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Synthesis and Characterization of Homoleptic and Heteroleptic Cobalt, Nickel, Copper, Zinc and Cadmium Compounds with the 2-(Tosylamino)-*N*-[2-(tosylamino)benzylidene]aniline Ligand

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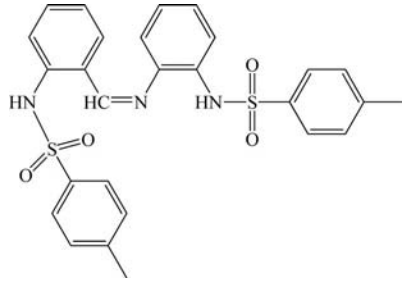
The electrochemical oxidation of anodic metal (cobalt, nickel, copper, zinc and cadmium) in an acetonitrile solution of the Schiff-base ligand 2-(tosylamino)-*N*-[2-(tosylamino)-benzylidene]aniline (H_2L) afforded the homoleptic compounds [ML]. The addition of 1,1-diphenylphosphanylmethane (dppm), 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) to the electrolytic phase gave the heteroleptic complexes [NiL(dppm)], [ML(bipy)] and [ML(phen)]. The crystal structures of H_2L (**1**), [NiL] (**2**), [CuL] (**3**), [NiL(dppm)] (**4**), [CoL(phen)] (**5**), [CuL(bipy)] (**6**) and [Zn(Lphen)] (**7**) were determined by X-ray diffraction. The homoleptic compounds [NiL] and [CuL] are mononuclear with a distorted square planar [MN_3O] geometry with the Schiff base acting as a dianionic ($N_{amide}N_{amide}N_{imine}O_{tosyl}$) tetradentate ligand. Both compounds exhibit an unusual π–π stacking interaction between a six-membered chelate ring containing the metal and a phenylic ring of the ligand. In the heteroleptic complex [NiL(dppm)], the nickel atom is in a distorted tetrahedral [NiN_3P] environment defined by the imine, two amide nitrogen atoms of the L^{2-} dianionic tridentate ligand and one of the phosphorus atoms of the dppm molecule. In the other heteroleptic complexes, [CoL(phen)], [CuL(bipy)] and [ZnL(phen)], the metal atom is in a five-coordinate environment defined by the imine, two amide nitrogen atoms of the dianionic tridentate ligand and the two bipyridine or phenanthroline nitrogen atoms. The compounds were characterized by microanalysis, IR and UV/Vis (Co, Ni and Cu complexes) spectroscopy, FAB mass spectrometry and ^{1}H NMR ([NiL] and Zn and Cd complexes) and EPR spectroscopy (Cu complexes).

Introduction

The chemistry of metal complexes with amide ligands has been widely studied, partly due to the use of such compounds as antibacterial drugs in the field of medicine.[1] In particular, copper(II)[2] and zinc(II)[3] complexes have been used in the treatment of numerous diseases and carbonic anhydrase inhibitory properties have been studied for Ni^{II} complexes.[4] However, it is well known that metal complex formation by the substitution of an amide proton by a metal ion is not an easy process.[5] This complexation process is facilitated by the presence in the amide groups of electron-withdrawing substituents, such as a sulfonyl group, which increases the acidity of the N–H group and makes deprotonation of the ligand, and thus metal complex formation, easier.[6]

For the reasons outlined above, and as a result of our continued interest in the chemistry of metal complexes with amide ligands, we report herein the synthesis of metal(II) complexes with 2-(tosylamino)-*N*-[2-(tosylamino)benzylidene]aniline, a molecule that contains two weakly acidic N–H groups and an imine group (Scheme 1). Owing to the presence in the ligand of these weakly acidic groups, homoleptic complexes were prepared by using an electrochemical procedure in which the metal was the anode of a cell containing the Schiff-base ligand in acetonitrile solution. The presence in the electrolytic cell of the Schiff base and co-



Scheme 1.

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ligands, such as 1,1-diphenylphosphanylmethane, 2,2′-bipyridine or 1,10-phenanthroline, allowed the synthesis of heteroleptic compounds in one step. This method has been successfully used for the synthesis of metal compounds with other ligands that contain weak acid groups, such as thiol,[7–10] NH[11–13] or hydroxy groups.[14–17]

Results and Discussion

Synthesis and General Characterization

The analytical data of the products show that the electrochemical procedure described can be satisfactorily used to obtain good yields in the synthesis of complexes of homo- and heteroleptic cobalt, nickel(II), copper(II), zinc(II) and cadmium(II) sulfonamide complexes [ML], [NiL(dppm)] and [MLL′] (L′ = phen or bipy). This method represents a simple alternative to other standard chemical procedures.

The electrochemical efficiency, defined as mole of metal dissolved per Faraday of charge, was close to 1 mol F^{-1} for the copper complexes, which shows that anodic oxidation leads initially to a Cu^{I} compound. However, the analytical data show that the complex is [CuL] or [CuLL′]. This suggests that the ligand oxidizes Cu^{I} to Cu^{II} in solution as soon as it is formed.

Cathode: $H_2L + 2\,e^- \longrightarrow L^{2-} + H_2(g)$

Anode: $Cu \longrightarrow Cu^+ + e^-$

Solution: $2\,Cu^+ + H_2L \longrightarrow 2\,Cu^{2+} + L^{2-} + H_2(g)$

Overall: $Cu + H_2L \longrightarrow [CuL] + H_2(g)$

or: $Cu + H_2L + L' \longrightarrow [CuLL'] + H_2(g)$

where L' is bipy or phen

This behaviour has been observed previously in the synthesis of other copper complexes by electrochemical procedures.[11,12,14]

For the other metals, the electrochemical efficiency of the cell was close to 0.50 mol F^{-1}. This fact, along with the evolution of hydrogen at the cathode, is compatible with the following reaction mechanisms:

Cathode: $H_2L + 2\,e^- \longrightarrow H_2(g) + L^{2-}$

Anode: $M \longrightarrow M^{2+} + 2\,e^-$

Overall: $H_2L + M \longrightarrow [ML] + H_2(g)$

or: $H_2L + M + L' \longrightarrow [MLL'] + H_2(g)$

where M = Co, Ni, Zn or Cd and L' is bipy or phen

or: $H_2L + Ni + dppm \longrightarrow [NiL(dppm)]$

Structure of the Ligand (H_2L)

The crystal structure of the ligand has been published previously.[18] However, the crystal packing was not described and this aspect is of great interest in terms of understanding the interactions that influence the packing arrangements in the complexes and this topic is discussed in the Supporting Information.

Homoleptic Complexes

The electrochemical oxidation of anodic cobalt, nickel, copper, zinc or cadmium in a cell containing 2-(tosylamino)-*N*-[2-(tosylamino)benzylidene]aniline (H_2L) in acetonitrile gave the complexes [ML]. The complexes were obtained as crystalline materials by concentration of the acetonitrile solution by evaporation in air.

