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Electrochemical synthesis of cobalt, nickel, copper, zinc and cadmium complexes with *N*[(2-hydroxyphenyl)methylidine]-*N*′-tosylbenzene-1,2-diamine. The crystal structures of {(1,10-phenanthroline)[*N*-(2-oxophenyl)methylidine]-*N*-tosylbenzene-1,2-diaminato}nickel(II) and {(1,10-phenanthroline)[*N*-(2-oxophenyl)-methylidine]-*N*′-tosylbenzene-1,2-diaminato}copper(II)

Mar Bernal [a], José A. García-Vázquez [a], Jaime Romero [a], Cristina Gómez [a], María L. Durán [a], Antonio Sousa [a,*], Antonio Sousa-Pedrares [a], David J. Rose [b], Kevin P. Maresca [b], Jon Zubieta [b]

[a] *Departamento de Química Inorgánica, Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Spain*
[b] *Department of Chemistry, Syracuse University, Syracuse, NY 13244, USA*

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Abstract

The electrochemical oxidation of cobalt, nickel, copper, zinc or cadmium anodes in an acetonitrile solution containing *N*[(2-hydroxyphenyl)methylidine]-*N*′-tosylbenzene-1,2-diamine (H_2L) yielded compounds of general formula [ML]. When 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy) is added to the cell, mixed ligand complexes are obtained. The crystal structures of {(1,10-phenanthroline)[*N*-(2-oxophenyl)methylidine]-*N*′-tosylbenzene-1,2-diaminato}nickel(II) (**1**) and {(1,10-phenanthroline)-[*N*-(2-oxophenyl)methylidine]-*N*′-tosylbenzene-1,2-diaminato}copper(II) (**2**) were determined by X-ray diffraction. Compound **1** consists of a binuclear $[Ni_2L_2{}^1(phen)_2]$ complex with phenolic oxygen atoms bridging both nickel atoms. Each nickel atom is in a distorted octahedral $[NiN_4O_2]$ environment. Compound **2** is monomeric, with the copper atom in a $[CuN_4O]$ distorted square pyramidal geometry. The electronic, IR and NMR spectra of the complexes are discussed and related to the structure. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Electrochemistry; Cobalt complexes; Copper complexes; Amide complexes

1. Introduction

The application of electrochemical procedures to the preparation of metal complexes of ligands having acid groups has been extensively investigated [1]. Compounds with Schiff bases containing phenol [2–6] or pyrrole [7–13] groups have been synthesised starting with the metal as the anode of an electrolytic cell containing the ligand in an appropriate solvent. In addition to its simplicity and high yield, the method allows the one-step preparation of mixed complexes by addition of a second ligand to the cell. This paper is an extension of our previous work on the electrochemical synthesis of complexes with Schiff bases containing phenol and tosyl amide as acid groups, shown below.

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* Corresponding author. Tel.: +34-981-563 100; fax: +34-981-597 525.

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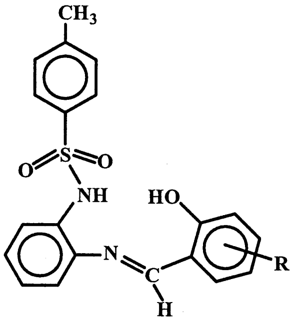

	H_2L^1	H_2L^2	H_2L^3
R	**H**	**(3,5)-Br_2**	**5-Cl**

2. Experimental

Acetonitrile, 2-hydroxybenzaldehyde, 1,2-diaminobenzene, and all other reagents were commercial products and were used as supplied. Metals (Ega Chemie) were used as plates (approximately 2 × 2 cm^2).

N-tosyl-1,2-diaminobenzene was prepared by the reaction of a solution of *o*-phenylenediamine (5 g, 46.3 mmol) in pyridine (30 cm^3) and *p*-toluenesulphonyl chloride (9 g, 47.5 mmol) in an ice-bath with continuous magnetic stirring. The reaction mixture was then poured into cold water (60 cm^3) with stirring affording a black oil in the bottom of the flask. The oil was isolated and treated with a hot 1:1 ethyl alcohol 95%–water mixture. After cooling, the solid obtained was recrystallised in 1:1 ethyl alcohol–water affording a white spongy compound. Yield: 8.9 g, 77.5%, m.p. 135–136°C.

The Schiff bases were prepared by direct reaction of equimolar amounts of the aldehyde and *N*-tosyl-1,2-diaminobenzene in ethanol using a Dean–Stark trap. After removal of the water produced in the reaction, the solution was concentrated and the isolated solid was recrystallised from ethanol. Its purity was checked by recording its IR and ^1H NMR spectra.

2.1. Electrochemical synthesis

An acetonitrile solution of the ligand containing about 15 mg of tetramethylammonium perchlorate as a current carrier was electrolysed using a platinum wire as the cathode and a metal plate as the anode. The cell can be summarised as: $Pt(-)/LH_2 + CH_3CN/M(+)$, where H_2L stands for the Schiff bases and M represents the metal. When mixed complexes were prepared, the corresponding additional ligand was added to the electrochemical cell. When a crystalline solid was obtained after the electrochemical reaction, the product was filtered in vacuo using a sintered funnel, washed with acetonitrile and diethyl ether, and dried. In those cases where no solid was produced after the electrochemical reaction, the solution was filtered and the filtrate was slowly evaporated at room temperature or on a vacuum line until a solid was crystallised. The solution composition and the experimental conditions are given in Table 1.

