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The synthesis of zinc(II) complexes of 2-(2-mercaptophenyl)-iminophenol by electrochemical cleavage of a disulfide bond; the crystal structure of {(2,2′-bipyridine)[2-(2-mercaptophenyl)iminophenoxy]}zinc(II)

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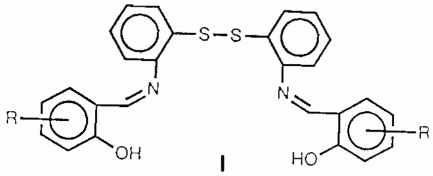
Abstract

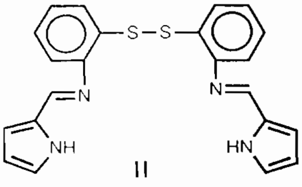
The electrochemical oxidation of anodic zinc in an acetonitrile solution of the Schiff base derived from the required salicylaldehyde and bis-(2-aminophenyl)disulfide, L_2H_2, yields compounds having the formulation ZnL. When 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy) is added to the electrolytic phase [ZnLphen] or [ZnLbipy] are obtained. The crystal structure of {2,2′-bipyridine[2-(2-mercaptophenyl)]iminophenoxy}zinc(II) [ZnL^{1}bipy] has been determined. The compound crystallises in the triclinic space group $P1$(No. 1) with two molecules in the unit cell and cell constants $a = 6.526(2)$, $b = 11.686(3)$, $c = 13.346(4)$ Å; $\alpha = 107.72(2)$, $\beta = 92.08(2)$, $\gamma = 91.79(2)°$. The zinc atom has a distorted trigonal bipyramidal geometry. The IR and ^{1}H NMR spectra of complexes are discussed and related to the structure.

Introduction

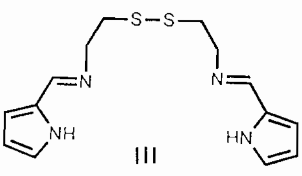
The synthesis of metal complexes of Schiff bases containing an anionic sulfur atom by electrochemical reductive cleavage of a disulfide bond has been the object of several studies. Starting from preformed Schiff bases such as I–III, nickel(II), copper(II), cadmium(II) and tin(IV) complexes have been synthesised [1–3]. In continuation of this work we have synthesised neutral complexes of zinc(II) derived from I. We report the crystal structure of {(2,2-bipyridine)[2-(2-mercaptophenyl)iminophenoxy]}zinc(II) [ZnL^{1}bipy].



I



II



III

Experimental

Acetonitrile, bis(2-aminophenyl)disulfide, 1,10-phenanthroline and 2,2′-bipyridine were all commercial products and were used without further purification. Zinc (Ega-Chemie) was used as plates (*c.* 2×2 cm).

Schiff base formation

The Schiff bases (I) were prepared by reaction of bis(2-aminophenyl)disulfide and the corresponding salicylaldehyde in a molar relation 1:2 in $CHCl_3$ as solvent in a Dean-Stark trap. After concentration, the oil obtained was stirred with hexane to give a cream solid. The purity of the Schiff bases was checked by IR and ^{1}H NMR spectroscopies prior to use in the electrochemical synthesis.

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Electrochemical synthesis

The electrochemical method used in synthesising the metal complexes is similar to that described by Tuck and co-workers [4]. The cell was a tall-form beaker (100 cm^3). The anode in foil form was suspended from a platinum wire and the cathode was a platinum wire. All experiments were carried out under an atmosphere of dry nitrogen which also served to agitate the mixture as it was gently bubbled through the solution. The ligand (*c.* 0.2–0.3 g) was dissolved in *c.* 50 cm^3 hot acetonitrile and tetramethylammonium perchlorate (*c.* 10 mg) was added as supporting electrolyte. For the synthesis of mixed complexes the corresponding ligand (1,10-phenanthroline or 2,2′-bipyridine) was added to the solution. Direct current was obtained from a purpose built d.c. power supply. The cells can be summarised as $Pt(-)/CH_3CN + L_2H_2/Zn(+)$ and $Pt(-)/CH_3CN + L_2H_2 + L'/Zn(+)$ (L′ = phen or bipy). As electrolysis proceeded hydrogen gas was evolved at the cathode, and after 2 h a small amount of insoluble solid, sometimes contaminated with metal from the anode was removed by filtration. We were not able to recover any characterisable product from these solids. The solution phase was concentrated by slow evaporation of the solvent and crystalline solids were deposited; in some cases with crystallisation acetonitrile. These solids were collected, washed with acetonitrile and diethyl ether and dried *in vacuo*. The crystals of ZnL^{1}bipy obtained were suitable for X-ray studies. Details of solution composition and electrochemical synthesis are given in Table 1.

