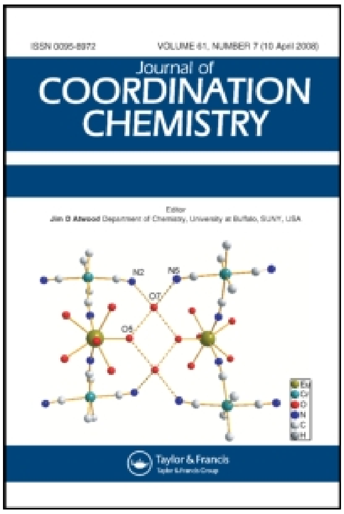

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SYNTHESIS AND STRUCTURE OF BIPYRIDINEBIS {2-[(2-PYRROLE)METHYLIMINO] -5-METHYLPHENOLATO} ZINC(II)

Jesús A. Castro[a]; Jaime Romero[a]; José A. Garcia-Vazquez[a]; Antonio Sousa[a]; Eduardo E. Castellano[b]; Julio Zukerman-Schpector[b]
[a] Departamento de Química Inorgánica, Universidad de Santiago de Compostela, Galicia, Spain [b] Universidad de Sao Paulo, Instituto de Física e Química, Sao Carlos, Brazil

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SYNTHESIS AND STRUCTURE OF BIPYRIDINEBIS {2-[(2-PYRROLE)METHYLIMINO] -5-METHYLPHENOLATO} ZINC(II)

JESUS A. CASTRO, JAIME ROMERO, JOSÉ A. GARCIA-VAZQUEZ, ANTONIO SOUSA,* EDUARDO E. CASTELLANO[a] and JULIO ZUKERMAN-SCHPECTOR[a]

Departamento de Química Inorgánica, Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Galicia, Spain [a]*Universidad de Sao Paulo, Instituto de Física e Química, Sao Carlos, Brazil*

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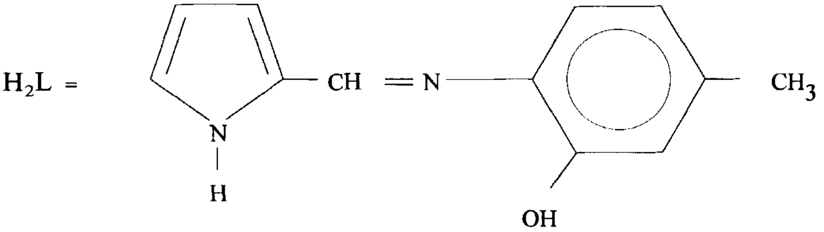
Electrochemical oxidation of zinc in acetonitrile containing 2, 2'-bipyridine and the Schiff base H_2L derived from H-pyrrole-2-carbaldehyde and 5-methyl-2-aminophenol gave a solution from which a crystalline product with the formula $Zn(HL)_2$.bipy was isolated. Its crystal structure was determined by X-ray diffraction methods. It crystallized in the monoclinic space group $P2_1/c$ (No. 14) with a = 10.111(1), b = 16.029(2), c = 20.293(3)Å and β = 97.71(1)°. The Zn environment is a distorted octahedron, with the metal coordinated to two bipyridine nitrogen atoms (2.195(6) and 2.178(5)Å from the metal atom), two phenolate oxygens (1.955(5) and 1.978(4)Å) and two imino nitrogen atoms (2.318(5) and 2.515(6) Å). The pyrrole nitrogens are not coordinated. There is a hydrogen bond between the N-H of the pyrrole group of each Schiff base and the phenolic oxygen of the other.

KEYWORDS: Zinc, Schiff base, H-pyrrole-2-carbaldehyde, 2,2'-bipyridine, electrochemical synthesis, X-ray structure

INTRODUCTION

Metal complexes with Schiff bases containing weakly acid groups can easily be synthesized electrochemically.[1–3] This procedure has been used to prepare metal complexes with pyrrolaldimines.[4–7] We report here the synthesis and crystal structure of a complex of Zn(II) with a ligand, H_2L, with two acids deprotonable groups.