2.2. Physical measurements

The C, N, H and S contents of the complexes were determined on a Perkin–Elmer 240B microanalyser. IR

Table 1
Experimental conditions for the synthesis of complexes [a]

Compound	Amount of H_2L (g) [b]	Amount of L′ (g)	Time (h)	Metal dissolved (mg)	E_f (mol F^{-1})
$[CoL^1]$	0.154	–	2	22.5	0.51
$[CoL^2]$	0.154	–	2	23.2	0.53
$[NiL^1(phen)]$	0.154	0.230	4	46.1	0.52
$[NiL^2(phen)]$	0.154	0.430	2	22.8	0.51
$[NiL^2(bipy)]$	0.200	0.230	2	22.3	0.49
$[CuL^1]$	0.200	–	1.5	37.1	1.04
$[CuL^1(bipy)]$	0.200	0.180	2	47.2	0.99
$[CuL^1(phen)]$	0.305	0.150	3	70.3	0.98
$[CuL^2]$	0.200	–	1.2	30.2	1.06
$[CuL^2(bipy)]$	0.200	0.240	1	22.4	0.95
$[CuL^2(phen)]$	0.305	0.110	3	74.3	1.04
$[CuL^3]$	0.200	–	1.5	40	1.12
$[ZnL^1]$	0.140	–	2	24.2	0.49
$[ZnL^2]$	0.200	–	2	24.0	0.49
$[ZnL^3]$	0.200	–	3	36	0.49
$[CdL^1]$	0.140	–	2	42.2	0.50
$[CdL^1(phen)]$	0.383	0.210	4	89.4	0.53
$[CdL^2]$	0.200	–	2	39.5	0.47
$[CdL^3]$	0.200	–	3	60	0.48

[a] Intensity of current 10 mA.

[b] Plus $[NMe_4]ClO_4$ (approximately 10 mg).

spectra were recorded as KBr mulls on a Perkin–Elmer 130 spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker WM 350 MHz spectrophotometer, using DMSO-d_6 as solvent. Chemical shifts were referenced to TMS as internal standard. The electronic spectra in the solid were recorded on a Hitachi 4-3200 spectrophotometer.

2.3. Crystal structure determination

The data collection was carried out on a Rigaku AFC5S for **1** and on an Enraf–Nonius CAD4 for **2**, using graphite-monochromatised Mo Kα radiation, $\lambda = 0.71073$ Å, 293 K. The $\omega/2\theta$ scan technique was employed to measure the intensities for 18 455 and 2278 reflections up to a maximum Bragg angle of 28.27 and 22.46° for **1** and **2**, respectively. Cell parameters were refined by a least-squares procedure on setting angles of 25 reflections. No decomposition of the crystal occurred during the data collection. Corrections were applied for Lorentz and polarisation effects and for absorption ($\mu = 0.776$ and 0.941 mm^{-1} for **1** and **2**) [14].

The structures were solved by direct methods and refined by a full-matrix least-squares procedure based on F^2. Non-hydrogen atoms were refined with anisotropic displacement parameters. The structural disorder of the acetonitrile molecules explains the high values of the R factor in the case of the nickel compound. The atomic scattering factors were taken from International Tables for X-ray Crystallography [15]. The calculations were carried out on a Micro VAXII using the crystallographic software TEXSAN [16] for **1** and SHELX86 [17] for **2**. The crystal parameters and other experimental details of data collection and refinement are summarised in Table 2.

3. Results and discussion

The analytical results of Table 3 show that the electrochemical procedure is an effective method for obtaining compounds of general formula [ML], where M is cobalt, nickel, copper, zinc and cadmium and L stands for the dianionic form of the Schiff bases. When the synthesis was carried out in presence of additional ligands (1,10-phenanthroline or 2,2′-bipyridine), mixed complexes of general formula [ML(phen)] or [ML(bipy)] were obtained.

In the case of copper complexes, the electrochemical efficiency was close to 1.0 mol F^{-1}. This value is indicative of the formation of Cu$^+$ at the anode, which is subsequently oxidised to Cu^{2+} in solution. This fact together with the H_2 evolution at the cathode are compatible with the following reaction scheme:

$$\begin{aligned}
&\text{Cathode:} && H_2L + e^- \rightarrow HL^- + 1/2H_2 \\
&\text{Anode:} && Cu \rightarrow Cu^+ + e^- \\
& && Cu^+ + HL^- \rightarrow [CuL] + 1/2H_2
\end{aligned}$$

In the case of cobalt, nickel, zinc and cadmium complexes, the electrochemical efficiency is close to

Table 2
Summary of crystal data for $[Ni_2L_2{}^1(phen)_2]$ (**1**) and $[CuL^1(phen)]$ (**2**)

	$[Ni_2L_2{}^1(phen)_2]$	$[CuL^1(phen)]$
Empirical Formula	$C_{68}H_{54}N_{10}O_6S_2Ni_2$	$C_{32}H_{24}CuN_4O_3S$
Formula weight	1287.4	608.15
Size	0.12 × 0.10 × 0.10	0.50 × 0.25 × 0.15
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	11.06530(10)	8.840(2)
b (Å)	13.13320(10)	9.972(2)
c (Å)	21.08370(10)	15.813(5)
α (°)	93.0930(10)	104.36(3)
β (°)	97.1830(10)	87.44(3)
γ (°)	100.6370(10)	99.13(3)
V (Å^3)	2978.32(4)	1333.3(5)
Z	2	2
D_{calc} (g cm^{-3})	1.437	1.515
λ (Å) (Mo Kα radiation)	0.71073	0.71073
μ (mm^{-1}) (Mo Kα)	0.766	0.941
T (K)	293(2)	293(2)
No. reflections collected	18 455	2278
No. independent reflections	12 923	2082
F(000)	1336	626
R [a]	0.074	0.0214
R_w [b]	0.194	0.0570