Instrumentation

Microanalyses were determined using a Carlo-Erba EA1108 microanalyzer. The analytical data are given in Table 2. IR spectra were recorded as KBr discs in a Perkin-Elmer 180 spectrophotometer. ^{1}H NMR spectra were recorded in a Bruker WM 250 MHz spectrometer, using CDCl$_3$ as solvent for ZnLphen and ZnLbipy and in DMSO-d$_6$ in the case of ZnL for solubility reasons. Chemical shifts were determined against TMS as internal standard.

Crystal structure determination of ZnL^{1}bipy

A yellow crystal having approximate dimensions 0.05×0.1×0.3 mm was mounted on an Enraf Nonius CAD4 four-circle diffractometer. Cell constants were determined from setting angles for 25 reflections. Intensity data were collected at 273 K by the ω scan technique in the range $1 < \theta < 27°$. From 4466 reflections measured, 2637 unique reflections with $I > 1.5\sigma(I)$ were considered as observed and used for refinement. Data reduction included an empirical absorption correction (PSI scans, [5] maximum and minimum transmission factors 94.6 and 100%, respectively). Three standards reflections showed no significant variation of intensity over the course of data collection.

Space group symmetry required origin fixing in three dimensions. Therefore the origin was arbitrarily located in one zinc atom. Coordinates of the other zinc atom were obtained from the highest peak of a Patterson synthesis. The remaining non-hydrogen atoms were located in successive difference Fourier syntheses. In the final least-squares refinement Zn, S, O and N atoms were refined anisotropically. For the carbon atoms isotropic temperature factors were $R = 0.072$, $R_w = 0.059$ ($w = 1/\sigma^2(I)$). A final difference Fourier map showed a local maximum of 0.6 electrons/Å^3 close to C112. Scattering factors and corrections for anomalous dispersion were taken from the SDP program system [6]. Calculations were performed on a VAXstation 3100 computer with the SDP system and the program ORTEP [7]. The crystal data are summarised in Table 3, with

TABLE 1. Experimental conditions for the electrochemical syntheses

R	Compound	Amount of H_2L_2 (g[a])	Amount of L′	Initial voltage (V)[b]	Time (h)	Metal dissolved (mg)	E_f (mol F^{-1})
H	ZnL^1	0.30		20	3.5	78	0.47
H	ZnL^{1}bipy	0.30	0.20	13	3.5	78.6	0.46
H	ZnL^{1}phen	0.17	0.15	26	2	46.8	0.48
4,6-OCH$_3$	ZnL	0.21		11	2	47	0.48
4,6-OCH$_3$	ZnLbipy	0.21	0.12	20	2	45	0.46
4,6-OCH$_3$	ZnLphen	0.21	0.15	15	2	48	0.49
5-Br	ZnL	0.12		17	1.5	37.6	0.51
5-Br	ZnLbipy	0.15	0.12	20	2	47.8	0.48
5-Br	ZnLphen	0.15	0.15	18	2	48.8	0.50

[a] Plus [NMe$_4$]ClO$_4$ (*c.* 10 mg). [b] Voltage to produce a current of 20 mA.