Structures of [NiL] (2) and [CuL] (3)

The molecular structures of complexes **2** and **3** are shown in Figure 1 along with the atomic numbering schemes adopted. Selected bond lengths and angles are given in Table 1. The two compounds are isostructural and consist of monomer units. In both complexes the metal atom is tetracoordinated to two amide nitrogen atoms, the imine nitrogen atom and one of the oxygen atoms of one of the tosyl groups of the dianionic tetradentate Schiff base. In both compounds the coordination polyhedron around the metal atom is distorted square planar with the amide nitrogen atoms in a *trans* disposition. This distortion is caused mainly by the small bite angle, 68.20(13)° for [CuL] and 72.59(19)° for [NiL] complexes with a four-membered chelate ring, and to a lesser extent by other angles involving five- {85.62(14)° for [CuL] and 86.0(2)° for [NiL]} and six-membered {92.87(15)° for [CuL] and 94.4(2)° for [NiL]} chelating ligand rings, which also deviate from the theoretical value. The square-planar geometry of the metal(II) ions in both compounds show a tetrahedral distortion. However, the dihedral angle between the two planes, each encompassing the metal and two donor atoms (N–M–N), of 14.85(17)° for [CuL] indicates a higher distortion from the square-planar geometry than the value of 7.98(22)° for the [NiL] complex (for a square-planar geometry the value would be 0° and for a tetrahedral geometry 90°). Thus, this tetrahedral distortion is more pronounced in the copper complex. This situation is also apparent because in [CuL] the copper atom is located –0.141 Å below the mean plane formed by O(1), N(1), N(2) and N(3), whereas in [NiL] the nickel is almost in the mean plane (–0.040 Å) that contains the same donor atoms.

In the case of [NiL], the Ni–N_{imine} bond length of 1.842(4) Å is slightly shorter than the value found in other complexes containing tetracoordinate nickel(II) and a Schiff base as ligand [1.860(2)–2.000(3) Å].[19–23] The Ni–N_{amide} bond lengths [1.833(5) and 1.895(4) Å] are significantly different to each other. In addition, both bonds are shorter than the range [2.030(6)–1.905(2) Å] described for tetracoordinate Ni^{II} complexes with Schiff bases containing nitrogen amide donor atoms.[19–23] The Ni–O_{tosyl} bond length of 2.004(4) Å is also shorter than those found in hexacoordinate complexes with ligands containing sulfon-

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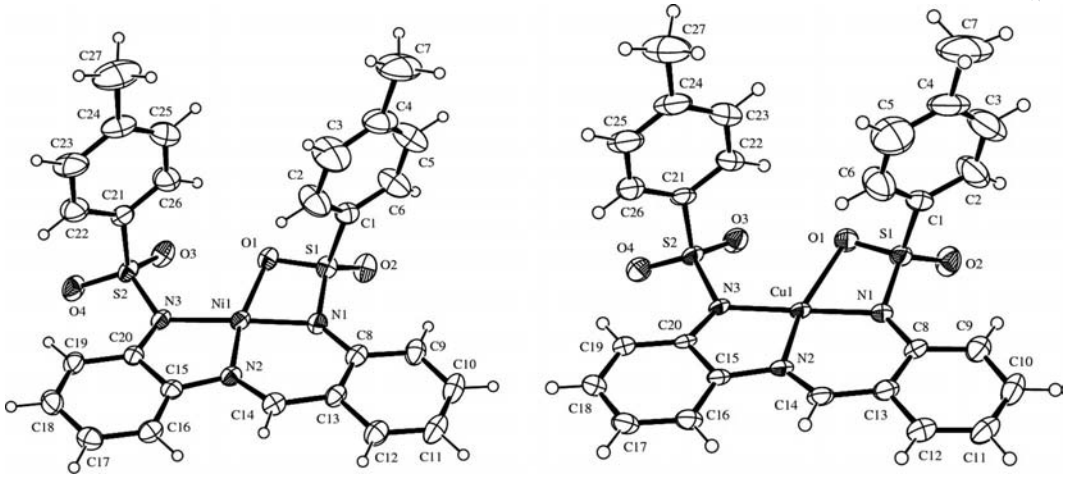

Figure 1. ORTEP diagram of the molecular structures of [NiL] (left) and [CuL] (right).

Table 1. Selected bond lengths [Å] and angles [°] for [NiL] and [CuL].

	M = Ni	M = Cu		M = Ni	M = Cu
M(1)–N(1)	1.833(5)	1.899(3)	M(1)–N(2)	1.842(4)	1.906(3)
M(1)–N(3)	1.895(4)	1.935(3)	M(1)–O(1)	2.004(4)	2.203(3)
M(1)–O(3)	3.189(4)	3.114(3)	N(2)–C(14)	1.314(6)	1.293(5)
N(1)–M(1)–N(2)	94.4(2)	92.87(15)	N(1)–M(1)–N(3)	177.0(2)	177.15(15)
N(2)–M(1)–N(3)	86.0(2)	85.62(14)	N(1)–M(1)–O(1)	72.59(19)	68.20(13)
N(2)–M(1)–O(1)	164.66(17)	156.96(14)	N(3)–M(1)–O(1)	107.38(18)	112.68(13)

amide groups coordinated through one oxygen atom of the SO_2 group (2.095–2.131 Å),[24,25] a situation that reflects the lower coordination number in [NiL]. To the best of our knowledge, the Ni–O_{tosyl} bond lengths in tetracoordinate nickel(II) complexes have not previously been estimated, which means that comparisons cannot be made with the Ni–O_{tosyl} bond length in [NiL].

In the case of [CuL], the Cu–N_{amide} [1.899(3) and 1.906(3) Å] bond lengths are similar to each other, but they are slightly shorter than the usual range (2.088–1.956 Å) found in tetracoordinate copper(II) complexes derived from ligands containing tosyl groups.[21–23,26–28] The Cu–N_{imine} distance [1.935(3) Å] is also slightly shorter than those found in tetracoordinate complexes with Schiff-base ligands (ranging from 1.954–1.981 Å).[23,24,28] Once again, complexes of tetracoordinate copper with a Cu–O_{tosyl} bond have not been studied by X-ray diffraction, but the Cu–O_{tosyl} distance of 2.203(3) Å in [CuL] is comparable to those found in pentacoordinate copper complexes containing different substituted *N*-(2-pyridyl)sulfonamide ligands [2.209(6)–2.2914(18) Å].[12]

In both complexes, the bond lengths and angles within the Schiff base are as expected. In particular, the imine C–N bond length, 1.314(6) for [NiL] and 1.293(5) Å for [CuL], is consistent with the value of 1.30 Å proposed for a C=N bond.[29]

As in the free ligand (see the Supporting Information), the crystal packing in the complexes [NiL] and [CuL] is mainly due to C–H···O hydrogen-bonding interactions. All of the oxygen atoms of the SO_2 groups, apart from that directly coordinated to the metal (O1), establish C–H···O interactions with different C–H groups. These C–H···O interactions only occur in two dimensions and they give rise to layers of molecules parallel to the crystallographic *ab* plane (see Figure S1 in the Supporting Information for [NiL]). The parameters for the hydrogen-bonding interactions in both compounds are given in Table S1.