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* Author for correspondence.

EXPERIMENTAL

Materials and methods

Acetonitrile, H-pyrrole-2-aldehyde, 5-methyl-2-aminophenol, 2,2'-bipyridine (bipy) and all other reagents were commercial products and were used as supplied. Zinc (Ega Chemie) was used as ca 2 × 2 cm plates.

The ligand H_2L was prepared by direct reaction of equimolecular amounts of the aldehyde and the amine in chloroform, using a Dean-Stark trap. After removal of the water produced in the reaction, the solution was concentrated and the isolated solid washed with diethyl ether and dried *in vacuo*. Its purity was checked by IR and ^{1}H NMR spectra.

Preparation of the complex

The complex was obtained by an electrochemical method similar to that described by Tuck.[8] The electrochemical oxidation of a zinc anode in acetonitrile (50 cm^3) containing 2,2'-bipyridine (0.15 g), the Schiff base 2-(2-pyrrole)methylimino-5-methylphenol (H_2L, 0.3 g) and a small amount of tetramethylammonium perchlorate (ca 10 mg) produced a yellow solution from which, by slow evaporation of the solvent at room temperature, yellow crystals suitable for X-ray studies were obtained and identified by elemental analysis as $Zn(HL)_2 \cdot CH_3CN$. Found: C, 65.0; H, 5.1, N, 14.5%. Calc. for $\{[Zn(C_{12}H_{11}\ N_2O)_2\ (C_{10}N_2H_8)]CH_3CN\}$: C, 65.4; H, 4.9; N, 14.8 %.

Crystal Data

$C_{36}H_{33}N_7O_2Zn$; M = 661.08, monoclinic, a = 10.111(1), b = 16.029 (2), c = 20.293(3)Å, β = 97.71(1)°, V = 3259(1)Å^3 (by least-squares refinement of diffractometer angles for 24 automatically centred reflections, $8 < \theta < 21°$, λ = 0.71073 Å), space group $P2_1/c$ (No.14), Z = 4, Dx = 1.347 g cm^{-3}, μ (MoKα) = 8.12 mm^{-1}. Irregular crystal of maximum and minimum dimensions 0.40 and 0.01 mm.

Data collection and processing

CAD4 diffractometer, graphite monochromated Mokα radiation, (λ = 0.71073 Å), $\omega/2\theta$ mode with ω scan width $(0.65 + 0.35 \tan\theta)°$, 4750 reflections measured ($0 < \theta < 25°$, $-1 \leq h \leq 11$, $0 \leq k \leq 24$, $0 \leq l \leq 24$), 4623 unique (merging R = 0.030), 2452 with $I > 3\sigma(I)$; Lorentz and polarization corrections. Absorption corrections were applied at a later stage in the refinement[9] (max., min. transmission factors 1.29, 0.81). The intensities of two standard reflections were essentially constant throughout the experiment.

Structure analysis and refinement

The structure was solved by standard direct methods followed by normal difference Fourier techniques. Blocked matrix least — squares refinement was used with non-H atoms anisotropic except those of the acetonitrile solvent molecule; hydrogens found in difference syntheses (slightly modified on stereochemical grounds when possible) were included as fixed contributors, with an overall isotropic temperature factor which refined to $U_{iso} = 0.113(5)Å^2$. The acetonitrile solvent molecule was found to be disordered, occupying two slightly different positions with approximately the same occupancy; it was decided to refine them isotropically, with a fixed occupancy factor of 0.5. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + 0.0002F_o^2]$; final $R = [\Sigma w(|F_o| - |F_c|)/\Sigma w(|F_o|)]$ and $R' = \{[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}\}$ values were 0.057 and 0.054, respectively. Programs used were SHELX76[10] and ORTEP.[11] Scattering factors for non-H atoms were taken from Cromer and Mann[12] with corrections for anomalous dispersion from Cromer and Liberman.[13] (for H from Stewart, Davidson and Simpson[14]). The relevant crystallographic data have been deposited as Supplementary Publication CSD 56829. Copies can be obtained through the Fachinformationszentrum Energie, Physik, Mathematik D-7514 Eggenstein-Leopoldshafen.

