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# Direct electrochemical synthesis of cobalt(II) complexes of tosylamides: crystal structures of $[CoL_2py_2]$ , $[CoL_2DMF_2]$ , $[CoL_2bipy]$ and $[CoL_2phen]$ , L = [(4-methylphenyl)sulfonyl]-2-pyridylamide

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#### Abstract

Several complexes with tosylamides were synthesised by the electrochemical oxidation of cobalt in an acetonitrile solution of [(4-methylphenyl)sulfonyl]-imino-1H-pyridine (HL) and the appropriate neutral coligand: L' (pyridine, 2,2'-bipyridine, 1,10-phenanthroline or *N*,*N*-dimethylformamide). The structures of bis-(*N*,*N*-dimethylformamide)bis{[(4-methylphenyl)sulfonyl]-2-pyridyl-amide}cobalt(II), bis-(pyridine)bis{[(4-methylphenyl)sulfonyl]-2-pyridyl-amide}cobalt(II), 2,2'-bipyridine bis{[(4-methylphenyl)sulfonyl]-2-pyridyl-amide}cobalt(II), and 1,10-phenanthroline bis{[(4-methylphenyl)sulfonyl]-2-pyridyl-amide}cobalt(II) were determined by X-ray diffraction methods. In these monomeric complexes, the cobalt atom is in a distorted octahedral environment. The vibrational and electronic spectra of the complexes are discussed and are shown to agree with the structures. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Electrochemical synthesis; Cobalt(II) complexes; Crystal structures; Tosylamide complexes

## 1. Introduction

The coordination chemistry of amides is scarce due to the difficulty of the substitution of a metal ion for an amide proton. However, if a sulfonamide group substitutes the amide group, the electron withdrawal of the sulfonyl group causes important changes and the formation of the complexes is facilitated [1].

This is one of the reasons why the coordination chemistry of sulfonamide ligands has been investigated in recent years [2,3]. Electron withdrawal of the sulfonyl group causes important changes in both the neutral ligand and in the complexes. Free molecules, such as tosylsulfonylimino-1*H*-pyridine, are expected to exist in



the form I. However, crystallographic and spectroscopic data show that the most stable is II [3]. This electron withdrawal of the sulfonyl group increases the acidity of the hydrogen on the pyridine group and complexes are easily obtained by the deprotonation of

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the ligand. This deprotonation may be carried out with an electrochemical procedure.

Electrochemical methods have been widely used for the synthesis of metallic complexes, especially those of weakly acid organic ligands [4-8]. Of particular relevance to the present work are metal complexes with heterocyclic ligands, such as pyridine derivatives containing, apart from the nitrogen atom, sulfur [9,10], oxygen and sulfur [11] or selenium [12] atoms as additional donor atoms.

In this paper, we now report the electrochemical synthesis and characterisation of several cobalt(II) complexes with the mentioned ligand, where an *N*-tosylamido group substitutes a pyridine ring, and the additional atom is another nitrogen atom.

### 2. Experimental

Acetonitrile, dichloromethane, 2-aminopyridine, tosyl chloride, pyridine, 2,2'-bipyridine, 1,10-phenanthroline, N,N-dimethylformamide and all other reagents were commercial products and were used as supplied. Cobalt (Aldrich Chemie) was used as  $2 \times 2$  cm plates.

The proligand, HL, was prepared by reaction of the amine and the tosyl chloride following the method previously described [3]. Before its use, the product was recrystallized from  $CH_3CN/(CH_3)_2CO$ .

## 2.1. Preparation of complexes. General procedure

The complexes were obtained following an electrochemical procedure [8]. A solution of the proligand and the appropriated coligand (either pyridine, DMF, 2,2'bipyridine or 1,10-phenanthroline) in a mixture of acetonitrile-dichloromethane containing about 20 mg of tetraethylammonium perchlorate as a current carrier was electrolysed using a platinum wire as the cathode and a cobalt plate as the sacrificial anode. In all cases, hydrogen was evolved at the cathode.