TABLE 2. Analytical data for complexes (%)[a]

R	Compound	N (%)	C (%)	H (%)
H	ZnL^1	4.4(4.3)	48.3(47.5)	3.5(3.9)
H	ZnL^{1}bipy	9.2(9.4)	61.7(61.6)	4.0(3.8)
H	ZnL^{1}phen	8.9(8.9)	62.8(63.5)	3.8(4.1)
4,6-OCH_3	ZnL·2CH_3CN[b]	9.3(9.7)	52.4(52.5)	4.8(4.4)
4,6-OCH_3	ZnLbipy·CH_3CN[b]	8.4(8.0)	57.0(57.0)	4.7(4.4)
4,6-OCH_3	ZnLphen	7.9(7.9)	60.7(60.9)	5.0(4.9)
5-Br	ZnL	3.6(3.8)	42.3(42.0)	2.0(2.0)
5-Br	ZnLbipy	8.7(8.0)	52.2(52.4)	3.5(3.0)
5-Br	ZnLphen·CH_3CN[b]	10.1(9.5)	53.5(54.7)	3.3(3.2)

[a] Calculated values in parentheses. [b] IR show a band at 2190 cm^{-1} attributable to CH_3CN.

TABLE 3. Summary of crystal data for ZnL^{1}bipy

Formula	$C_{28}H_{17}N_3OSZn$
M	448.85
Crystal system	triclinic
Space group	$P1$ (No. 1)
a (Å)	6.526(2)
b (Å)	11.686(3)
c (Å)	13.346(4)
α (°)	107.72(2)
β (°)	92.08(2)
γ (°)	91.79(2)
U (Å^3)	968(1)
Z	2
D_c (g cm^{-3})	1.540
F(000)	460
Radiation, (Å)	Mo Kα, 0.7093
μ (cm^{-1})	14.21
R	0.072
R_w	0.059

TABLE 4. Positional parameters and their e.s.d.s for ZnL^{1}bipy

Atom	x	y	z	B_{iso} (Å)^2
Molecule 1				
Zn1	0.000	0.000	0.000	3.00(3)
S1	0.2176(5)	−0.1597(3)	−0.0481(3)	4.02(8)
O1	−0.093(1)	0.1373(7)	−0.0406(6)	4.1(2)
N10	−0.214(1)	−0.1166(8)	−0.1071(6)	2.6(2)
N12	0.205(1)	0.1161(8)	0.1203(7)	3.1(2)
N13	−0.139(1)	0.0111(7)	0.1443(7)	2.9(2)
C1	−0.353(2)	−0.078(1)	−0.1569(9)	3.4(2)
C101	0.023(2)	−0.270(1)	−0.1087(9)	3.3(2)
C102	−0.175(2)	−0.241(1)	−0.1297(8)	2.8(2)
C103	−0.328(2)	−0.330(1)	−0.1713(9)	3.6(3)
C104	−0.279(2)	−0.449(1)	−0.1946(9)	4.1(3)
C105	−0.87(2)	−0.479(1)	−0.176(1)	5.1(3)
C106	0.068(2)	−0.391(1)	−0.1325(9)	4.0(3)
C111	−0.266(2)	0.145(1)	−0.0923(8)	2.9(2)
C112	−0.400(2)	0.043(1)	−0.1445(8)	2.9(2)
C113	−0.585(2)	0.063(1)	−0.1923(9)	4.1(3)
C114	−0.642(2)	0.175(1)	0.186(1)	4.1(3)
C115	−0.513(2)	0.274(1)	−0.137(1)	4.6(3)
C116	−0.331(2)	0.257(1)	−0.0922(9)	4.2(3)
C121	0.156(2)	0.135(1)	0.2202(9)	3.1(2)
C122	0.287(2)	0.208(1)	0.305(1)	4.3(3)
C123	0.460(2)	0.254(1)	0.280(1)	4.2(3)
C124	0.514(2)	0.239(1)	0.1767(9)	3.6(3)
C125	0.374(2)	0.16(6)	0.0975(9)	2.9(2)
C131	−0.035(2)	0.075(1)	0.2343(9)	3.1(2)
C132	−0.105(2)	0.080(1)	0.333(1)	4.3(3)
C133	−0.287(2)	0.016(1)	0.336(1)	5.2(3)
C134	−0.400(2)	−0.049(1)	0.248(1)	5.2(3)
C135	−0.316(2)	−0.048(1)	0.1500(9)	3.8(3)
Molecule 2				
Zn2	−0.4560(2)	−0.3499(1)	0.4280(1)	3.05(3)
S2	−0.2253(5)	−0.4769(3)	0.4742(3)	4.16(8)
O2	−0.545(1)	−0.1860(7)	0.4664(6)	4.3(2)
N20	−0.643(1)	−0.3924(8)	0.5376(7)	2.9(2)
N22	−0.275(1)	−0.3155(7)	0.3082(7)	2.8(2)
N23	−0.626(1)	−0.4410(8)	0.2847(7)	3.1(2)
C2	−0.767(2)	−0.320(1)	0.5914(9)	3.8(3)
C201	−0.406(2)	−0.549(1)	0.5314(9)	3.4(2)
C202	−0.598(2)	−0.502(1)	0.5574(8)	2.9(2)
C203	−0.744(2)	−0.563(1)	0.5980(8)	3.4(2)
C204	−0.694(2)	−0.671(1)	0.614(1)	5.1(3)
C205	−0.504(2)	−0.716(1)	0.591(1)	4.7(3)
C206	−0.359(2)	−0.657(1)	0.5509(9)	3.8(3)
C211	−0.822(2)	−0.207(1)	0.5802(8)	2.8(2)
C212	−0.707(2)	−0.142(1)	0.5228(8)	3.0(2)
C213	−0.777(2)	−0.031(1)	0.5239(9)	3.7(3)
C214	−0.948(2)	0.018(1)	0.5731(9)	4.0(3)
C215	−1.058(2)	−0.046(1)	0.627(1)	4.2(3)
C216	−0.991(2)	−0.151(1)	0.6324(9)	3.9(3)
C221	−0.344(2)	−0.369(1)	0.2095(9)	3.1(2)
C222	−0.234(2)	−0.354(1)	0.1248(9)	4.0(3)
C223	−0.055(2)	−0.290(1)	0.147(1)	4.3(3)
C224	0.024(2)	−0.238(1)	0.2493(9)	3.7(3)
C225	−0.098(2)	−0.2517(9)	0.3299(8)	2.9(2)
C231	−0.540(2)	−0.437(1)	0.1958(8)	2.8(2)
C232	−0.628(2)	−0.499(1)	0.098(1)	5.0(3)
C233	−0.813(2)	−0.567(1)	0.093(1)	5.8(4)
C234	−0.903(2)	−0.568(1)	0.182(1)	5.6(3)
C235	−0.804(2)	−0.503(1)	0.276(1)	3.9(3)