DISCUSSION

The electrochemical oxidation of zinc in the presence of the Schiff base H_2L and 2,2'-bipyridine gives a solution which upon concentration in air at room temperature yields a solid complex of formula $Zn(HL)_2$.bipy. The electrochemical efficiency E_f, defined as moles of metal dissolved per Faraday of charge, is 0.52

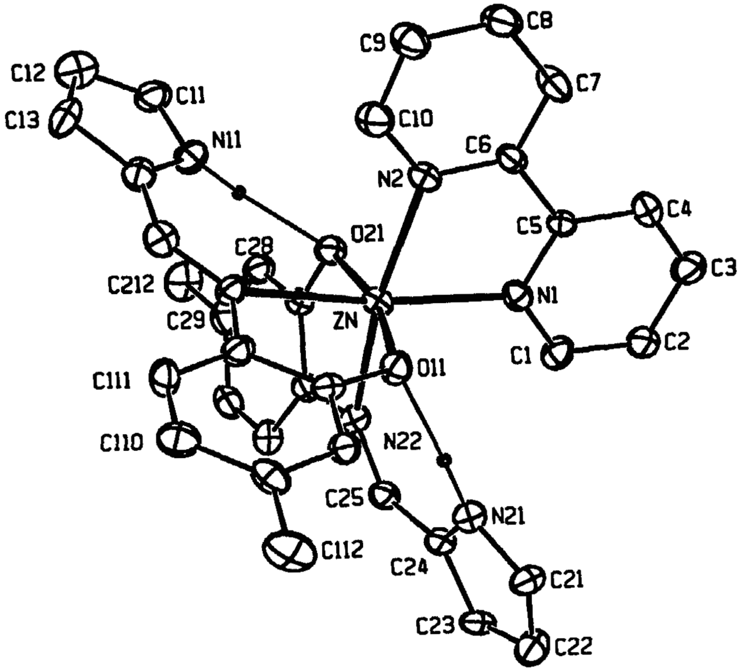

Figure 1 The title molecule drawn using ORTEP.[11]

mol F^{-1}, indicating that the synthesis of the complex involves the following processes.

$$\text{Cathode: } H_2L + 2e^- \rightarrow 2HL^- + H_2$$

$$\text{Anode: } 2HL^- + \text{bipy} + Zn \rightarrow Zn(HL)_2.\text{bipy} + 2e^-$$

The molecular structure of $Zn(HL)_2$. bipy is illustrated in Figure 1. Figure 2 shows a partial packing diagram. Positional parameters are listed in Table 1 and bond distances and angles around the zinc atom, with estimated standard deviations, are listed in Tables 2 and 3. The zinc atom is coordinated to the phenolic oxygen and the imino nitrogen of each of two bidentate Schiff base monoanions, and to a bidentate bipyridine molecule. The pyrrole nitrogen atoms are not coordinated to the metal. The bidentate character of the ligands gives the zinc atom a distorted octahedral environment. Deviation from perfect octahedral geometry is shown by the angles defined by *trans* donors atoms and the zinc atom, (161.7(2) and 165.8(2)°) and by the internal angles of the chelate rings at the metal atom (74.1(2) and 77.7(2)° for the OZnN angles of the Schiff base, 74.9(2)° for NZnN in bipyridine).