# 2.1.1. $[CoL_2 py_2]$ (1)

Electrolysis of an acetonitrile-dichloromethane (25 + 25 ml) solution containing the proligand HL (201.4 mg, 0.81 mmol), pyridine (ca. 1 ml) and tetraethylammonium perchlorate (ca. 20 mg) at 10 mA and 14 V for 2 h dissolved 21.1 mg of cobalt ( $E_f = 0.48$ ). At the end of the experiment the pale pink solid product was filtered, washed with hot acetonitrile and ether and dried in vacuo. The compound was characterised as [CoL<sub>2</sub>py<sub>2</sub>]: *Anal*. Found: H, 4.7; C, 57.2; N, 11.8; S, 8.7. Calc. for [C<sub>34</sub>H<sub>32</sub>CoN<sub>6</sub>O<sub>4</sub>S<sub>2</sub>]: C, 57.4; H, 4.5; N, 11.8; S, 9.0%. IR (KBr, cm<sup>-1</sup>): 3071(m), 3069(m), 2973(sh), 1593(s), 1463(s), 1315(b), 1135(b), 1038(s), 981(vb), 702(s), 662(s), 579(s), 559(b), 531(s), 430(m). Crystals suitable for X-ray diffraction studies were obtained by crystallisation from  $(CH_3)_2CO-CH_3CN$ .

# 2.1.2. $[CoL_2(DMF)_2]$ (2)

Electrolysis of an acetonitrile–*N*,*N*-dimethylformamide (50 + 10 ml) solution containing HL (327.8 mg, 1.3 mmol) and tetraethylammonium perchlorate (ca. 20 mg) at 10 mA and 14 V for 2.2 h dissolved 22.2 mg of cobalt ( $E_f = 0.46$ ). At the end of the experiment the pale pink solid product was filtered, washed with hot acetonitrile and ether and dried in vacuo. The compound was characterised as [CoL<sub>2</sub>DMF<sub>2</sub>]: *Anal.* Found: H, 4.93; C, 51.6; N, 12.09; S, 9.52. Calc. for [C<sub>30</sub>H<sub>36</sub>CoN<sub>6</sub>O<sub>6</sub>S<sub>2</sub>]: C, 51.50; H, 5.19; N, 12.01; S, 9.17%. IR (KBr, cm<sup>-1</sup>): 3082(w), 3064(vw), 2923(m), 2851 (w), 1650(s), 1596(m), 1466(s), 1450(m), 1392(m), 1321(s), 1265(m), 1137(m), 1090(m), 784(m), 661(m), 577(m), 554(m). Crystals were obtained by recrystallisation from (CH<sub>3</sub>)<sub>2</sub>CO–CH<sub>3</sub>CN.

## 2.1.3. $[CoL_2 bipy]$ (3)

Electrolysis of an acetonitrile-dichloromethane (25 + 25 ml) solution containing HL (201.0 mg, 0.81 mmol), 2,2'-bipyridine (67.2 mg, 0.43 mmol) and tetraethylammonium perchlorate (ca. 20 mg) at 10 mA and 10 V for 2.16 h dissolved 22.1 mg of cobalt ( $E_f = 0.47$ ). At the end of the experiment the pale pink solid was filtered, washed with hot acetonitrile and ether and dried in vacuo. The compound was characterised as [CoL<sub>2</sub>bipy]. *Anal.* Found: C, 57.5; H, 4.5; N, 11.8; S, 8.9. Calc. for [C<sub>34</sub>H<sub>30</sub>CoN<sub>6</sub>O<sub>4</sub>S<sub>2</sub>]: C, 57.5; H, 4.3; N, 11.8; S, 9.0%. IR (KBr, cm<sup>-1</sup>): 3107(w), 3064(vw), 2919(m), 1595(s), 1465(s), 1319(s), 1138(s), 1138(s), 1088(m), 1011(m), 976 (m), 764(m), 736(s), 667(s). Crystals were obtained by crystallisation from (CH<sub>3</sub>)<sub>2</sub>CO-CH<sub>3</sub>CN.