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[b] $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 3
Analytical data for complexes (%) [a]

Compound	%C	%H	%N	%S
$[CoL^1]$	56.5(56.7)	3.6(3.8)	6.2(6.6)	7.2(7.5)
$[CoL^2]$	41.2(41.3)	2.7(2.4)	4.8(4.8)	5.3(5.5)
$[NiL^1(phen)]\cdot CH_3CN$	64.2(64.7)	4.1(4.1)	10.9(10.5)	5.1(4.8)
$[NiL^2(bipy)]$	48.4(48.9)	3.0(3.1)	7.4(7.6)	3.9(4.3)
$[NiL^2(phen)]$	52.2(51.9)	2.8(3.0)	7.4(7.1)	4.2(4.1)
$[CuL^1]$	56.4(56.1)	3.9(3.8)	6.3(6.6)	7.2(7.5)
$[CuL^1(bipy)]$	61.7(61.7)	3.7(4.1)	9.4(9.6)	5.5(5.5)
$[CuL^1(phen)]$	64.3(64.6)	3.3(3.8)	9.4(8.9)	5.8(5.1)
$[CuL^2]$	41.3(40.9)	3.0(2.6)	4.5(4.8)	4.7(5.4)
$[CuL^2(bipy)]$	48.4(48.4)	3.0(3.2)	8.0(7.5)	4.4(4.3)
$[CuL^2(phen)]$	50.2(50.2)	2.9(3.0)	7.8(7.3)	4.4(4.2)
$[CuL^3]$	51.9(51.9)	3.4(3.5)	6.5(6.0)	6.9(6.9)
$[ZnL^1]$	55.5(55.9)	3.9(3.8)	6.5(6.5)	7.3(7.5)
$[ZnL^2]$	40.7(40.7)	3.0(2.7)	4.9(4.8)	4.7(5.4)
$[ZnL^3]$	52.1(51.7)	3.2(3.1)	6.0(6.0)	6.9(6.8)
$[CdL^1]$	50.2(50.4)	3.3(3.4)	6.0(5.9)	6.4(6.7)
$[CdL^1(phen)]$	59.8(59.9)	3.6(3.6)	8.6(8.2)	4.2(4.7)
$[CdL^2]$	37.2(37.7)	2.9(2.5)	4.5(4.4)	5.4(5.0)
$[CdL^3]$	46.7(46.9)	2.7(3.1)	5.3(5.4)	6.3(6.2)

[a] Calculated values in parentheses.

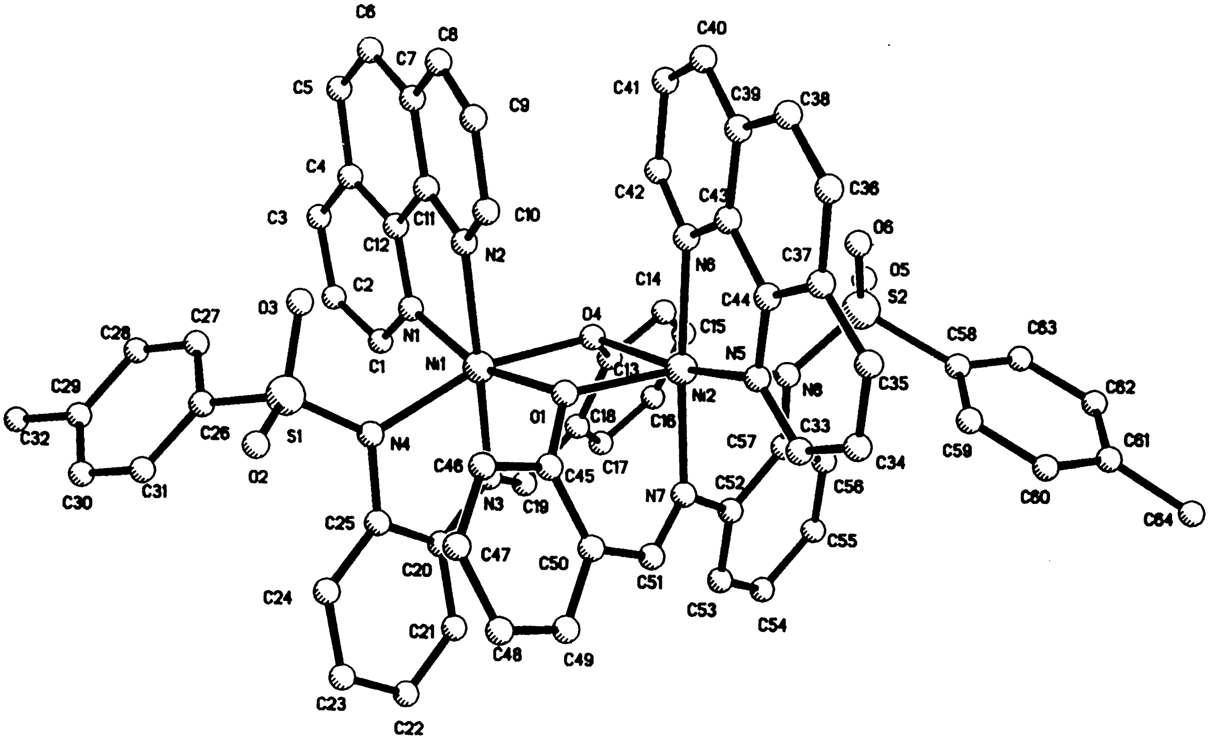

Fig. 1. Molecular structure of $[Ni_2L_2{}^1(phen)_2]$ (**1**).