The Zn-O bond distances, 1.955(5) and 1.978(4) Å, are in the range expected and similar to those found in several salicylaldiminate zinc complexes.[15–17] There are

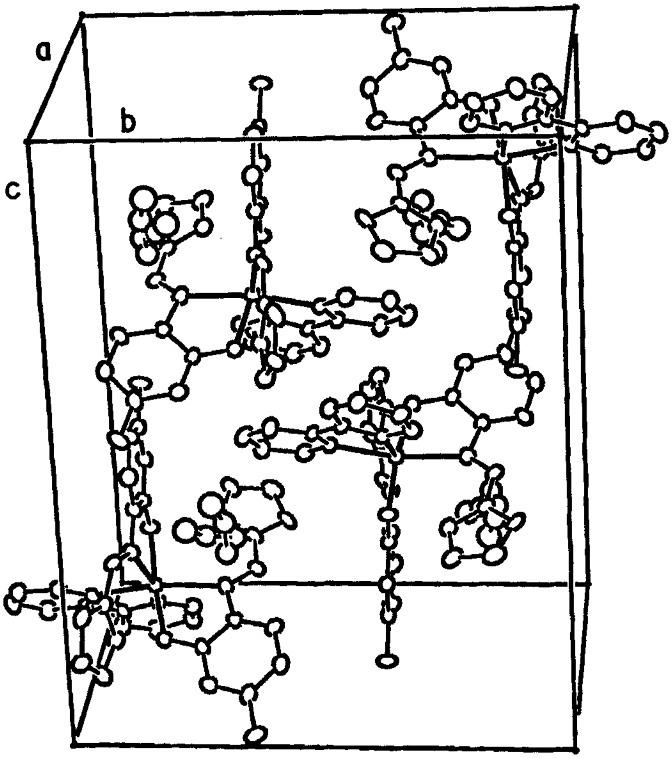

Figure 2 Partial packing diagram for the complex.

Table 1 Fractional atomic coordinates and equivalent isotropic temperature factors (Å^2).