# 2.1.4. $[CoL_2 phen]$ (4)

Electrolysis of an acetonitrile-dichloromethane (25+25 ml) solution containing HL (202.1, 0.81) mmol), 1,10-phenanthroline (83.3 mg, 0.46 mmol) and tetraethylammonium perchlorate (ca. 20 mg) at 10 mA and 13.5 V for 2.12 h dissolved 21.7 mg of cobalt  $(E_t = 0.46)$ . At the end of the experiment the pale pink solid was filtered, washed with hot acetonitrile and ether and dried in vacuo. The compound was characterised as [CoL2phen]: Anal. Found: C, 58.74; H, 4.23; N, 11.52, S, 8.41. Calc. for [C<sub>36</sub>H<sub>30</sub>CoN<sub>6</sub>O<sub>4</sub>S<sub>2</sub>]: C, 58.93; H, 4.12; N, 11.45; S, 8.74%. IR (KBr, cm<sup>-1</sup>): 3062(w), 3023(w), 2921(sh), 1588(s), 1559(s), 1515(m), 1495(m), 1315(m), 1178(m), 1134(m), 1038 (m), 981(m), 847(m), 727(s), 702(s), 662(m). Crystals by crystallisation from (CH<sub>3</sub>)<sub>2</sub>CO-CH<sub>3</sub>CN.

## 2.2. Physical measurements

The C, N, H and S contents of the compounds were determined on a Carlo–Erba EA 1108 microanalyser. IR spectra were recorded as KBr mulls on a Bruker Vector-22 spectrophotometer. The <sup>1</sup>H NMR spectrum of the ligand was recorded on a Bruker ARX-400 MHz spectrometer using Cl<sub>3</sub>CD as solvent. Solid-state electronic spectra were recorded on a Shimadzu UV 3101 PC. Magnetic measurements were made using a DMS VSM 1160 instrument.

## 2.3. Crystal structure determination

The data collection, in all the cases at room temperature, was taken on a MACH3 Enraf–Nonius using Mo K $\alpha$  radiation for [CoL<sub>2</sub>py<sub>2</sub>] and for [CoL<sub>2</sub>bipy]. Data were corrected for polarization and Lorentz effects.  $\Psi$ -scan absorption corrections were applied [13]. The data collection for [CoL<sub>2</sub>DMF<sub>2</sub>] and [CoL<sub>2</sub>phen] was taken on a Siemens Smart CCD area-detector diffractometer with graphite-monochromated Mo K $\alpha$  radiation. Absorption corrections were carried out using SADABS [14].

All the structures were solved by direct methods and refined by a full-matrix least-squares based on  $F^2$  [15]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Correct absolute structures of [CoL<sub>2</sub>phen] were determined by using the Flack parameter [16]. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken

Table 1

from the International Tables for X-ray Crystallography [17]. Details of crystal data and structural refinement are given in Table 1.

## 3. Results and discussion

Anodic oxidation of cobalt metal in a non-aqueous solution containing (4-methylphenyl)sulfonyl]imino-1*H*-pyridine and one coligand as pyridine (py), *N*,*N*dimethylformamide (DMF), 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) yields crystalline products of formulae [CoL<sub>2</sub>py<sub>2</sub>], [CoL<sub>2</sub>DMF<sub>2</sub>], [CoL<sub>2</sub>bipy] and [CoL<sub>2</sub>phen], respectively. The values of the electrochemical efficiency, defined as the amount of metal dissolved per number of Faradays, were close to 0.5 mol F<sup>-1</sup> in all cases. This value is compatible with the mechanism

Cathode:  $2HL + 2e^- \rightarrow 2L^- + H_2$ 

Anode:  $\text{Co} \rightarrow \text{Co}^{2+} + 2e^{-}$ 

The overall reactions can be described as

 $\operatorname{Co} + 2\operatorname{HL} + n\operatorname{L'} \rightarrow [\operatorname{CoL}_2\operatorname{L'}_n] + \operatorname{H}_2$ 

n = 1; L' = bipy or phen.

n = 2; L' = py or DMF.

3.1. Description of the structures of  $[CoL_2 py_2](1)$ ,  $[CoL_2 DMF_2]$  (2),  $[CoL_2 bipy]$  (3), and  $[CoL_2 phen]$  (4)

The molecular structures are shown in Figs. 1–4. Selected bond lengths and angles are given in Tables