0.5 mol F^{-1}. This is in accordance with the following reaction mechanism:

Cathode: $H_2L + 2e^- \rightarrow L^{2-} + H_2$
Anode: $M + L^{2-} \rightarrow [ML] + 2e^-$

3.1. Molecular structure of $[Ni_2L_2{}^1(phen)_2]\cdot 2CH_3CN$ *(1)*

Fig. 1 shows the molecular structure of **1** together with the atom labelling scheme used. Final atomic coordinates, bond distances and angles are given in Tables 4 and 5, respectively.

The structure consists of dimeric $[Ni_2L_2{}^1(phen)_2]$ molecules with both metal atoms bridged by phenolic oxygen atoms. This bridge is slightly asymmetric, with bond lengths O(1)–Ni(1) 2.135(4) Å, O(4)–Ni(2) 2.152(4) Å and O(1)–Ni(2) 2.064(4) Å, O(4)–Ni(1) 2.083(4) Å. The four-membered ring formed by the two nickel atoms and the oxygen bridging atoms is not planar (angle between Ni(1)–O(1)–O(4) and Ni(2)–O(1)–O(4) of 3.60(20)°). The coordination sphere around each metal is completed by the amide and the imino nitrogen atoms of the Schiff base and the two nitrogen atoms of the bidentate 1,10-phenanthroline.

Each nickel atom is in a $[NiN_4O_2]$ distorted octahedral environment with the donors of the terdentate Schiff base in a meridional disposition. The angles defined by the two *trans*-donor atoms and the nickel atom are significantly different from the idealised value of 180°. (N(1)–Ni(1)–O(1) = 164.1(2)°, N(8)–Ni(2)–O(1) = 164.5(2)°, N(7)–Ni(2)–N(6) = 175.4(2)°, O(4)–Ni(1)–N(4) = 164.0(2)°, N(5)–Ni(2)–O(4) = 165.5(2)°, N(2)–Ni(1)–N(3) = 173.3(2)°). The angles defined by the nickel atom and the two *cis*-donor atoms are also different from 90°, particularly in the case of the chelate ring, N(7)–Ni(2)–N(8) = 79.3(2)°, N(5)–Ni(2)–N(6) = 79.0(2)°, N(1)–Ni(1)–N(2) = 78.9(2)°, N(3)–Ni(1)–N(4) = 78.8(2)°. The Ni–N amide bond distances, 2.138(5) and 2.131(5) Å, are longer than the Ni–N imine bond distances and longer than that in the binuclear hexacoordinated nickel(II) complex {bis-(methanol)[2-(2-*N*-tosylaminophenyl) iminomethyl] phenolato}nickel(II) [18] of 2.093(13) Å. This distance is also longer than those found in tetrahedral amide Ni(II) complexes (1.916(3) [19] and 1.839(6) Å [20]), a feature reflecting the lower coordination number in the tetrahedral complexes.

The $Ni–N_{imine}$ bond distances, 2.042(4) and 2.030(4) Å, are similar to those found in other hexacoordinated nickel(II) salicylaldiminate complexes [4,21]. The two $Ni–N_{phen}$ bond distances are non-equivalent, 2.134(5) and 2.087(4) Å for Ni(1) and 2.132(5) and 2.084(5) Å for Ni(2), but similar to those found in other Ni(II) hexacoordinated complexes with 1,10-phenanthroline, 2.06(4) and 2.15(3) Å [22] in $[Ni(phen)_3]^{2+}$ [24] or 2.125(5) and 2.136(5) Å in 1,10-phenanthroline-bis{[2-(2 - pyrrole)methyleneimino]4 - methylphenolato}nickel-(II) [23].

Table 4
Atomic coordinates ($\times 10^4$) for $[NiL^1(phen)]_2 \cdot 2CH_3CN$ (**1**)