Furthermore, the molecules are arranged in such a way along the crystallographic *c* axis that the planar part of the complex and the 4-toluenesulfonate groups alternate. As shown in Figure 2 for M = Ni, three π–π stacking interactions are formed, all of them involving chelate rings, and it is reasonable that the metal atom is involved in the π delocalization. These interactions are termed "parallel displaced" (Janiack[30]), that is, the two rings are essentially parallel to one another but are not perfectly aligned. These interactions are strong, as shown by the distances between centroids, 3.433(3) and 3.466(3) Å for M = Ni and 3.318(2) and 3.422(2) Å for M = Cu (see Table S2 for complete data on the π-stacking interactions).

The packing arrangements present in the crystal structure show two types of chemical process that favour magnetic weak exchange interactions between the metal ions, and these are hydrogen-bonding and π–π stacking interactions. In the case of the Cu^{II} ion, the EPR analyses of the solid, powder and single crystal show collapsed lines with anisotropic *g* values and without hyperfine interactions (electron spin-nuclear spin), as widely described in ref.[31]

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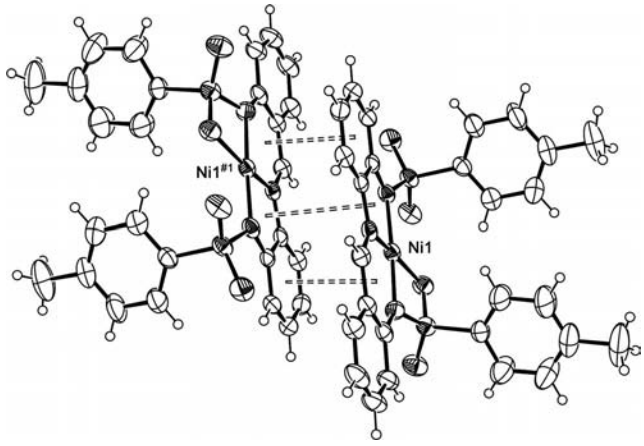

Figure 2. Crystal structure of [NiL] with π–π stacking interactions between the chelate ring and one of the phenyl rings shown as dotted lines.

Heteroleptic Complexes

Co-ligands such as 1,1-diphenylphosphanylmethane, 1,10-phenanthroline or 2,2′-bipyridine were added to the electrochemical cell with the intention of incorporating them as co-ligands for metal coordination. The electrochemical oxidation of the appropriate metal in a solution of 2-(tosylamino)-*N*-[2-(tosylamino)benzylidene]aniline and an equimolar amount of 2,2′-bipyridine or 1,10-phenanthroline in acetonitrile gave selectively the complexes [ML(phen)] or [ML(bipy)], which shows that the co-ligand had been incorporated into the complex. However, when the co-ligand 1,1-diphenylphosphanylmethane (dppm) was added to the electrochemical cell, only in the case of the nickel complex was the co-ligand incorporated into the metal coordination sphere. The complex isolated in this case was [NiL(dppm)] (**4**), as confirmed by X-ray diffraction. In all other cases, the analytical data and the spectroscopic studies performed on the resulting products showed no evidence for the incorporation of the additional co-ligand and the homoleptic compound [ML] was formed exclusively.

The heteroleptic metal(II) sulfonamide compounds were obtained as crystalline solids by concentration of the resulting acetonitrile solutions in air. These complexes were found to be more soluble than the homoleptic analogues in chloroform and a range of other chlorinated organic solvents.

Crystal Structure of [NiL(dppm)] (4)

The molecular structure of [NiL(dppm)] (**4**) is shown in Figure 3 and selected bond lengths and angles are given in Table 2. The compound consists of discrete molecules with the nickel atom coordinated to two amide nitrogen atoms and the imine atom of the Schiff base, which can be considered to act as a tridentate dianionic Schiff base. The coordination around the nickel atom is completed by one of the phosphorus atoms of a 1,1-diphenylphosphanylmethane (dppm) molecule, which acts as a monodentate ligand. The other phosphorus atom of dppm is not coordinated to the metal. A weak interaction between the nickel atom and one oxygen atom (O1) from one sulfonyl group is also observed. This weak Ni(1)–O(1) interaction causes the O(1)–S(1)–N(1) angle [100.6(2)°] to be smaller than one would expect for a regular tetrahedron.

The geometry around the nickel atom is best described as distorted tetrahedral [NiN_3P] as the dihedral angle between the P(1)–Ni(1)–N(1) and N(3)–Ni(1)–N(2) planes is 81.84(12)°. This distortion is shown by the angles between donor atoms and nickel atoms, which vary from 82.96(15) to 151.19(14)°. The widest angle is that between nickel and

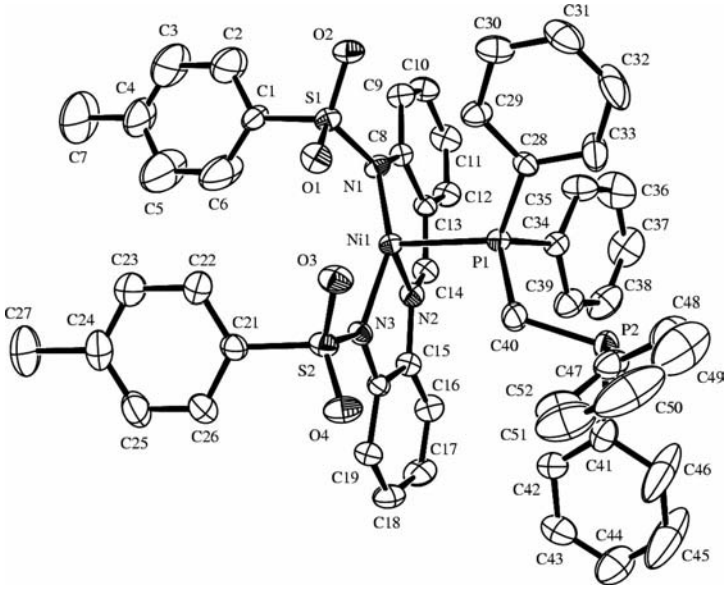

Figure 3. ORTEP diagram of the molecular structure of [NiL(dppm)].

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Table 2. Selected bond lengths [Å] and angles [°] for [NiL(dppm)].