Compound	$[CoL_2py_2]$	$[CoL_2DMF_2]$	[CoL <sub>2</sub> bipy]	[CoL <sub>2</sub> phen]
Empirical formula	C <sub>17</sub> H <sub>16</sub> Co <sub>0.5</sub> N <sub>3</sub> O <sub>2</sub> S	C <sub>15</sub> H <sub>18</sub> Co <sub>0.5</sub> N <sub>3</sub> O <sub>3</sub> S	C <sub>34</sub> H <sub>30</sub> CoN <sub>6</sub> O <sub>4</sub> S <sub>2</sub>	C <sub>36</sub> H <sub>30</sub> CoN <sub>6</sub> O <sub>4</sub> S <sub>2</sub>
Formula weight	355.85	349.85	709.69	733.71
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no 14)	$P2_1/n$ (no 14)	$P2_1/n$ (no. 14)	<i>P</i> 2 <sub>1</sub> (no. 4)
Unit cell dimensions				
a (Å)	9.5603(11)	9.5240(2)	10.8443(19)	9.4524(5)
b (Å)	18.934(2)	18.5979(3)	21.2416(6)	19.6321(10)
c (Å)	9.7615(15)	10.21420(10)	14.386(4)	9.6993(5)
β (°)	109.457(9)	111.4133(7)	93.90(3)	109.8834(11)
Volume (Å <sup>3</sup> )	1666.0(4)	1684.32(5)	3306.0(11)	1692.6(2)
Ζ	4	4	4	2
Absorption coefficient (mm <sup>-1</sup> )	0.688	0.683	0.693	0.680
Reflections collected	4226	11983	7059	9376
Independent reflections	4001 $[R_{int} = 0.0750]$	4113 $[R_{int} = 0.0226]$	6704 $[R_{int} = 0.1331]$	7312 $[R_{int} = 0.0410]$
Reflections observed $[>2\sigma(I)]$	1546	3452	2297	4864
Data/restraints/parameters	4001/0/266	4113/0/205	6703/0/424	7312/1/442
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0495,$	$R_1 = 0.0363,$	$R_1 = 0.0642,$	$R_1 = 0.0718,$
	$wR_2 = 0.0853$	$wR_2 = 0.0955$	$wR_2 = 0.1276$	$wR_2 = 0.1294$
Absolute structure parameter	-	-	2	-0.03(2)
Largest difference peak and hole (e $Å^{-3}$ )	0.345  and  -0.340	0.290  and  -0.423	0.540  and  -0.556	0.287 and -0.506



Fig. 1. Molecular structure of  $[CoL_2py_2]$  (1).



Fig. 2. Molecular structure of  $[CoL_2DMF_2]$  (2).

2-5 for each compound. In the four complexes the cobalt atom is in a highly distorted octahedral environment but they are different to each other. In the case of 1, 3 and 4, the environment is  $[CoN_6]$ , and in 2 is  $[CoO_2N_4]$ . Compounds 1 and 2 contain two N–N anionic ligands and two monodentate ligands, but 3 and 4 have three bidentate N–N ligands, two anionic and one neutral.

## 3.1.1. Molecular structure of $[CoL_2 py_2]$ (1)

The cobalt atom in  $[CoL_2py_2]$  is in an octahedral environment  $[CoN_6]$ . The nitrogen atoms of the two neutral pyridine molecules are in *trans* positions, and the nitrogen atoms of the two anionic tosylato ligands are in the equatorial plane. As the cobalt atom is in a symmetry center, the equivalent nitrogen atoms of the tosylato ligands are in *trans* positions. The Co–N bond lengths of the apical positions are slightly longer, 2.164(3) Å, than the Co–N bonds lengths on the equatorial plane, 2.125(3) and 2.138(3) Å. This is probably because the apical ligands are neutral, but the ligands in the equatorial plane are

anionic. Similar behaviour has been found in the pyridine complex containing other anionic ligands, such as in diaqua-dipyridyl-bis(N-(4-methyl-2-sulfamoyl- $\Delta^2$ -1, 3,4-thiadiazolin-5-ylidene)acetamide)cobalt(II) [18], with a Co(II)–N<sub>py</sub> distance of 2.198(2) Å and other



Fig. 3. Molecular structure of [CoL<sub>2</sub>bipy] (3).



Fig. 4. Molecular structure of [CoL<sub>2</sub>phen] (4).