	x	y	z	U_{eq}
Ni(1)	737(1)	817(1)	2814(1)	32(1)
Ni(2)	2115(1)	−641(1)	1964(1)	31(1)
S(1)	1528(2)	2977(1)	3815(1)	46(1)
S(2)	1430(2)	−2542(1)	757(1)	43(1)
O(1)	2540(3)	627(3)	2631(2)	35(1)
O(2)	2682(5)	3451(4)	4213(3)	65(1)
O(3)	1307(6)	3378(4)	3195(2)	64(1)
O(4)	288(3)	−412(3)	2106(2)	35(1)
O(5)	190(5)	−3061(4)	473(2)	61(1)
O(6)	1988(5)	−1676(4)	426(2)	57(1)
N(1)	−1107(4)	1111(4)	2727(2)	37(1)
N(2)	817(4)	1915(3)	2134(2)	36(1)
N(3)	439(4)	−278(4)	3458(2)	35(1)
N(4)	1323(5)	1744(4)	3702(2)	40(1)
N(5)	3979(4)	−473(4)	1763(2)	38(1)
N(6)	2048(5)	245(4)	1175(2)	38(1)
N(7)	2320(4)	−1514(4)	2722(2)	37(1)
N(8)	1557(5)	−2167(4)	1498(2)	39(1)
N(9)	4660(23)	2768(22)	6356(17)	69(8)
N(10)	5049(19)	−5891(16)	2408(11)	46(5)
C(1)	−2010(6)	774(5)	3065(3)	45(1)
C(2)	−3165(6)	1104(6)	2983(3)	52(2)
C(3)	−3369(6)	1790(6)	2533(4)	56(2)
C(4)	−2430(6)	2150(5)	2156(3)	45(1)
C(5)	−2574(7)	2850(6)	1664(4)	60(2)
C(6)	−1643(7)	3187(6)	1332(4)	61(2)
C(7)	−438(6)	2913(5)	1480(3)	46(1)
C(8)	607(7)	3347(5)	1210(3)	55(2)
C(9)	1730(7)	3100(5)	1430(3)	54(2)
C(10)	1803(6)	2371(5)	1895(3)	44(1)
C(11)	−283(5)	2202(4)	1949(3)	36(1)
C(12)	−1310(5)	1788(4)	2282(3)	36(1)
C(13)	−608(5)	−1227(4)	2129(3)	36(1)
C(14)	−1212(6)	−1800(5)	1558(3)	46(1)
C(15)	−2100(6)	−2682(6)	1559(4)	56(2)
C(16)	−2451(7)	−3044(6)	2127(4)	67(2)
C(17)	−1885(7)	−2499(6)	2702(4)	58(2)
C(18)	−963(6)	−1598(5)	2716(3)	42(1)
C(19)	−356(6)	−1135(5)	3342(3)	41(1)
C(20)	1029(5)	46(5)	4096(3)	38(1)
C(21)	1198(6)	−655(5)	4565(3)	50(2)
C(22)	1805(7)	−307(6)	5165(3)	57(2)
C(23)	2282(7)	746(7)	5298(3)	59(2)
C(24)	2152(7)	1453(6)	4840(3)	52(2)
C(25)	1514(6)	1117(5)	4223(3)	42(1)
C(26)	325(7)	3251(5)	4239(3)	49(2)
C(27)	−822(8)	3250(7)	3900(4)	70(2)
C(28)	−1797(8)	3433(8)	4228(5)	80(3)
C(29)	−1606(8)	3643(6)	4895(4)	66(2)
C(30)	−443(8)	3674(7)	5220(4)	67(2)
C(31)	526(8)	3484(6)	4900(4)	61(2)
C(32)	−2681(9)	3852(9)	5240(5)	89(3)
C(33)	4901(6)	−906(5)	2037(3)	49(2)
C(34)	6068(6)	−756(7)	1826(4)	61(2)
C(35)	6298(7)	−143(7)	1344(4)	63(2)
C(36)	5522(8)	1016(6)	543(4)	67(2)
C(37)	5371(7)	355(6)	1052(3)	53(2)
C(38)	4562(9)	1398(6)	252(3)	67(2)
C(39)	3314(8)	1143(5)	437(3)	53(2)
C(40)	2264(9)	1456(6)	130(3)	64(2)
C(41)	1145(8)	1140(5)	330(3)	58(2)
C(42)	1076(7)	537(5)	863(3)	48(1)
C(43)	3161(6)	528(4)	960(3)	39(1)
C(44)	4203(5)	139(4)	1276(3)	39(1)
C(45)	3400(5)	708(5)	3142(3)	37(1)
C(46)	4006(5)	1708(5)	3415(3)	45(1)
C(47)	4824(6)	1822(6)	3978(4)	59(2)
C(48)	5094(7)	959(7)	4284(3)	62(2)
C(49)	4539(6)	−13(6)	4025(3)	53(2)
C(50)	3685(5)	−169(5)	3454(3)	40(1)
C(51)	3060(6)	−1222(5)	3252(3)	42(1)
C(52)	1652(6)	−2557(4)	2601(3)	40(1)
C(53)	1335(7)	−3194(5)	3083(3)	50(2)
C(54)	646(8)	−4187(5)	2943(4)	63(2)
C(55)	249(8)	−4532(6)	2310(4)	64(2)
C(56)	524(7)	−3899(5)	1819(3)	51(2)
C(57)	1228(6)	−2894(5)	1945(3)	42(1)
C(58)	2377(6)	−3506(5)	708(3)	41(1)
C(59)	3560(7)	−3317(6)	1058(4)	63(2)
C(60)	4305(7)	−4058(7)	1032(5)	69(2)
C(61)	3884(8)	−4996(6)	666(4)	61(2)
C(62)	2716(8)	−5165(5)	313(4)	60(2)
C(63)	1961(6)	−4421(5)	337(3)	47(1)
C(64)	4682(10)	−5827(8)	667(6)	97(4)
C(65)	4326(27)	4346(28)	5793(13)	59(8)
C(66)	4534(23)	3397(29)	6086(15)	60(8)
C(67)	3404(15)	−4877(12)	2631(10)	27(4)
C(68)	4416(17)	−5457(14)	2521(9)	26(4)

The Ni–O bond distances, 2.135(4), 2.083(4), 2.064(4) and 2.152(4) Å, are longer than those observed in mononuclear salicylaldiminate hexacoordinated nickel(II) complexes (2.005(4) and 2.032(3) Å) [4,21,24] and display a relatively large range. The shorter bond lengths are similar to the values found in {bis(methanol)[2-(2-*N*-tosylaminophenyl)iminomethyl] phenolato}nickel(II), 2.051(11) and 2.063(10) Å [18].

The phenyl rings of the dianionic Schiff base ligand are planar. The 1,10-phenanthroline ligand is also essentially planar with bond distances and angles similar to those of other phenanthroline complexes. The N_{imine}–C bond distances have the expected values for a (C=N) azomethine bond [25]: N(3)–C(19) = 1.285(7) Å and N(3)–C(19) = 1.295(8) Å. The C–O distances are shorter than expected for a single bond, but longer than for a C=O double bond [26].

3.2. Molecular structure of [CuL^1(phen)] (**2**)

Fig. 2 shows the molecular structure of **2** together with the labelling scheme used. Final atomic coordinates, bond distances and angles are given in Tables 6 and 7, respectively.