Ni(1)–N(1)	1.951(3)	Ni(1)–N(3)	1.964(3)
Ni(1)–N(2)	1.968(3)	Ni(1)–P(1)	2.3287(13)
Ni(1)–O(1)	2.434(3)	Ni(1)–O(3)	3.054(3)
N(2)–C(14)	1.273(5)		
N(1)–Ni(1)–N(3)	151.19(14)	N(1)–Ni(1)–N(2)	90.82(15)
N(3)–Ni(1)–N(2)	82.96(15)	N(1)–Ni(1)–P(1)	109.05(11)
N(3)–Ni(1)–P(1)	99.71(10)	N(2)–Ni(1)–P(1)	98.95(11)
N(1)–Ni(1)–O(1)	63.64(12)	N(3)–Ni(1)–O(1)	107.70(12)
N(2)–Ni(1)–O(1)	145.22(12)	P(1)–Ni(1)–O(1)	111.16(8)
N(1)–Ni(1)–O(3)	129.61(12)	N(3)–Ni(1)–O(3)	52.39(11)
N(2)–Ni(1)–O(3)	135.17(12)	P(1)–Ni(1)–O(3)	86.33(7)
O(1)–Ni(1)–O(3)	66.04(9)		

the amide nitrogen atoms and this seems to be the result of an attempt to minimize the steric hindrance between the tosyl groups.[19–23]

The Ni–N_{amide} bond lengths [1.951(3) and 1.964(3) Å] are similar to each other but slightly greater than the values found in [NiL]. However, these values are within the usual range (1.905–2.030 Å) found in complexes with tetracoordinate nickel(II) and ligands containing tosyl groups. The Ni–N_{imine} bond length in [NiL(dppm)] [1.968(3) Å] is also longer than that observed in the aforementioned complex [NiL], but it is similar to those found in tetracoordinate nickel(II) complexes with Schiff-base ligands, which have values in the range 1.860(2)–2.000(3) Å.[19–23] The Ni–P bond length [2.3287(13) Å] does not differ significantly from the value observed in the tetracoordinate complex dibromo[*N*-2(diisopropylphosphanyl)benzyl]-*N*,*N*-dimethylaminonickel(II),[32] but is greater than those found in other tetracoordinate nickel(II) complexes in which phosphorus is a donor atom (2.168–2.199 Å).[33,34]

As in the complexes [NiL] and [CuL], the Schiff-base ligand is again orientated in such a way that one of the oxygen atoms from a tosyl group is close to the nickel atom [distance Ni(1)–O(1) 2.434(3) Å]. This value is higher than those observed in the complex [NiL] and in other nickel complexes that contain donor oxygen tosyl ligands. However, the distance is shorter than the sum of the van der Waals radii of these elements[35] and comparable to the distances in other tetracoordinate nickel complexes characterized by weak intramolecular Ni–O_{tosyl} interactions.[21,36]

The phenyl rings of the ligand are essentially planar, with a maximum deviation of less than 0.02 Å. The P and the S atoms are practically on the plane of the ring to which they are bonded.

The crystal packing in this compound is closely related to that of the homoleptic nickel complex discussed above, [NiL]. As in the case of [NiL], all of the oxygen atoms of the SO_2 groups are involved in C–H···O interactions with different C–H groups. These interactions also only occur in two dimensions, giving rise to layers parallel to the crystallographic *ab* plane. The data for these interactions are given in Table S1. The fundamental difference between the two compounds under discussion is evident if we consider the crystallographic *c* axis. The disposition of the complexes in this direction is similar to that in the homoleptic complex with the 4-toluenesulfonate groups and dppm units facing each other in an alternate manner. In the case of the homoleptic complex, the absence of co-ligands enables π–π stacking interactions between the planar parts of the two complexes, whereas in this case the presence of dppm ligands at this face does not allow such interactions to form.

Crystal Structures of [CoL(phen)] (5) and [ZnL(phen)] (7)

Complexes **5** and **7** are isostructural. [CoL(phen)] (**5**) is shown in Figure 4 along with the atomic numbering scheme adopted (molecular structures of **5** and **7** can be viewed in Figures S2 and S3). Selected bond lengths and angles for both compounds are listed in Table 3.

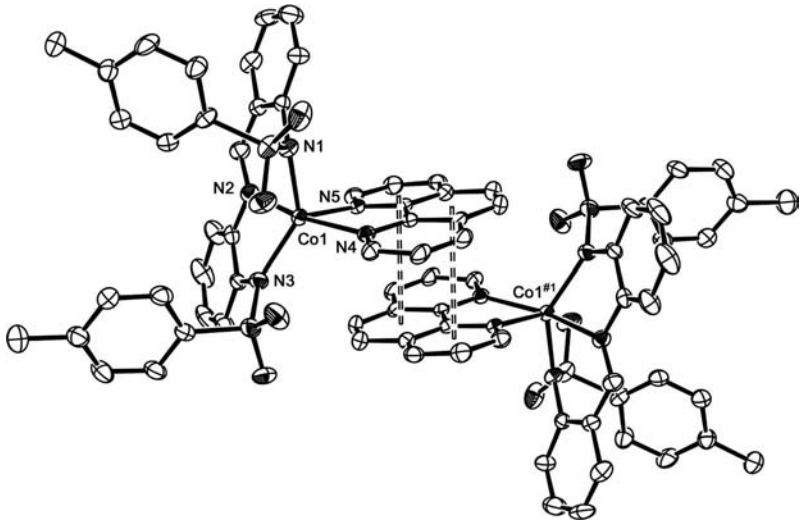

Figure 4. Crystal packing diagram of [CoL(phen)]. Intermolecular π–π stacking interactions between phenanthroline rings are represented by dotted lines.

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Table 3. Selected bond lengths [Å] and angles [°] for [CoL(phen)] and [ZnL(phen)].