final atomic coordinates listed in Table 4. See also 'Supplementary material'.

Results and discussion

The studies reported above show that an electrochemical reductive cleavage of the disulfide bond present in the preformed Schiff base H_2L_2 accompanied by deprotonation of the phenol group, can be used to obtain compounds of general formula [ZnL] which are otherwise difficult to prepare by conventional synthetic routes. The presence of aditional ligand L′ (phenanthroline or bipyridine) led to formation of mixed complexes ZnLL′.

The electrochemical efficiency, defined as the amount of metal dissolved per Faraday of charge, E_f, was close to 0.5 mol F^{-1}. This fact and the formation of H_2 at the cathode is compatible with the following reaction mechanism:

cathode: $\frac{1}{2}\,H_2L_2 + 2e^- \longrightarrow \frac{1}{2}\,H_2(g) + L^{2-}$

anode: $Zn + L^{2-} \longrightarrow ZnL + 2e^-$

$Zn + L^{2-} + L' \longrightarrow ZnLL' + 2e^-$

$L' =$ phen or bipy

Structure of ZnL¹bipy

In the cell there are two independent molecules of the complex. The structure of one of these molecules is shown in Fig. 1. Selected bond distances and angles, together with their associated estimated standard deviations, are given in Tables 5 and 6. The zinc atom is coordinated to one terdentate Schiff base molecule and one bidentate bipyridine ligand. The environment around the metallic atom may be described as a very distorted trigonal bipyramidal geometry. The oxygen and the sulfur atom of the Schiff base and one of the nitrogen atoms of the bipyridine molecule lie in the equatorial plane of the molecule. The zinc atom is coplanar with them, being deviated by 0.034 Å out of the best least-squares plane. Thus the angles between the nitrogen apical atoms and the zinc atom are very close to the required 180°; 175.1(3)° for one molecule and 176.3(3)° for the other. The equatorial angles are quite different from 120°, having average values of 105.4(4), 111.3(3) and 143.0(3)°, and serving as the principal source of distortion. However the sum of these angles is 359.8°, very close to 360°.