Table 2									
Selected	bond	lengths	(Å)	and	angles	(°)	for	[CoL	<sub>2</sub> py <sub>2</sub> ]

Co-N(11)	2.125(3)	Co-N(11 <sup>a</sup> )	2.125(3)
Co-N(12 <sup>a</sup> )	2.138(3)	Co-N(12)	2.138(3)
Co-N(21)	2.164(3)	Co-N(21 <sup>a</sup> )	2.164(3)
S(1)–N(12)	1.588(3)	S(1)-C(16)	1.772(4)
N(11)-C(11)	1.330(5)	N(11)-C(15)	1.350(5)
N(12)-C(15)	1.383(5)	N(21)-C(25)	1.323(5)
N(21)-C(21)	1.316(5)		
N(11)-Co-N(11 <sup>a</sup> )	180.0	N(11)-Co-N(12 a)	117.07(11)
N(11)-Co-N(12)	62.93(11)	N(12 a)-Co-N(12)	180.0
N(11)-Co-N(21)	91.71(13)	N(12)-Co-N(21)	87.93(12)
N(11)-Co-N(21 a)	88.29(13)	N(12)-Co-N(21 a)	92.07(13)
N(21)-Co-N(21 a)	180.0	N(12)-S(1)-C(16)	107.82(18)
C(11)-N(11)-C(15)	118.6(4)	C(15)-N(12)-S(1)	123.7(3)
N(11)-C(11)-C(12)	123.6(5)	N(11)-C(15)-N(12)	108.9(3)
C(21)-N(21)-C(25)	117.2(4)	N(21)-C(21)-C(22)	123.3(5)
N(21)-C(25)-C(24)	122.5(5)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: -x+1, -y+1, -z+1.

Co–N distance of 2.108(2) Å. Nevertheless, there are some examples where the Co–N<sub>py</sub> bond lengths are longer than the other Co–N bond lengths and all the ligands are neutral. That is the case for (1,3,5-tris-(pyridine-2-carboxaldimino)-cyclohexane- $N^1, N^2, N^3, N^4$ ,  $N^5, N^6$ )cobalt(II) diperchlorate [19], with average bond distances Co–N<sub>py</sub> of 2.231 Å and Co–N<sub>imino</sub> of 2.131 Å, or (1,1,1-tris(pyridine-2-aldiminomethyl)ethane)cobalt(II) diperchlorate [20] with average bond distances Co–N<sub>py</sub> of 2.150 Å and Co–N<sub>imino</sub> of 2.097 Å.

A tetrahedral coordination around the cobalt atom has been found for bis{[(4-methylphenyl)sulfonyl][2-(2-pyridyl)phenyl]amine}cobalt(II) [2]. In this case, the Co–N distances are shorter, average Co–N<sub>amide</sub> = 1.963(2) and Co–N<sub>py</sub> = 2.042(2) Å, as expected for a complex with a lower coordination number.

The ligand bond distances and angles are normal and do not deserve special discussion. The neutral pyridine is almost perpendicular to the pyridine ring belonging to the anionic ligand, with a dihedral angle of  $86.93(12)^\circ$ . The pyridine ring of the anionic ligand is almost coplanar with the small chelate ring Co-N(12)-C(15)-N(11), with a dihedral angle of  $3.92(14)^\circ$ .

The most important deviation of the octahedron from regularity is the small bite of the ligand,  $62.93(11)^\circ$ . This value is in the range for a four-member chelate ring found for complexes of cobalt(II): 55.3° in hexakis[( $\mu^2$ -methoxo)-( $\mu^2$ - $\sigma^3$ -1,5-di-*p*-tolyl-1,4-pentaazadienido)cobalt(II)] mesitylene solvate [21] and 65.8° in diaqua-bis[(N,N'-methylene-bis(L-prolinato)]cobalt(II) sesquihydrate [22] or 65.5° in diaqua-[N,N'methylene-bis(4-hydroxy-L-prolinato)]cobalt(II) [23].