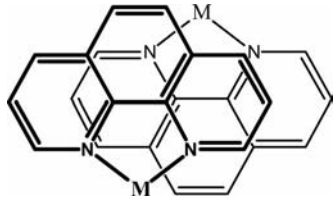
	M = Co	M = Zn		M = Co	M = Zn
M(1)–N(3)	2.034(6)	1.988(10)	M(1)–N(1)	1.994(6)	1.991(10)
M(1)–N(4)	2.133(6)	2.107(11)	M(1)–N(2)	2.132(6)	2.123(12)
M(1)–N(5)	2.156(6)	2.174(11)	N(2)–C(14)	1.242(10)	1.258(16)
N(1)–M(1)–N(3)	138.1(3)	134.8(4)	N(1)–M(1)–N(2)	84.7(3)	85.7(4)
N(3)–M(1)–N(2)	77.7(3)	77.0(4)	N(1)–M(1)–N(4)	95.5(2)	96.2(4)
N(3)–M(1)–N(4)	111.3(2)	112.3(4)	N(2)–M(1)–N(4)	164.4(2)	162.9(4)
N(1)–M(1)–N(5)	104.1(2)	105.2(4)	N(3)–M(1)–N(5)	112.2(3)	114.9(4)
N(2)–M(1)–N(5)	86.6(2)	86.8(4)	N(4)–M(1)–N(5)	78.2(2)	76.3(4)

The compounds consist of discrete molecules that contain a pentacoordinate metal atom. The geometrical parameter τ [$\tau = (\beta - \alpha)/60$, in which α and β are the N(2)–M(1)–N(4) and N(3)–M(1)–N(1) bond angles, respectively][37] has a value of 0.44 for [CoL(phen)] and 0.47 for [ZnL(phen)]. This suggests that the complexes have a geometry intermediate between a square pyramid ($\tau = 0$) and a trigonal bipyramid ($\tau = 1$). The environment around the cobalt metal is formed by one of the 1,10-phenanthroline nitrogen atoms, the imine nitrogen atom and the two deprotonated amide nitrogen atoms of the two 4-toluenesulfonamide groups, which occupy the basal sites, with the other 1,10-phenanthroline nitrogen atom in the apical site. In this arrangement, N(1) and N(3) are 0.41 and 0.45 Å (0.47 and 0.46 Å for the zinc complex) above the best least-squares plane of N(1)–N(2)–N(3)–N(4), and N(2) and N(4) are –0.52 and –0.34 Å below the plane (–0.57 and –0.37 Å for zinc complex). The cobalt and zinc atoms are 0.16 Å out of these planes. The low value of one of the chelate angles [N(3)–M(1)–N(2) 77.7(3)° for the cobalt complex and 77.0(4)° for the Zn complex] and the small bite angle of the phen ligand [78.2(2)° for Co and 76.3(4)° for Zn] are significantly different to those expected for a regular geometry and this deviation is the main source of the distortion.

The two Co–N_{amide} bond lengths in the complex [CoL(phen)] are similar [1.994(6) and 2.034(6) Å] and not very different to those observed in other amide complexes of Co^{II} with the same coordination number around the metal atom.[38] Similarly, the Co–N_{imine} bond length of 2.132(6) Å is in the range found for other pentacoordinate cobalt(II) complexes with Schiff bases.[38,39] The bond lengths between the cobalt atom and the two nitrogen atoms from the 1,10-phenanthroline molecule [2.133(6) and 2.156(6) Å] are very similar and can be considered as normal and consistent with those found in other pentacoordinate cobalt complexes that contain 1,10-phenanthroline as a chelating ligand.[40–42]

The bond lengths around the zinc atom are similar to those reported for other pentacoordinate complexes with the same donor atoms. Thus, the Zn–N_{amide} bond lengths [1.988(10) and 1.991(10) Å], although shorter than those in bis{1-[(4-methylphenyl)sulfonamido]-2-[(2-pyridylmethylene)-amino]benzene}zinc(II) [2.094(4) and 2.087(4) Å],[43] are of the same order as the values of 2.06(7) and 2.017(6) Å found for Zn–N_{amide} in the pentacoordinate compound (2,6-bis{1-[2-(tosylamino)phenylimino]ethyl}pyridine)zinc-(II).[44] In addition, the value of 2.123(12) Å for the Zn–N_{imine} bond length is similar to those found in the aforementioned complex[43,44] and in other pentacoordinate complexes of Zn with Schiff bases.[45,46] The Zn–N bond lengths formed with the phenanthroline ligand [2.107(11) and 2.174(11) Å] are similar to those found in other pentacoordinate phenanthroline complexes.[47–50]

In these cases the interactions largely responsible for the crystal packing are the C–H···O hydrogen-bonding interactions established between the oxygen atoms of the SO_2 groups of the ligands (H_2L) and different C–H groups, with π–π stacking interactions also evident between the nitrogenated co-ligands. The C–H···O interactions are similar to those already discussed for the free ligand and for the other complexes, although in these cases the interactions are established in three dimensions (see data in Table S1). On the other hand, as mentioned above, the nitrogenated co-ligands, 1,10-phenanthroline, are involved in π-stacking interactions with each other. These co-ligands are essentially planar and are arranged parallel to the crystallographic *ac* plane. The π–π stacking interactions are "parallel displaced" (see data in Table S2) and propagate along the crystallographic *b* axis (see Figure 4 for M = Co). The displacement of the rings is represented in Scheme 2, which shows a view of the interaction along the *b* axis. Analysis of the centroid–centroid distances shows that the strongest interactions are established between the central ring of one co-ligand and one of the lateral rings of the other co-ligand [3.605(5) Å for M = Co and 3.631(8) Å for M = Zn].



Scheme 2. Overlap of the phenanthroline rings of the neighbouring molecules in [ML(phen)] (M = Co, Zn) along the *b* axis.

Unfortunately, good quality crystals of [CuL(phen)] could not be obtained, with only a fine powder isolated. However, one would expect a very similar crystal structure and, in this case, the EPR signal was similar to that of the other Cu^{II} complexes, that is, weak exchange effects with collapsed lines without hyperfine interactions (electron spin–nuclear spin).

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Crystal Structure of [CuL(bipy)] (6)

The molecular structure of [CuL(bipy)] is shown in Figure 5 along with the atom numbering system used. Selected bond lengths and angles are listed in Table 4.

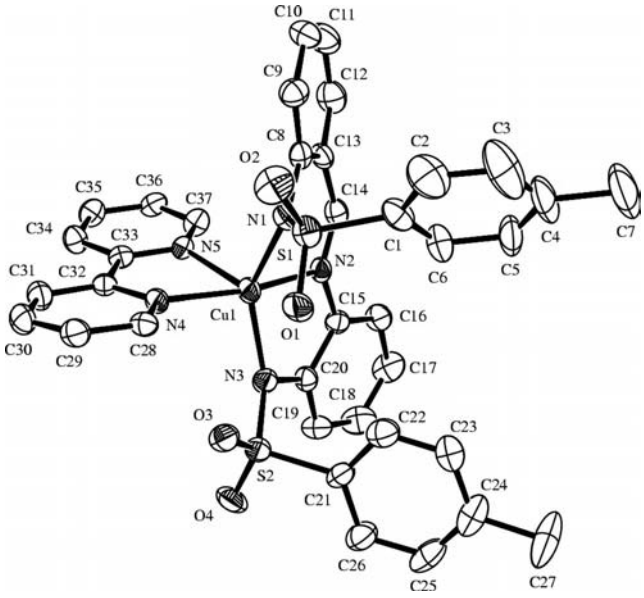

Figure 5. ORTEP diagram of the molecular structure of [CuL(bipy)].

Table 4. Selected bond lengths [Å] and angles [°] for [CuL(bipy)].