Atom	*X/A*	*Y/B*	*Z/C*	B_{iso}[a]
Zn	0.4507(1)	0.1334(1)	0.8500(1)	3.74(3)
N(1)	0.6201(6)	0.1188(3)	0.9289(3)	3.5(2)
C(1)	0.6953(8)	0.1803(5)	0.9584(4)	4.4(3)
C(2)	0.7963(8)	0.1674(5)	1.0108(4)	4.9(3)
C(3)	0.8181(8)	0.0869(5)	1.0353(4)	5.2(3)
C(4)	0.7405(8)	0.0239(5)	1.0059(4)	4.7(3)
C(5)	0.6432(7)	0.0410(4)	0.9520(3)	3.3(3)
N(2)	0.4596(6)	-0.0002(3)	0.8721(3)	3.6(2)
C(6)	0.5577(7)	-0.0255(4)	0.9186(3)	3.4(3)
C(7)	0.5804(8)	-0.1099(5)	0.9324(4)	5.2(3)
C(8)	0.4973(9)	-0.1690(5)	0.8972(4)	5.9(4)
C(9)	0.3987(8)	-0.1431(5)	0.8499(4)	5.4(3)
C(10)	0.3803(8)	-0.0579(4)	0.8384(4)	4.8(3)
O(11)	0.5582(5)	0.1196(3)	0.7775(2)	4.0(2)
N(11)	0.0874(6)	0.0896(4)	0.8431(3)	4.4(2)
N(12)	0.2875(6)	0.1079(3)	0.7471(3)	3.7(2)
C(11)	-0.0287(9)	0.0724(5)	0.8688(4)	5.2(4)
C(12)	-0.1219(9)	0.0436(5)	0.8198(5)	5.7(4)
C(13)	-0.0644(8)	0.0437(5)	0.7602(5)	5.3(3)
C(14)	0.0670(8)	0.0737(4)	0.7766(4)	4.2(3)
C(15)	0.1651(9)	0.0836(5)	0.7334(4)	4.2(3)
C(16)	0.3666(8)	0.1103(4)	0.6948(4)	3.7(3)
C(17)	0.5052(7)	0.1144(4)	0.7146(4)	3.4(3)
C(18)	0.5900(7)	0.1132(4)	0.6650(4)	3.9(3)
C(19)	0.5402(9)	0.1098(4)	0.5966(4)	4.4(3)
C(110)	0.4041(9)	0.1085(5)	0.5791(4)	5.1(3)
C(111)	0.3183(8)	0.1084(5)	0.6268(4)	4.8(3)
C(112)	0.6334(9)	0.1096(5)	0.5452(4)	6.9(4)
O(21)	0.3107(4)	0.1612(3)	0.9058(2)	3.8(2)
N(21)	0.7217(6)	0.2499(4)	0.7993(3)	4.5(2)
N(22)	0.4612(5)	0.2778(3)	0.8543(3)	3.8(2)
C(21)	0.8461(9)	0.2637(5)	0.7836(4)	5.2(3)
C(22)	0.8793(9)	0.3458(6)	0.7956(5)	6.3(4)
C(23)	0.7722(9)	0.3836(4)	0.8209(4)	5.0(3)
C(24)	0.6734(8)	0.3230(4)	0.8239(3)	4.0(3)
C(25)	0.5483(8)	0.3344(4)	0.8473(3)	3.9(3)
C(26)	0.3452(7)	0.3040(4)	0.8812(3)	3.6(3)
C(27)	0.2749(7)	0.2408(4)	0.9093(3)	3.5(3)
C(28)	0.1645(8)	0.2623(5)	0.9413(4)	4.3(3)
C(29)	0.1213(8)	0.3443(5)	0.9434(4)	4.4(3)
C(210)	0.1888(9)	0.4060(5)	0.9118(4)	4.8(3)
C(211)	0.2995(8)	0.3862(4)	0.8818(4)	4.1(3)
C(212)	0.0008(9)	0.3661(5)	0.9782(4)	6.7(4)
N(31)	0.084(2)	0.203(1)	0.111(1)	9.7(5)
C(31)	0.199(2)	0.190(1)	0.224(1)	6.9(6)
C(32)	0.158(2)	0.186(1)	0.161(1)	7.1(6)
N'(31)	0.016(2)	0.250(1)	0.1361(9)	8.8(5)
C'(31)	0.249(2)	0.175(1)	0.211(1)	6.3(6)
C'(32)	0.104(2)	0.219(1)	0.169(1)	6.3(5)

[a] $B_{iso} = 4/3\Sigma_i\Sigma_j B_{ij}(a_i.a_j)$.

Table 2 Bond distances (Å) for the compound.

Zn-N(1)	2.195(6)	Zn-N(2)	2.187(5)
Zn-O(11)	1.955(5)	Zn-N(12)	2.515(6)
Zn-O(21)	1.978(4)	Zn-N(22)	2.318(5)
N(1)-C(1)	1.336(9)	N(1)-C(5)	1.342(9)
C(1)-C(2)	1.39(1)	C(2)-C(3)	1.39(1)
C(3)-C(4)	1.37(1)	C(4)-C(5)	1.40(1)
C(5)-C(6)	1.48(1)	N(2)-C(6)	1.337(9)
N(2)-C(10)	1.349(9)	C(6)-C(7)	1.39(1)
C(7)-C(8)	1.40(1)	C(8)-C(9)	1.35(1)
C(9)-C(10)	1.39(1)	O(11)-C(17)	1.319(9)
N(11)-C(11)	1.37(1)	N(11)-C(14)	1.36(1)
N(12)-C(15)	1.29(1)	N(12)-C(16)	1.41(1)
C(11)-C(12)	1.36(1)	C(12)-C(13)	1.41(1)
C(13)-C(14)	1.41(1)	C(14)-C(15)	1.42(1)
C(16)-C(17)	1.41(1)	C(16)-C(111)	1.40(1)
C(17)-C(18)	1.41(1)	C(18)-C(19)	1.41(1)
C(19)-C(110)	1.37(1)	C(19)-C(111)	1.50(1)
C(110)-C(111)	1.38(1)	O(21)-C(27)	1.331(8)
N(21)-C(21)	1.36(1)	N(21)-C(24)	1.388(9)
N(22)-C(25)	1.285(9)	N(22)-C(26)	1.422(9)
C(21)-C(22)	1.37(1)	C(22)-C(23)	1.40(1)
C(23)-C(24)	1.40(1)	C(24)-C(25)	1.42(1)
C(26)-C(27)	1.40(1)	C(26)-C(211)	1.40(1)
C(27)-C(28)	1.41(1)	C(28)-C(29)	1.39(1)
C(29)-C(210)	1.40(1)	C(29)-C(211)	1.53(1)
C(210)-C(211)	1.38(1)	C(31)-C(32)	1.29(3)
N(31)-C(32)	1.21(3)	C'(31)-C'(32)	1.74(3)
N'(31)-C'(32)	1.15(3)		