## 3.1.2. Molecular structure of $[CoL_2 DMF_2]$ (2)

In this compound, the metal environment is  $[CoN_4O_2]$ . The cobalt atom is in a centre of symmetry coordinated by two *N*,*N*-bidentate anionic ligands and by two molecules of DMF through the oxygen atom. The coordination polyhedron can be described as an octahedron with the neutral DMF ligands in the axial positions and the anionic ligands in the equatorial plane. As happens in  $[CoL_2py_2]$ , the ligands in the apical positions are slightly farther than the ligands in the equatorial plane. All the other features are very

Table 3 Bond lengths (Å) and angles (°) for [CoL<sub>2</sub>DMF<sub>2</sub>]

Co–N(1 <sup>a</sup> )	2.1194(15)	Co-N(1)	2.1194(15)
Co–N(2 <sup>a</sup> )	2.1415(14)	Co-N(2)	2.1415(13)
Co-O(21 <sup>a</sup> )	2.1635(14)	Co-O(21)	2.1635(14)
S-N(2)	1.5856(14)	S-C(6)	1.7808(18)
N(1)-C(1)	1.344(2)	N(1)-C(5)	1.353(2)
N(2)-C(5)	1.387(2)	N(21)-C(22)	1.473(3)
O(21)-C(21)	1.229(3)	N(21)-C(21)	1.321(2)
N(21)-C(23)	1.434(3)		
N(1 <sup>a</sup> )–Co–N(2 <sup>a</sup> )	62.97(5)	N(1)-Co-N(2 a)	117.03(5)
N(1 <sup>a</sup> )–Co–N(2)	117.03(5)	N(1)-Co-N(2)	62.97(5)
N(2 <sup>a</sup> )–Co–N(2)	180.0	N(1 <sup>a</sup> )–Co–O(21 <sup>a</sup> )	87.97(6)
N(1)-Co-O(21 <sup>a</sup> )	92.03(6)	N(2 <sup>a</sup> )–Co–O(21 <sup>a</sup> )	86.41(6)
N(2)-Co-O(21 <sup>a</sup> )	93.59(6)	N(1 <sup>a</sup> )-Co-O(21)	92.03(6)
N(1)-Co-O(21)	87.97(6)	N(2 <sup>a</sup> )–Co–O(21)	93.59(6)
N(2)-Co-O(21)	86.41(6)	O(21 <sup>a</sup> )–Co–O(21)	180.0
N(1 <sup>a</sup> )–Co–N(1)	180.0	N(2)-S-C(6)	108.91(8)
C(23)-N(21)-C(22)	117.8(2)	C(21)-O(21)-Co	127.91(14)
O(21)-C(21)-N(21)	125.5(2)	C(21)-N(21)-C(23)	121.1(2)
C(21)-N(21)-C(22)	121.0(2)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: 1-x+, 1-y, 1-z.

Table 4

Selected bond lengths (Å) and angles (°) for [CoL2bipy]

Co-N(21)	2.065(5)	Co-N(31)	2.107(6)
Co-N(32)	2.120(5)	Co-N(11)	2.120(5)
Co-N(12)	2.185(5)	Co-N(22)	2.259(5)
S(1)-N(12)	1.606(6)	S(1)-C(16)	1.774(7)
S(2)-N(22)	1.586(5)	S(2)-C(26)	1.774(7)
N(11)-C(11)	1.345(8)	N(11)-C(15)	1.353(8)
N(12)-C(15)	1.357(8)	N(21)-C(21)	1.332(8)
N(21)-C(25)	1.361(8)	N(22)-C(25)	1.369(8)
N(31)-C(36)	1.336(8)	N(31)-C(310)	1.347(8)
N(32)-C(31)	1.332(8)	N(32)-C(35)	1.341(8)
N(21)-Co-N(31)	111.3(2)	N(21)-Co-N(32)	94.3(2)
N(31)-Co-N(32)	76.6(2)	N(21)-Co-N(11)	145.0(2)
N(31)-Co-N(11)	96.4(2)	N(32)-Co-N(11)	113.1(2)
N(21)-Co-N(12)	96.0(2)	N(31)-Co-N(12)	152.0(2)
N(32)-Co-N(12)	95.7(2)	N(11)-Co-N(12)	61.4(2)
N(21)-Co-N(22)	61.36(19)	N(31)-Co-N(22)	94.0(2)
N(32)-Co-N(22)	149.1(2)	N(11)-Co-N(22)	97.01(19)
N(12)-Co-N(22)	105.0(2)	N(12)-S(1)-C(16)	108.3(3)
N(22)-S(2)-C(26)	107.3(3)	C(11)–N(11)–C(15)	119.2(6)
C(11)-N(11)-Co	144.1(5)	C(15)-N(11)-Co	96.6(4)
C(15)–N(12)–S(1)	123.4(5)	N(11)-C(15)-N(12)	108.5(6)
N(11)-C(15)-C(14)	120.6(7)	N(12)-C(15)-C(14)	131.0(7)