In **2**, the copper atom is pentacoordinated by the imine nitrogen atom, the amide group nitrogen atom and the phenolic oxygen atom of the dianionic Schiff base and the nitrogen atoms of phenanthroline. A comparison of the metrical parameters of **2** given in Table 4 with the ideal values for the limiting coordina-

Table 5
Selected bond distances and angles for $[NiL^1(phen)]_2 \cdot 2CH_3CN$ (**1**)

Bond lengths			
Ni(1)–N(3)	2.042(4)	Ni(1)–O(4)	2.083(4)
Ni(1)–N(2)	2.087(4)	Ni(1)–N(1)	2.134(5)
Ni(1)–O(1)	2.135(4)	Ni(1)–N(4)	2.138(5)
Ni(2)–N(7)	2.030(4)	Ni(2)–O(1)	2.064(4)
Ni(2)–N(6)	2.084(5)	Ni(2)–N(5)	2.132(5)
Ni(2)–N(8)	2.131(5)	Ni(2)–O(4)	2.152(4)
S(1)–O(3)	1.444(5)	S(1)–O(2)	1.452(6)
S(1)–N(4)	1.594(5)	S(1)–C(26)	1.773(7)
S(2)–O(6)	1.448(5)	S(2)–O(5)	1.453(5)
S(2)–N(8)	1.595(5)	S(2)–C(58)	1.793(6)
O(1)–C(45)	1.331(6)	O(4)–C(13)	1.326(7)
N(l)–C(1)	1.323(7)	N(1)–C(12)	1.354(7)
N(2)–C(10)	1.316(7)	N(2)–C(11)	1.357(7)
N(3)–C(19)	1.285(7)	N(3)–C(20)	1.426(7)
N(4)–C(25)	1.425(8)	N(5)–C(33)	1.342(8)
N(5)–C(44)	1.351(8)	N(6)–C(42)	1.318(8)
N(6)–C(43)	1.360(8)	N(7)–C(51)	1.295(8)
N(7)–C(52)	1.424(8)	N(8)–C(57)	1.410(7)
N(9)–C(66)	1.05(4)	N(10)–C(68)	1.02(3)
Bond angles			
N(3)–Ni(1)–O(4)	86.7(2)	N(3)–Ni(1)–N(2)	173.3(2)
O(4)–Ni(1)–N(2)	92.0(2)	N(3)–Ni(1)–N(1)	94.6(2)
O(4)–Ni(1)–N(1)	93.7(2)	N(2)–Ni(1)–N(1)	78.9(2)
N(3)–Ni(1)–O(1)	99.0(2)	O(4)–Ni(1)–O(1)	78.94(14)
N(2)–Ni(1)–O(1)	87.2(2)	N(1)–Ni(1)–O(1)	164.1(2)
N(3)–Ni(1)–N(4)	78.8(2)	O(4)–Ni(1)–N(4)	164.0(2)
N(2)–Ni(1)–N(4)	103.2(2)	N(1)–Ni(1)–N(4)	94.0(2)
O(1)–Ni(1)–N(4)	96.8(2)	N(7)–Ni(2)–O(1)	86.2(2)
N(7)–Ni(2)–N(6)	175.4(2)	O(1)–Ni(2)–N(6)	94.5(2)
N(7)–Ni(2)–N(5)	96.4(2)	O(1)–Ni(2)–N(S)	92.9(2)
N(6)–Ni(2)–N(5)	79.0(2)	N(7)–Ni(2)–N(8)	79.3(2)
O(1)–Ni(2)–N(8)	164.5(2)	N(6)–Ni(2)–N(8)	100.4(2)
N(5)–Ni(2)–N(8)	94.1(2)	N(7)–Ni(2)–O(4)	95.0(2)
O(1)–Ni(2)–O(4)	78.96(14)	N(6)–Ni(2)–O(4)	89.6(2)
N(5)–Ni(2)–O(4)	165.5(2)	N(8)–Ni(2)–O(4)	96.8(2)

tion polyhedron, square pyramidal and trigonal bipyramid, together with the value of 0.248 found for the geometrical parameter, τ, defined as $(\beta - \alpha)/60$, where β and α represents the bond angles N(3)–Cu–N(2) and O(3)–Cu–N(4), respectively, suggest that the complex has a geometry closer to a square pyramid, $\tau = 0$, than to a trigonal bipyramid, $\tau = 1$ [27].

The oxygen atom from the phenolato group, the imine nitrogen atom and the amide nitrogen atom from the Schiff base, and one of the 1,10-phenanthroline nitrogen atoms are in the basal plane, with the second 1,10-phenanthroline nitrogen atom occupying the apical position. The angles around the metal involving the apical nitrogen atom are different from 90°, due to the small bite of the phenanthroline ligand: N(1)–Cu–N(2), 76.63(11)°; N(1)–Cu–N(4), 93.98(10)°; N(1)–Cu–N(3), 99.83(11)° and N(1)–Cu–O(3), 104.76(10)°.

The Cu–O distance, 1.932(2) Å, is not very different from others found in pentacoordinated copper complexes, for example 1.936 Å, the average value for the bis-(*N*-dimethylaminoethylsalicylaldiminato)copper(II) [28], or 1.944(7) and 1.957(6) Å in 1,10-phenanthroline{2-[(2-oxyphenyl)iminomethyl]phenolato}copper(II) [29]. Similarly, the Cu–N_{imine} bond distance, 1.940(3) Å, conforms to that found in the above complexes with average values of 1.946 and 1.93(1) Å, respectively.