two essentially different Zn-N distances. The Zn-N (pyridine) distances, 2.178(5) and 2.195(6) Å, are in agreement with those observed in hexacoordinate Zn complexes containing similar bidentate ligands, for instance 2.162(6) and 2.202(7)Å for Zn-N(phenanthroline) in 1,10-phenanthrolinebis(pyridine-2-thionate)zinc(II).[18] The two Zn-N(imino) bond distances, 2.318(5) and 2.515(6) Å, are smaller than the sum of the covalent radii of N and octahedral Zn (*ca* 2.85 Å), but are greater than those of Zn-N(imino) bonds in other complexes with pyrrolealdimines as ligands, e.g., 2.057(3)Å in tetracoordinate bis {2-[pyrrol-2-ylmethyleneamino] thiophenolate-*S*,*N*}zinc(II),[19] 2.169(2) in pentacoordinate acetonitrile-bis -{2-[(2-pyrrole)methylimino] 3,5-dimethylphenolato}zinc(II).[20] No Zn-N(imino) bond distance for hexacoordinate zinc complexes with related ligands has been published; the values here reported are indicative of weak interaction between Zn and the imino nitrogens.

Between the pyrrolic nitrogen of each Schiff base and the phenolic oxygen of the other there is a strong hydrogen bond (Table 4) [N...O 2.695(8) and 2.664(8) Å, somewhat shorter than expected for N...O hydrogen bonds, 2.73–3.22. Å].[21] As a consequence of this hydrogen bond, the ν(N-H) IR band, which in the spectrum of the free ligand appears at 3400 cm^{-1}, is shifted to 2700–2900 cm^{-1}. In addition, the ^1H NMR signal of the pyrrole proton is shifted to 14.2 ppm in the complex; this contrasts with the value of 11.8–12 ppm found for pyrrole complexes in which the N-H group is not involved in a hydrogen bond.[19] The absence of a band attributable

Table 3 Bond angles (°) for the compound.