Table 5 Selected bond lengths (Å) and angles (°) for [CoL<sub>2</sub>phen]

Co-N(31)	2.113(5)	Co-N(22)	2.120(6)
Co-N(32)	2.122(5)	Co-N(12)	2.140(5)
Co-N(11)	2.143(5)	Co-N(21)	2.215(6)
S(1)-N(12)	1.587(5)	S(1)-C(16)	1.782(7)
S(2)-N(22)	1.586(6)	S(2)-C(26)	1.779(6)
N(12)-C(15)	1.399(8)	N(11)-C(15)	1.349(8)
N(11)-C(11)	1.351(8)	N(21)-C(21)	1.341(9)
N(21)-C(25)	1.342(8)	N(22)-C(25)	1.390(8)
N(31)-C(31)	1.339(8)	N(31)-C(311)	1.340(8)
N(32)-C(310)	1.329(8)	N(32)-C(312)	1.363(7)
N(31)-Co-N(22)	100.6(2)	N(31)-Co-N(32)	78.4(2)
N(22)-Co-N(32)	104.5(2)	N(31)-Co-N(12)	99.0(2)
N(22)-Co-N(12)	154.2(2)	N(32)-Co-N(12)	95.6(2)
N(31)-Co-N(11)	159.4(2)	N(22)-Co-N(11)	99.7(2)
N(32)-Co-N(11)	93.8(2)	N(12)-Co-N(11)	62.5(2)
N(31)-Co-N(21)	96.6(2)	N(22)-Co-N(21)	61.8(2)
N(32)-Co-N(21)	164.7(2)	N(12)-Co-N(21)	99.5(2)
N(11)-Co-N(21)	95.3(2)	O(11)-S(1)-N(12)	106.9(3)
O(12)-S(1)-N(12)	112.0(3)	O(11)-S(1)-C(16)	107.3(3)
O(12)-S(1)-C(16)	106.3(3)	N(12)-S(1)-C(16)	106.1(3)
N(22)-S(2)-C(26)	105.8(3)	C(15)-N(12)-S(1)	122.6(4)
C(15)–N(11)–C(11)	118.5(6)		

similar to those in  $[CoL_2py_2]$ . The Co–O bond length (2.1635(14) Å) and the angles C–O–Co (127.91(14)°) are in the range for Co(II) complexes with DMF as the ligand, like, for example, *trans*-bis(benzo(1,3)-thiazole)-bis(*N*,*N* - dimethylformamide) - bis(isothiocyanato)co-balt(II) [24], with values of 2.118 Å and 126.14°, respectively.

#### 3.1.3. Molecular structure of $[CoL_2 bipy]$ (3)

The cobalt atom in 3 is in a distorted octahedral environment  $[CoN_6]$ , with the two anionic tosyl ligands and the neutral bipyridine molecule as N,N-bidentate ligands. The small bite angles of the ligands, especially in the case of the anionic ligand, are the main reason for the distortion. So, the angles  $N_{\text{amide}}$ -Co- $N_{\text{pyridine}}$  are 61.3(2) and  $61.4(2)^{\circ}$  in each anionic ligand, with a chelate ring of four members (see above) and 76.6(2)° in the bipyridine, with a chelate ring of five members. The pyridine fragments of the anionic ligands are in trans positions, and consequently if these are considered as the apical positions, the equatorial plane is formed by the amide nitrogen atoms of the tosylamide ligands and the nitrogen atoms of the bipyridine molecule. The cobalt atom is 0.024(3) Å out of this equatorial plane. The pyridine rings in trans positions are also almost perpendicular between them, dihedral angle of 80.5(2)°, and form dihedral angles with the equatorial plane of 76.5(2) and 79.3(2)°. It is worth noting that while the Co-N bond distances in the case of one of the tosyl ligands are quite similar, 2.121(6) and 2.185(6) Å, for the other one, one of the distances is significantly

shorter than the other, 2.259(6) and 2.066(6) Å. Such disposition of the ligands around the metal corresponds approximately to non-crystallographic two-fold point symmetry.