The bond distances between the copper atom and the two nitrogen atoms of the 1,10-phenanthroline molecule are significantly different at 2.028(3) and 2.320(3) Å, with the longer distance associated with the apical nitrogen atom. The value of 2.028(3) Å can be considered as normal and similar to those found in other copper complexes with bidentate 1,10-phenanthroline or 2,2′-bipyridine ligands [30,31]. However, the 2.320(3) Å value is unusually high and similar to the longest Cu–N distance found in $[Cu(phen)_3]^{2+}$ [31], a

Table 6
Atomic coordinates ($\times 10^4$) for $[CuL^1(phen)]$ (**2**)

	x	y	z	U_{eq}
Cu	2174(1)	1517(1)	3335(1)	27(1)
S	4684(1)	−48(1)	2083(1)	27(1)
O(1)	4867(3)	−1279(2)	1407(2)	36(1)
O(2)	5444(2)	89(2)	2890(1)	32(1)
O(3)	1335(3)	2314(2)	4466(2)	37(1)
N(1)	2252(3)	3230(3)	2567(2)	31(1)
N(2)	4150(3)	2815(3)	3742(2)	25(1)
N(3)	224(3)	391(3)	2935(2)	25(1)
N(4)	2937(3)	100(3)	2303(2)	26(1)
C(1)	1374(5)	3391(4)	1962(3)	42(1)
C(2)	1628(5)	4537(4)	1591(3)	49(1)
C(3)	2822(5)	5560(5)	1870(3)	45(1)
C(4)	3802(4)	5446(3)	2512(2)	34(1)
C(5)	5072(5)	6465(4)	2856(3)	42(1)
C(6)	5982(5)	6285(4)	3457(3)	40(1)
C(7)	5728(4)	5030(3)	3769(2)	30(1)
C(8)	6696(4)	4775(4)	4372(2)	36(1)
C(9)	6374(5)	3555(4)	4624(3)	35(1)
C(10)	5091(4)	2611(4)	4302(2)	29(1)
C(11)	4470(4)	4018(3)	3466(2)	25(1)
C(12)	3465(4)	4231(3)	2832(2)	27(1)
C(13)	−1116(4)	838(3)	4318(2)	27(1)
C(14)	34(4)	1870(3)	4796(2)	28(1)
C(15)	−276(5)	2412(4)	5685(2)	37(1)
C(16)	−1591(4)	1951(4)	6083(3)	37(1)
C(17)	−2693(5)	936(4)	5618(3)	37(1)
C(18)	−2457(4)	406(4)	4755(2)	33(1)
C(19)	−957(4)	186(4)	3416(2)	28(1)
C(20)	267(4)	−328(3)	2041(2)	27(1)
C(21)	1736(4)	−482(3)	1698(2)	26(1)
C(22)	1833(5)	−1180(4)	821(2)	38(1)
C(23)	546(5)	−1661(4)	316(3)	42(1)
C(24)	−862(5)	−1478(4)	653(3)	43(1)
C(25)	−1018(5)	−815(4)	1514(3)	37(1)
C(26)	5498(4)	1432(3)	1690(2)	29(1)
C(27)	4855(5)	1713(4)	985(3)	40(1)
C(28)	5435(5)	2891(4)	707(3)	49(1)
C(29)	6640(5)	3821(4)	1124(3)	49(1)
C(30)	7287(5)	3531(4)	1823(3)	47(1)
C(31)	6722(4)	2338(4)	2108(3)	37(1)
C(32)	7260(11)	5144(7)	833(6)	87(2)

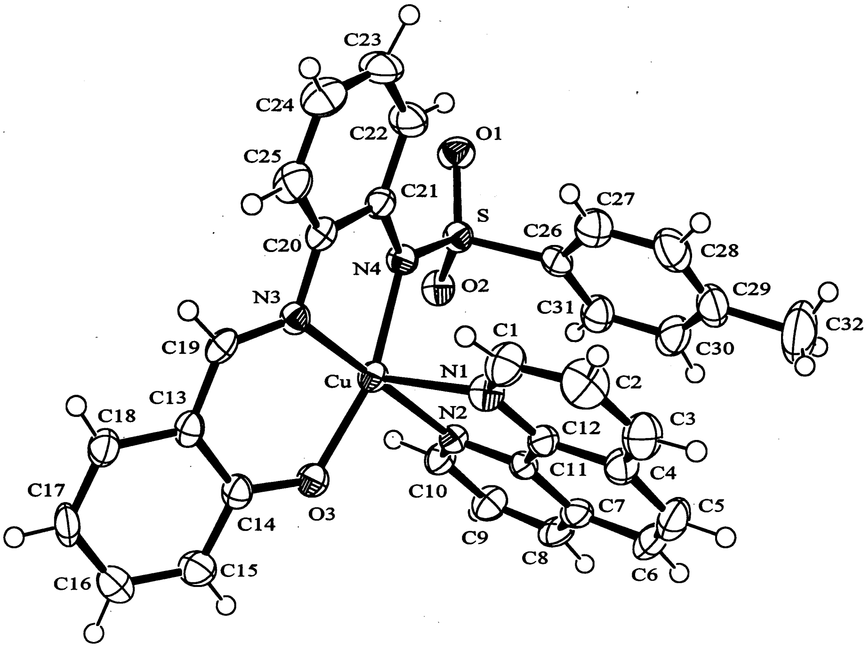

Fig. 2. Molecular structure of [CuL^1(phen)] (**2**).

compound with a very pronounced Jahn–Teller distortion. A similar behaviour is found in the case of 1,10-phenanthroline{2 - [2 - (oxyphenyl)iminomethyl]phenolato}copper(II) [29]. The Cu–N$_{\text{amide}}$ bond length, 2.044(3) Å, is not different from that found in pentacoordinated copper(II) complexes, i.e., 2.041(5) and 2.031(5) Å in [CuL$_2$dmf], with HL standing for *N*-(*p*-tolyl-sulphonyl)-*o*-phenylenediamine) [32]. The two phenyl rings from the Schiff base, including the oxygen donor atoms, are planar, and the 1,10-phenanthroline molecule is also planar.