Cu(1)–N(2)	1.987(5)	Cu(1)–N(3)	2.014(5)
Cu(1)–N(1)	2.027(4)	Cu(1)–N(4)	2.032(4)
Cu(1)–N(5)	2.290(4)	N(2)–C(14)	1.273(6)
N(2)–Cu(1)–N(3)	81.64(19)	N(2)–Cu(1)–N(1)	86.92(18)
N(3)–Cu(1)–N(1)	144.29(18)	N(2)–Cu(1)–N(4)	164.13(18)
N(3)–Cu(1)–N(4)	101.66(18)	N(1)–Cu(1)–N(4)	98.50(18)
N(2)–Cu(1)–N(5)	87.22(18)	N(3)–Cu(1)–N(5)	102.48(17)
N(1)–Cu(1)–N(5)	110.65(16)	N(4)–Cu(1)–N(5)	76.91(19)
N(5)–C(33)–C(32)	116.7(5)	N(5)–C(37)–C(36)	124.2(5)

The complex consists of monomer units in which a pentacoordinate [CuN_5] copper atom is bound to two amide nitrogen atoms and the imine nitrogen atom of the tridentate dianionic Schiff-base ligand. A neutral 2,2′-bipyridine molecule acting as an (N,N) bidentate chelating donor completes the coordination sphere of the metal. Consequently, the environment around the copper atom may be described as a distorted square pyramid (τ = 0.33) with one of the nitrogen [N(5)] atoms of the 2,2′-bipyridine molecule as the apical atom. The copper atom and the basal donor atoms are coplanar within the limits of experimental accuracy.

The Cu–N_{imine} bond length [1.987(5) Å] is similar to those found in other five-coordinate copper compounds, for example, in bis(dimethylaminoethylsalicylaldiminato)copper(II)[51] (mean value of 1.946 Å) or 2,2′-bipyridine-{2-[2′-(*N*-tosylamino)benzylideneamino]phenolato}copper(II)[52] [1.973(17) Å]. The Cu–N_{bipy} bond lengths are different with the basal bond [2.032(4) Å] shorter than the apical bond [2.290(4) Å]. The shorter Cu–N_{bipy} bond length can be considered as normal and is similar to the bond lengths found in other five-coordinate copper(II) complexes with bidentate 2,2′-bipyridine ligands; 2.002(4) Å in di-μ-hydroxo-bis[(2,2′-bipyridine)(trifluoromethanesulfonato-*O*)copper(II)][53] and 2.0037(18) Å in 2,2′-bipyridine-{2-[2′-(*N*-tosylamino)benzylideneamino]phenolato}copper(II).[52] However, the bond length of 2.290(4) Å is unusually high and similar to the longest Cu–N distance found in [Cu(phen)$_3$]$^{2+}$, a compound with a very pronounced Jahn–Teller distortion.[54] Similar behaviour has been found in the cases of 1,10-phenanthroline{2-[2-(oxyphenyl)iminomethyl]phenolato}copper(II),[55] 1,10-phenanthroline-{*N*-[(2-oxophenyl)methylidene]-*N*-4-toluenesulfonylbenzene-1,2-diaminato}copper(II)[56] and 2,2′-bipyridine-{2-[2′-(*N*-tosylamino)benzylideneamino]phenolato}copper(II).[52] The Cu–N_{amide} bond lengths [2.014(5) and 2.027(4) Å] are not different to those found in other pentacoordinate copper(II) complexes,[57] for example, 2.041(5) and 2.031(5) Å in [CuL_2dmf], with HL representing *N*-(*p*-tolylsulfonyl)-*o*-phenylenediamine,[58] or 2.003(2) and 2.044(3) Å in the above-mentioned sulfonamide complexes.[52,56]

The crystal packing in this compound is very similar to that described above for other heteroleptic complexes with 1,10-phenanthroline ligands (compounds **5** and **7**). Thus, all the oxygen atoms of the SO_2 groups are involved in C–H···O interactions that extend in three dimensions, although they are weaker than in the other complexes reported (see data in Table S1). The bipyridine co-ligands are also oriented parallel to the crystallographic *ac* plane, leading to π–π stacking interactions along the *b* axis between one ring of the co-ligand and a symmetry equivalent of the other ring, as shown in Figure 6. These interactions are also "parallel displaced" (see data in Table S2) and quite strong

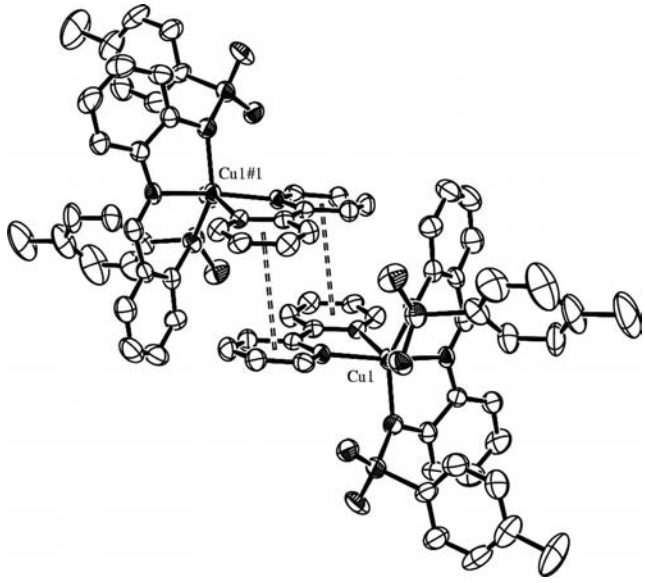

Figure 6. Crystal packing diagram of [CuL(bipy)]. Intermolecular π–π stacking interactions between bipyridine rings are represented by dotted lines.

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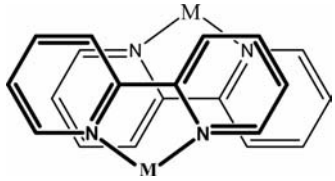
[centroid–centroid distance 3.552(7) Å]. The displacement of the rings can be seen in Scheme 3, which shows a view of the interaction along the *b* axis.



Scheme 3. A view along the *b* axis showing the overlap between bipyridine rings of two neighbouring molecules of [CuL(bipy)].

As far as the EPR spectrum of [CuL(bipy)] is concerned, the results were similar to those obtained for other Cu^{II} complexes.