TABLE 5. Bond distances (Å) for ZnL¹bipy

Molecule 1		Molecule 2	
Zn1–S1	2.327(4)	Zn2–S2	2.340(4)
Zn1–O1	1.950(8)	Zn2–O2	1.939(8)
Zn1–N10	2.097(8)	Zn2–N20	2.100(9)
Zn1–N12	2.15(1)	Zn2–N22	2.150(9)
Zn1–N13	2.13(1)	Zn2–N23	2.13(1)
S1–C101	1.77(1)	S2–C201	1.75(1)
O1–C111	1.32(1)	O2–C212	1.34(1)
N10–C1	1.28(1)	N20–C2	1.26(1)
N10–C102	1.42(1)	N20–C202	1.42(1)
N12–C121	1.34(1)	N22–C221	1.33(1)
N12–C125	1.32(1)	N22–C225	1.33(1)
N13–C131	1.35(1)	N23–C231	1.34(1)
N13–C135	1.35(1)	N23–C235	1.34(1)
C1–C112	1.41(2)	C2–C211	1.42(2)
C101–C102	1.39(1)	C201–C202	1.40(1)
C101–C106	1.40(2)	C201–C206	1.40(2)
C102–C103	1.39(1)	C202–C203	1.40(1)
C103–C104	1.38(2)	C203–C204	1.39(2)
C104–C105	1.35(2)	C204–C205	1.37(2)
C105–C106	1.39(2)	C205–C206	1.37(2)
C111–C112	1.43(1)	C211–C212	1.45(1)
C111–C116	1.39(2)	C211–C216	1.40(2)
C112–C113	1.41(1)	C212–C213	1.39(2)
C113–C114	1.35(2)	C213–C214	1.37(2)
C114–C115	1.39(2)	C214–C215	1.38(2)
C115–C116	1.36(2)	C215–C216	1.34(2)
C121–C122	1.43(2)	C221–C222	1.41(2)
C121–C131	1.45(2)	C221–C231	1.46(2)
C122–C123	1.33(2)	C222–C223	1.34(2)
C123–C124	1.40(2)	C223–C224	1.39(2)
C124–C125	1.42(2)	C224–C225	1.41(1)
C131–C132	1.39(2)	C231–C232	1.38(2)
C132–C133	1.39(2)	C232–C233	1.41(2)
C133–C134	1.36(2)	C233–C234	1.35(2)
C134–C135	1.44(2)	C234–C235	1.38(2)

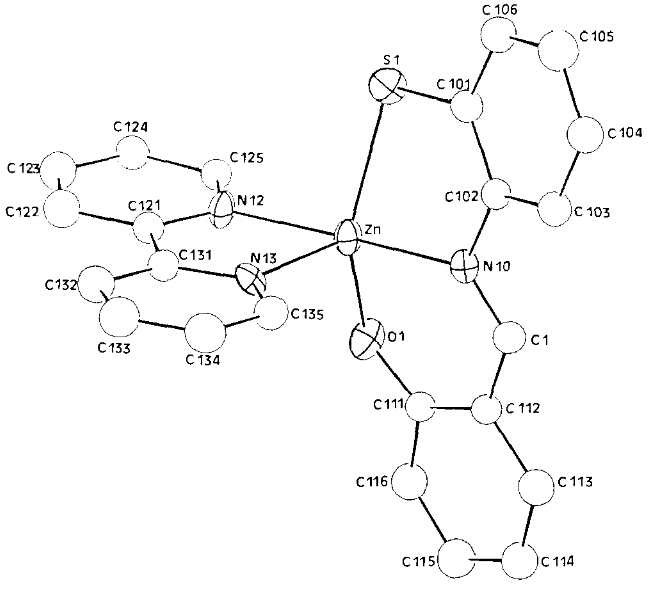

Fig. 1. The crystal structure of ZnL¹bipy.