N(1)-Zn-N(2)	74.9(2)	N(1)-Zn-O(11)	94.5(2)
N(1)-Zn-N(12)	161.7(2)	N(1)-Zn-O(21)	98.9(2)
N(1)-Zn-N(22)	93.0(2)	N(2)-Zn-O(11)	91.8(2)
N(2)-Zn-N(12)	90.9(2)	N(2)-Zn-O(21)	96.7(2)
N(2)-Zn-N(22)	165.8(2)	O(11)-Zn-N(12)	74.1(2)
O(11)-Zn-O(21)	165.6(2)	O(11)-Zn-N(22)	96.5(2)
N(12)-Zn-O(21)	94.1(2)	N(12)-Zn-N(22)	102.4(2)
O(21)-Zn-N(22)	77.7(2)	C(1)-N(1)-C(5)	117.8(6)
N(1)-C(1)-C(2)	123.3(7)	C(1)-C(2)-C(3)	118.5(7)
C(2)-C(3)-C(4)	118.4(7)	C(3)-C(4)-C(5)	120.0(7)
N(1)-C(5)-C(4)	121.8(6)	N(1)-C(5)-C(6)	116.5(6)
C(4)-C(5)-C(6)	121.6(6)	C(6)-N(2)-C(10)	119.0(6)
C(5)-C(6)-N(2)	116.0(6)	C(5)-C(6)-C(7)	122.5(6)
N(2)-C(6)-C(7)	121.5(7)	C(6)-C(7)-C(8)	118.9(7)
C(7)-C(8)-C(9)	119.3(8)	C(8)-C(9)-C(10)	119.2(7)
N(2)-C(10)-C(9)	122.0(7)	C(11)-N(11)-C(14)	108.4(7)
C(15)-N(12)-C(16)	118.0(6)	N(11)-C(11)-C(12)	109.6(8)
C(11)-C(12)-C(13)	107.6(8)	C(12)-C(13)-C(14)	106.4(7)
N(11)-C(14)-C(13)	108.1(7)	N(11)-C(14)-C(15)	124.5(7)
C(13)-C(14)-C(15)	127.4(8)	N(12)-C(15)-C(14)	129.1(7)
N(12)-C(16)-C(17)	115.4(6)	N(12)-C(16)-C(111)	125.6(7)
C(17)-C(16)-C(111)	119.0(7)	O(11)-C(17)-C(16)	122.6(6)
O(11)-C(17)-C(18)	119.1(6)	C(16)-C(17)-C(18)	118.3(6)
C(17)-C(18)-C(19)	122.2(7)	C(18)-C(19)-C(110)	117.8(7)
C(18)-C(19)-C(112)	120.7(7)	C(110)-C(19)-C(112)	121.5(7)
C(19)-C(110)-C(111)	121.3(8)	C(16)-C(111)-C(110)	121.4(7)
C(21)-N(21)-C(24)	109.2(6)	C(25)-N(22)-C(26)	116.5(6)
N(21)-C(21)-C(22)	109.1(7)	C(21)-C(22)-C(23)	107.3(8)
C(22)-C(23)-C(24)	107.9(7)	N(21)-C(24)-C(23)	106.4(6)
N(21)-C(24)-C(25)	126.9(6)	C(23)-C(24)-C(25)	126.7(7)
N(22)-C(25)-C(24)	126.9(7)	N(22)-C(26)-C(27)	115.6(6)
N(22)-C(26)-C(211)	124.9(6)	C(27)-C(26)-C(211)	119.5(6)
O(21)-C(27)-C(26)	121.0(6)	O(21)-C(27)-C(28)	119.8(6)
C(26)-C(27)-C(28)	119.2(6)	C(27)-C(28)-C(29)	121.2(7)
C(28)-C(29)-C(210)	118.6(7)	C(28)-C(29)-C(212)	120.3(7)
C(210)-C(29)-C(212)	121.1(7)	C(29)-C(210)-C(211)	120.8(7)
C(26)-C(211)-C(210)	120.6(7)	N(31)-C(32)-C(31)	154.(1)
N’(31)-C’(32)-C’(31)	173.(1)		

Table 4 Hydrogen bonds between ligands in the complex.

O...H-N	O...N	O...H	O...H-N
O(21)...H(11)-N(11)	2.695(8)	1.718(4)	157.1(4)
O(11)...H(21)-N(21)	2.664(8)	1.669(5)	176.6(4)

to ν(O-H), and the shift to lower frequency of the ν(C = N) of the imino group, indicate that the phenolic hydrogen is lost during the electrosynthetic process and that the imino nitrogen is coordinated to the metal. Therefore the effective ligand is monoanionic and bidentate. This is in keeping with the absence of a phenolic proton peak in the ^{1}H NMR spectrum and with the downfield shift of the azomethine hydrogen signal.

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