3.3. Spectroscopic studies

The IR spectra of the complexes show the absence of the ν(OH) and ν(NH) bands which, in the free ligands, appear in the 3100–2800 and 3250 cm^{-1} ranges, respectively. This observation indicates that the phenol hydrogen atom and the amide hydrogen atom are lost during the electrochemical process. The band attributable to ν(CO) of the phenol group is shifted to higher frequencies and the band assignable to the azomethine group is shifted to lower frequencies upon complexation. All these data suggest that the Schiff bases are coordinated in the dianionic form through the phenol oxygen atom and the amide and imine nitrogen atoms, and exhibit the terdentate character of the ligands in the complexes. This conclusion is supported by the X-ray diffraction structures of [Ni$_2$L$_2$^{1}(phen)$_2$] and [CuL^1(phen)]. Therefore, it is reasonable to propose for complexes of general formulae [ML] dimeric or polymeric structures in the solid state, as the metallic atoms would be in a coordinatively unsaturated tricoordinated environment if the compounds were monomeric. The spectra of the mixed complexes show bands of the coordinated phenanthroline at 1510, 850 and 730 cm^{-1} [33], or bipyridine at 760 and 740 cm^{-1} [34].

The solid state electronic spectra of [CoL] show three d–d bands at approximately 9000, 14 000 and 18 000 cm^{-1}, which are in the expected range for hexacoordinated cobalt(II) complexes [35] and can be assigned to the transitions $^4T_{1g} \rightarrow {^4T_{2g}}(\nu_1)$, $^4T_{1g} \rightarrow {^4A_{2g}}(\nu_2)$ and $^4T_{1g} \rightarrow {^4T_{1g}}(P)(\nu_3)$, respectively. These data suggest a

Table 7
Selected bond distances (Å) and angles (°) for [CuL^1(phen)] (**2**)

Bond lengths			
Cu–O(3)	1.936(2)	Cu–N(3)	1.940(3)
Cu–N(2)	2.028(3)	Cu–N(4)	2.044(3)
Cu–N(1)	2.320(3)	S–O(2)	1.434(2)
S–O(1)	1.440(2)	S–N(4)	1.590(3)
S–C(26)	1.778(3)	O(3)–C(14)	1.300(4)
N(1)–C(1)	1.314(5)	N(1)–C(12)	1.347(4)
N(2)–C(10)	1.314(4)	N(2)–C(11)	1.361(4)
N(3)–C(19)	1.283(4)	N(3)–C(20)	1.420(4)
N(4)–C(21)	1.413(4)	C(1)–C(2)	1.394(5)
Bond angles			
O(3)–Cu–N(3)	92.34(11)	N(3)–Cu–N(2)	175.88(11)
O(3)–Cu–N(2)	86.58(10)	N(3)–Cu–N(4)	81.00(11)
O(3)–Cu–N(4)	160.97(10)	O(3)–Cu–N(1)	104.76(10)
N(2)–Cu–N(4)	101.24(10)	N(2)–Cu–N(1)	76.63(11)
N(3)–Cu–N(1)	99.83(11)	O(2)–S–O(1)	115.67(14)
N(4)–Cu–N(1)	93.98(10)	O(1)–S–N(4)	112.74(14)

polymeric hexacoordinated structure for the cobalt complexes.

The solid reflectance spectra of the [CuL] complexes show a broad band around 16 000 cm^{-1} typical of copper(II) species with a square-planar geometry [35]. This environment can be achieved by dimerisation of the compound through the oxygen atom. The dimeric nature of the compound could not be confirmed by determination of the molecular weight for solubility reasons. The solid reflectance spectra for the mixed complexes [CuLL′] show bands around 10 500, 13 000 and 16 000 cm^{-1} in accordance with a pentacoordinated geometry for these complexes [35], which is the structure of [CuL^1(phen)] as established by X-ray diffraction.

The electronic spectra in the solid state for mixed nickel(II) complexes [NiLL′] show bands at approximately 11 000 and 16 000 and between 20 300 and 26 500 cm^{-1} in accord with a hexacoordinated environment around the nickel atom [35]. We propose a binuclear structure for these complexes with the metallic atoms hexacoordinated, through phenoxy groups acting as bridging ligands, as found for the structure of [$Ni_2L_2{}^1(phen)_2$].

The ^1H NMR spectra of the zinc and cadmium complexes show no signals due to the hydrogen atoms from the –NH and –OH groups, reinforcing the IR conclusion that the ligands are coordinated to the metal in its dianionic form. Furthermore, the signal of the azomethine hydrogen atom is shifted towards lower field, around 0.4–0.7 ppm, upon complexation. This behaviour is a consequence of the coordination of the imine nitrogen atom to the metal.

The ^1H NMR of [CdL^1(phen)] complex shows, in addition to the signals of the Schiff base, resonances due to the 1,10-phenanthroline hydrogen atoms around 8.7, 8.2, 7.8 and 7.2 ppm, slightly shifted in comparison with the same signals in the free ligand. This can be taken as a demonstration of coordination of the phenanthroline to the cadmium atom.

4. Supplementary material

Atomic positions, full list of bond distances and angles and other crystallographic data have been deposited as supplementary material.

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