The distances Co–N<sub>bipy</sub>, 2.106(6) and 2.119(6) Å, are slightly shorter that those found in tris(2,2'bipyridine)cobalt(II) dichloride [25], average 2.130 Å, or in *cis*-dichloro-bis(2,2'-bipyridyl-N,N')cobalt(II) [26], average 2.154 Å.

The distances and angles of the anionic ligands are normal, with dihedral angles between the rings of 83.5(2) and  $78.2(2)^\circ$ , this last one in the case of the anisodentate ligand. The free ligand shows dihedral angles of 83.7(1) and  $87.6(1)^\circ$  [3].

## 3.1.4. Molecular structure of $[CoL_2 phen]$ (4)

Compound 4 contains a cobalt atom in a distorted octahedral geometry coordinated by two nitrogen atoms of an neutral ligand (phen), and by four nitrogen atoms of two anionic ligands. This is similar to 3, but there is an important difference between these compounds in the disposition of the ligands around the metal. In the case of 4, the amide nitrogen atoms of the anionic ligands occupy the axial positions, and the equatorial plane is formed by the pyridine nitrogen atoms of the anionic ligands and the nitrogen atoms of the phenanthroline molecule. This structure corresponds to that of the  $\Lambda$  isomer. This geometry has also been found in the corresponding Ni(II) complexes with this ligands and either bipyridine or phenanthroline [3].

The Co–N distances to one of the anionic ligands are very similar, 2.140(5) and 2.143(5) Å, but the other anionic ligand again shows an anisobidentate behaviour, Co–N distances 2.120(6) and 2.215(6) Å. The dihedral angle between the pyridine ring and the phenyl ring is 85.12(18) and  $81.98(23)^\circ$  in each ligand, respectively. The disposition of the pyridine rings of the ligands are almost perpendicular, with a dihedral angle between the pyridine rings of  $89.95(22)^\circ$ .

The distances Co– $N_{phen}$  (2.113(5) and 2.122(5) Å) are quite similar to those found in 1,10-phenanthroline bis{2-[(2-pyrrole)methylimino]phenolato}cobalt(II) [27], 2.22 and 2.16 Å, and in tris(1,10-phenanthroline)cobalt(II) diperchlorate monohydrate [28] (average 2.128 Å, max. 2.141 Å, min. 2.109 Å).

#### 3.2. Spectroscopic and magnetic studies

The IR spectra of the complexes do not show the band attributable to v(N-H), which in the free ligand appears at 3230 cm<sup>-1</sup>, confirming that the hydrogen atom of the amide group is lost during the electrolysis. The IR spectra of the mixed complexes show IR absorptions typical of coordinated pyridine (662 and 430

cm<sup>-1</sup>), *N*,*N*-dimethylformamide (2923, 2850, 1650 and 1392 cm<sup>-1</sup>), 2,2'-bipyridine (764 and 736 cm<sup>-1</sup>) and 1,10-phenanthroline (1515, 847 and 727 cm<sup>-1</sup>).

The magnetic moments of  $[CoL_2py_2]$ , 4.49 BM  $[CoL_2DMF_2]$ , 4.39 BM  $[CoL_2bipy]$ , 4.41 BM and  $[CoL_2phen]$  4.66 BM, are in the low limit for high-spin Co(II) complexes (4.7–5.2 BM). The solid reflectance spectra of  $[CoL_2py_2]$ ,  $[CoL_2DMF_2]$ ,  $[CoL_2bipy]$  and  $[CoL_2phen]$  show three bands at 28 170, 21 500, 9700, 28 450, 20 325, 8740, 25 757, 20 800, 8830 and 25 850, 20 600, 8925 cm<sup>-1</sup>, respectively. They can be assigned to the  ${}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}(F)$ ,  ${}^{4}A_{2g} \leftarrow {}^{4}T_{1g}$  and  ${}^{4}T_{2g} \leftarrow {}^{4}T_{1g}$  transitions, and are in accordance with an octahedral geometry for the complex. These conclusions are in keeping with the X-ray diffraction results.

#### 4. Supplementary material

The atomic positions, full list of bond lengths and angles and other crystallographic data are available on request from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk), quoting the deposition numbers CCDC 139406–139409.

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