In the dianionic Schiff base each of the phenyl rings is planar as are the four-atom C–C–N–C planes across the imine double bonds. However the two phenyl rings are twisted from the imine four-atom plane with dihedral angles between planes of 13.78° for the thiophenolate ring and 16.66° for the phenolate ring. In addition the donor sulfur and oxygen atoms are both out of the phenyl ring (0.091 Å in both cases). This ensures that the angles subtended at the zinc in both sulfur-containing five-numbered and oxygen-containing six-numbered chelate rings are close to 90°, average value of 84.8 and 91.8°, respectively. The angle including the nitrogen donor atom of the bipyridine and the metal atom (average value 75.5°) is similar to those found in other bipyridine complexes [8–10].

The bond distances around the zinc atom are similar to those reported for other pentacoordinated zinc complexes containing the same donor atoms. Thus, the average value of 2.334(4) Å for the Zn–S bond distance is practically equal to the value of 2.335(2) Å found in the pentacoordinated complex of zinc with the Schiff base derivative of 2,6-diacetylpyridine and 2-aminobenzenethiol [11]. The bond distance Zn–N(imine),

TABLE 6. Bond angles (°) for ZnL^{1}bipy

Molecule 1		Molecule 2	
S1–Zn1–O1	142.4(3)	S2–Zn2–O2	143.7(3)
S1–Zn1–N10	85.0(3)	S2–Zn2–N20	84.6(2)
S1–Zn1–N12	96.0(4)	S2–Zn2–N22	95.7(2)
S1–Zn1–N13	111.6(3)	S2–Zn2–N23	111.1(3)
O1–Zn1–N10	91.5(4)	O2–Zn2–N20	92.1(4)
O1–Zn1–N12	90.6(4)	O2–Zn2–N22	89.8(4)
O1–Zn1–N13	105.8(4)	O2–Zn2–N23	105.0(4)
N10–Zn1–N12	175.1(3)	N20–Zn2–N22	176.3(3)
N10–Zn1–N13	100.3(4)	N20–Zn2–N23	100.5(3)
N12–Zn1–N13	74.9(4)	N22–Zn2–N23	76.0(4)
C1–N10–C102	122.9(9)	C2–N20–C202	122(1)
C121–N12–C125	121(1)	C221–N22–C225	122(1)
C131–N13–C135	119(1)	C231–N23–C235	118(1)
N10–C1–C112	128(1)	N20–C2–C211	127(1)
S1–C101–C102	122.0(9)	S2–C201–C202	121.3(8)
S1–C101–C106	119.0(9)	S2–C201–C206	120.0(9)
C102–C101–C106	119(1)	C202–C201–C206	119(1)
N10–C102–C101	118(1)	N20–C202–C201	118(1)
N10–C102–C103	122(1)	N20–C202–C203	121(1)
C101–C102–C103	121(1)	C201–C202–C203	121(1)
C102–C103–C104	119(1)	C202–C203–C204	119(1)
C103–C104–C105	121(1)	C203–C204–C205	121(1)
C104–C105–C106	121(1)	C204–C205–C206	121(1)
C101–C106–C105	119(1)	C201–C206–C205	120(1)
O1–C111–C112	123(1)	O2–C212–C211	123(1)
O1–C111–C116	119(1)	O2–C212–C213	120(1)
C112–C111–C116	117(1)	C212–C211–C216	117(1)
C1–C112–C111	125(1)	C2–C211–C212	124(1)
C1–C112–C113	117(1)	C2–C211–C216	119(1)
C111–C112–C113	118(1)	C211–C212–C213	117(1)
C112–C113–C114	122(1)	C212–C213–C214	124(1)
C113–C114–C115	121(1)	C213–C214–C215	119(1)
C114–C115–C116	119(1)	C214–C215–C216	119(1)
C111–C116–C115	124(1)	C211–C216–C215	124(1)
N12–C121–C122	120(1)	N22–C221–C222	120(1)
N12–C121–C131	115(1)	N22–C221–C231	116(1)
C122–C121–C131	124(1)	C222–C221–C231	123(1)
C121–C122–C123	117(1)	C221–C222–C223	118(1)
C122–C123–C124	124(1)	C222–C223–C224	122(1)
C123–C124–C125	115(1)	C223–C224–C225	116(1)
N12–C125–C124	122(1)	N22–C225–C224	121(1)
N13–C131–C121	115(1)	N23–C231–C221	116(1)
N13–C131–C132	122(1)	N23–C231–C232	122(1)
C121–C131–C132	123(1)	C221–C231–C232	122(1)
C131–C132–C133	118(1)	C231–C232–C233	118(1)
C132–C133–C134	124(1)	C232–C233–C234	121(2)
C133–C134–C135	115(1)	C233–C234–C235	117(2)
N13–C135–C134	123(1)	N23–C235–C234	124(1)