Spectroscopic Studies

The cobalt(II), nickel(II) and copper(II) complexes were also studied by electronic spectroscopy in the solid state.[59] Compound [CoL] shows a multicomponent band at 78130 and 9025 cm^{-1}, which has been assigned to $^4A_2 \rightarrow {}^4T_1$ (F), and another at 17800 cm^{-1} due to $^4A_2 \rightarrow {}^4T_1$(P), both of which are the result of a distorted tetrahedral environment. The spectra of the heteroleptic complexes of cobalt(II), with signals between 22000 and 5000 cm^{-1}, are similar to each other but differ from that of the [CoL] complex. The spectra of these complexes show the characteristic features of five-coordinate cobalt(II) ions with a distorted square-pyramidal stereochemistry. Thus, the complexes [CoL(bipy)] and [CoL(phen)] give rise to bands at around 7500 and 7600, 11180 and 11140, 16835 and 17200, and 22030 and 22030 cm^{-1}, respectively, and these have been assigned to $^4E_g(^4T_{1g}) \rightarrow {}^4E_g(^4T_{2g})$, $^4E_g(^4T_{1g}) \rightarrow B_{1g}$, $^4E_g(^4T_{1g}) \rightarrow {}^4Eg(^4T_{1g})$ and $^4E_g[^4T_{1g}(P)] \rightarrow A_{2g}[^4T_{1g}(P)]$ transitions, respectively, in a square-pyramidal geometry. This environment was found in the X-ray structure determination of [CoL(phen)] (**5**).

The solid-state electronic spectrum of the complex [NiL] shows three bands at 10820, 15780 and 23500 cm^{-1}, which can be attributed to the $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ transitions, respectively. These are characteristic of nickel(II) compounds in a square-planar environment. The diffuse reflectance spectrum of [NiL(dppm)] exhibits two d–d bands well within the range of tetrahedral complexes of nickel(II) (ca. 7200 and 15600 cm^{-1}), which can be assigned to the $^3T_1(F) \rightarrow {}^3A_2$ and $^3T_1(F) \rightarrow {}^3T_1(P)$ transitions, respectively. The solid-state electronic spectra of the mixed nickel complexes [NiL(bipy)] and [NiL(phen)] are consistent with a pentacoordinate environment around the nickel atom. The bands observed in these spectra cannot be unequivocally assigned to specific electronic transitions, but the bands in the visible region at 16200, 16700 and 22800, 22030 cm^{-1} have been assigned to $^3B_1 \rightarrow {}^3E$ and $^3B_1 \rightarrow {}^3A_2$, $^3E(P)$. The bands in the near-IR region at about 8830, 8790 and 10640, 11040 cm^{-1} have been assigned to $^3B_1 \rightarrow {}^3E$ and $^3B_1 \rightarrow {}^3B_2$ and the shoulders at 12500 and 12400 cm^{-1} to $^3B_1 \rightarrow {}^3A_2$ transitions, respectively. These data are consistent with a distorted square-pyramidal geometry for these complexes.

The diffuse reflectance spectrum of [CuL] shows a broad band at around 17800 cm^{-1}, in agreement with the values reported for square-planar copper(II) complexes. The electronic reflectance spectra of [CuL(bipy)] and [CuL(phen)] contain two broad bands in the ranges 11470–13270 and 15150–15200 cm^{-1}, in agreement with a square-pyramidal environment of a CuN_5 chromophore. This geometry was identified in the X-ray structure determination of [CuL(bipy)] (**6**).

The IR spectra of these complexes do not show the band attributed to ν(N–H), which in the ligand appears at 3297 cm^{-1}, confirming the loss of the amide protons during the electrolysis and showing that the ligand is in the dianionic amidate form in the complex. On the other hand, the band attributable to ν(C=N) of the imine group is shifted to a lower frequency on going from the free ligand (1618 cm^{-1}) to the complexes (1593–1612 cm^{-1}) as a result of coordination of the imine nitrogen to the metal. These observations suggest that the imine nitrogen and two amide nitrogen atoms of the dianionic Schiff base are coordinated to the metal atom. In addition, the two bands in the ranges 1340–1325 and 1115–1143 cm^{-1}, assignable to the asymmetric and symmetric modes of the SO_2 group, respectively, are shifted to significantly lower frequencies, with this shift being more marked in the complexes [NiL] and [CuL]. This behaviour can be considered as evidence of an interaction between the oxygen atom of the sulfonyl group and the metal atom. This conclusion is confirmed by the X-ray structures of **2** and **3**.

The IR spectra of the heteroleptic complexes show similar bands to those described above for the homoleptic complexes and these are characteristic of a coordinated Schiff-base ligand. Additional bands are also observed at around 758 and 735, and 725, 845 and 1510 cm^{-1}, and 1470, 1125, 785, 745 and 699 cm^{-1}, which are typical of coordinated 2,2′-bipyridine,[60] 1,10-phenanthroline[60,61] and dppm,[62] respectively.

NMR Spectra

The diamagnetic nature of the complex [NiL] allowed us to carry out an NMR study in solution. The room-temperature ^1H NMR spectra of this nickel complex and of the zinc and cadmium complexes show that the singlets attributable to the NH hydrogens, which appear in the free ligand at δ = 10.80 and 9.85 ppm, are not present in the complexes, again reinforcing the conclusion from the IR data that the ligands are coordinated to the metal in the dianionic form as a result of deprotonation of the ligand. Furthermore, the signal of the azomethine hydrogen atom is shifted to a lower field, around 0.3–0.5 ppm, upon complexation. This behaviour is a consequence of the coordination of the imine nitrogen to the metal. In the spectra of the heteroleptic complexes [CdL(bipy)] and [CdL(phen)], two low intensity

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peaks are also observed around this signal and these correspond to coupling of the imine nitrogen with the ^{113}Cd isotope [$^3J(^1H–^{113}Cd)$ = 17 Hz]. This coupling provides evidence for the coordination of the ligand to the metal through the imine nitrogen. The multiplet resonances in the aromatic region (δ = 8.0–6.79 ppm) and also the signals corresponding to the methyl groups (δ = 2.40–2.20 ppm) appear slightly shifted with respect to those in the free ligand. This change is due to the coordination of the ligand. In addition, in the ^{1}H NMR spectra of the heteroleptic complexes [ML(phen)] (M = Zn and Cd) the signals of the 1,10-phenanthroline can be distinguished at low field from those due to the aromatic sulfonamide ligand. In these cases the signals attributable to the 2,9- and 3,8-protons of 1,10-phenanthroline (between δ = 9.32–9.14 and δ = 8.13–8.30 ppm, respectively) experience a small downfield shift with respect to the corresponding signals in the free ligand. This shift provides evidence for the coordination of the 1,10-phenanthroline molecule.[63] The room-temperature ^{1}H NMR spectra of [ML(bipy)] (M = Zn, Cd) show signals that can be assigned to the hydrogen atoms of 2,2′-bipyridine in addition to the signals corresponding to the hydrogen atoms of the deprotonated sulfonamide ligands. The downfield shift of the signal attributable to the 3,3′ protons (δ = 8.04–8.11 ppm) and the upfield shift of the signal for the 6,6′-protons (δ = 8.98–8.79 ppm) provide evidence to support the coordination of the 2,2′-bipyridine ligand.[64]

