering due to disorder of the solvent. The crystal parameters and other experimental details regarding data collection and refinement are summarised in Table 1.

Crystallographic data for the structures have been deposited with Cambridge Crystallographic Data Centre, CCDC, numbers 170824 to 170828 respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

Acknowledgements. We thank the Xunta de Galicia (PGIDT00PXI20305PR) and (PGIDT99PXI20306B) for financial support.

All the crystallographic calculations were performed on the *fergus.uvigo.es* system *(http://angus.uvigo.es/)*.

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