average value 2.098(8) Å, is also similar to that found in *N,N'*-disalicylideneethylenediaminato Zn(II) monohydrate, 2.08 Å, [12] and in the dimeric bis(*N*-methylsalicylaldiminato)Zn(II), 2.06 Å [13]. In addition, the bond distance Zn–O, mean 1.944(8), is also similar to these found in the above-mentioned pentacoordinated zinc complexes.

IR spectra

The IR spectra of the complexes are consistent with the structural data presented above. The ν(O–H) band of the free ligand is absent from the spectra of the complexes, confirming that it is the deprotonated ligand that is present in the latter. The band attributable to the azomethine ν(C=N) is shifted to lower frequencies in the complexes indicating that the azomethine nitrogen is coordinated to zinc. These results show that the ligand behaves in a terdentate manner binding to the zinc through the phenolic oxygen, the sulfur and azomethine nitrogen. For this reason it is not unreasonable to propose that the ZnL complexes are at least dimeric and possibly polymeric in the solid state as a consequence of the metal atom in the monomer unit being coordinatively unsaturated in the three coordinate environment provided by the terdentate ligand. In addition, bands at *c.* 1500, 800 and 730 cm^{-1} in the phenanthroline compounds and 760, 740 cm^{-1} in the bipyridine compounds confirm the coordination of these ligands in the mixed complexes and hence that the zinc is pentacoordinated in these complexes.

NMR studies

The spectra of the complexes (Table 7), show that the peak about 12.9 ppm assignable to the phenolic proton is absent confirming the deprotonation of the ligand in the electrochemical procedure. The signals of HC=N between 8.6–9.0 ppm are shifted as compared with the free ligand. The spectra also show, in the mixed complexes, the signal of the hydrogen of the coligands bipy and phen. In the phenanthroline complexes the signals of the hydrogens undergoe small shifts with respect to the free ligands and this can be taken as proof of coordination of the phenanthroline to the metal [14, 15]. In the bipyridine complexes the coordination of this ligand is inferred by the downfield shift of the 3–3′ protons and the upfield shift of the signal of the 6–6′ hydrogen in accordance with the work of Castellano *et al.* [16]. This confirms that the coordination number of the zinc in all mixed complexes is five.

Supplementary material

Crystallographic data have been deposited as Supplementary Publication No. CSD 56325. Copies can be obtained through the Fachinformationszentrum Energie, Physik, Mathematik D-7514 Eggenstein-Leopoldshafen.

TABLE 7. Chemical shift data for complexes in $CDCl_3$

R	Compound	$-OH$	$-N{=}CH$	L′(phen or bipy)			
$-H$	$H_2L^1{}_2$	12.8	8.6				
$-H$	$H_2L^1{}_2{}^a$	12.6	9.0				
$-H$	ZnL^{1a}		8.7				
$-H$	ZnL^1bipy		8.7	8.6(3,3′)	8.2(4,4′)	8.0(5,5′)	7.6(6,6′)
$-H$	ZnL^1phen		8.7	8.9(2,9)	8.4(4,7)	7.9(5,6)	7.8(3,8)
4,6-OCH_3	H_2L_2	12.9	9.0				
4,6-OCH_3	ZnLbipy		9.2	8.6(3,3′)	8.2(4,4′)	8.0(5,5′)	7.6(6,6′)
4,6-OCH_3	ZnLphen		9.2	8.9(2,9)	8.4(4,7)	7.9(5,6)	7.8(3,8)
5-Br	H_2L_2	12.8	8.5				
5-Br	$H_2L_2{}^a$	12.5	9.0				
5-Br	ZnL^a		8.6				
5-Br	ZnLbipy		8.7	8.6(3,3′)	8.2(4,4′)	8.0(5,5′)	7.6(6,6′)
5-Br	ZnLphen		8.7	8.9(2,9)	8.4(4,7)	7.9(5,6)	7.8(3,8)

[a] In DMSO-d_6 as solvent.

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