EPR Spectra

The EPR spectra of the Cu compounds [CuL] (**3**), [CuL(bipy)] (**6**) and [CuL(phen)] are shown in Figures 7, 8 and 9, respectively, in which (a) are the spectra of powder samples and (b) are the spectra of the frozen solution samples. All of the powder samples gave rise to EPR spectra without resolution of the hyperfine structure of the Cu nuclear spin (I = 3/2). In accord with the X-ray structure results, which show intermolecular interactions between Cu^{II} ions, such as hydrogen bonding and π–π stacking, the EPR results for the powder samples are in agreement with the weak exchange interaction that collapses hyperfine lines, with anisotropic g values. This phenomenon is very well-studied in Cu^{II} amino acids, dipeptides and other molecular compounds.[31,65–71] When the samples were diluted (low concentration) in appropriate solvents, the frozen EPR spectra showed hyperfine structure from the Cu nuclear spin (I = 3/2), which indicates paramagnetic dilution. The samples of [CuL] (**3**) and [CuL(bipy)] (**6**) as frozen solutions show two EPR components, one similar to the powder spectrum and another as a diluted paramagnetic compound. These results suggest that these two compounds have low solubility. Simulation using the EasySpin[72] program gave the EPR parameters shown in Table 5. The EPR parameters are compatible with a $d_{x^2-y^2}$ orbital describing the unpaired electron with a small rhombic distortion ($g_x \neq g_y$). However, the second compo-

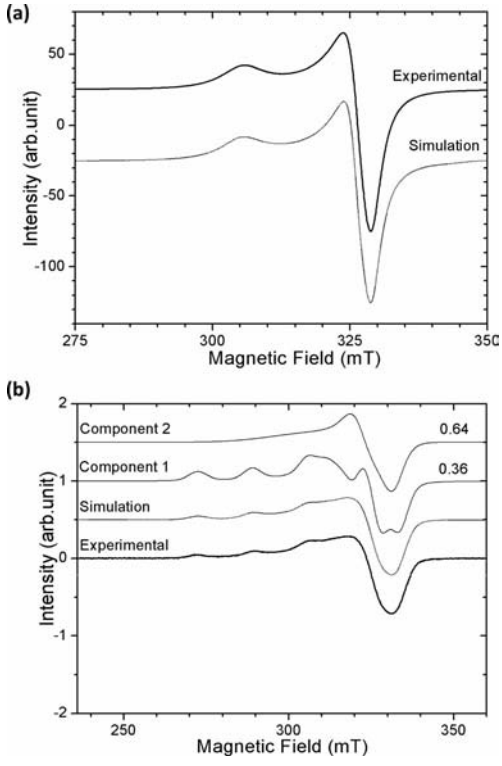

Figure 7. Experimental EPR spectra of the complex [CuL] (**3**): (a) powder sample (solid line) and (b) frozen solution sample (solid line) with spectral simulations (broken lines) obtained by using the EasySpin programme.[72]

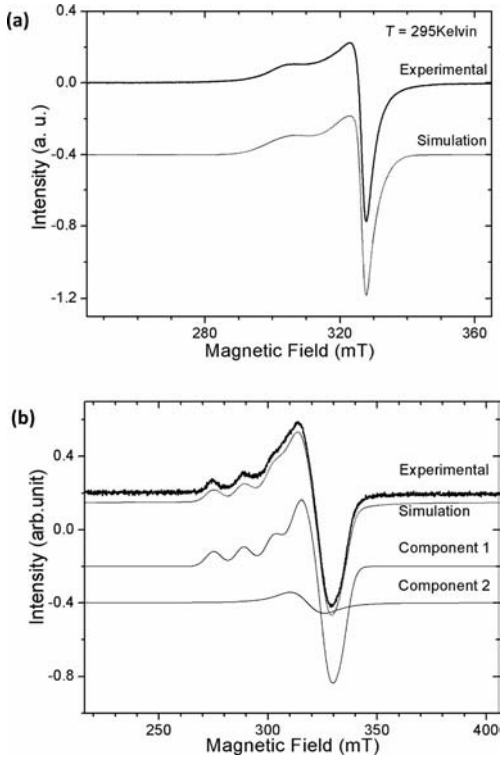

Figure 8. Experimental EPR spectra of the complex [CuL(bipy)] (**6**): (a) powder sample (solid line) and (b) frozen solution sample (solid line) with spectral simulations (broken lines) obtained by using the EasySpin programme.[72]

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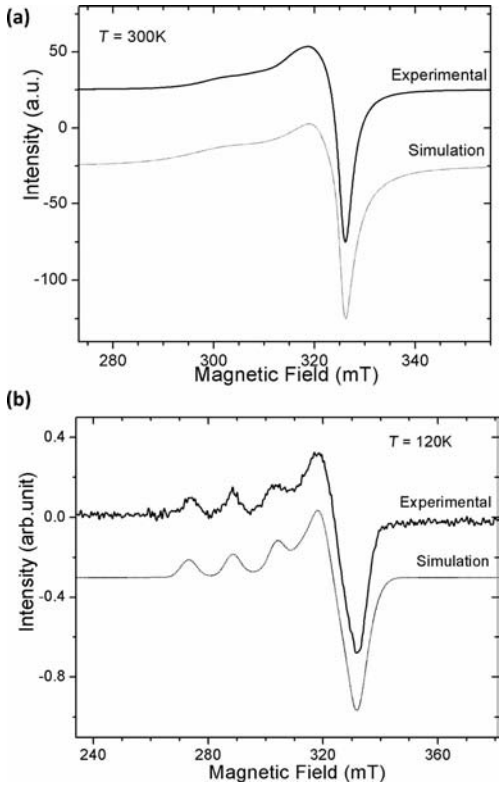

Figure 9. Experimental EPR spectra of the complex [CuL(phen)]: (a) powder sample (solid line) and (b) frozen solution sample (solid line) with spectral simulations (broken lines) obtained by using the EasySpin programme.[72]

nent of diluted [CuL] (**3**) and [CuL(bipy)] (**6**) presents a stronger rhombicity, which suggests a possible steric distortion induced by the action of solvent. [CuL] (**3**) and [CuL(bipy)] (**6**) gave good single crystals and the detailed measurement of the EPR spectra, as a function of magnetic field orientation relative to the single crystal axes, is in progress to obtain information concerning the weak exchange interaction and the role of the interactions involving hydrogen-bonding and ring-stacking, as discussed in the crystallography section.

Conclusions

In this paper the one-pot synthesis of several new metal complexes is reported. The highly pure isolated compounds were analysed spectroscopically and, when possible, by single-crystal X-ray diffraction. The synthesis involved an electrochemical procedure. Homoleptic complexes [ML] were obtained by oxidation of a metal anode in a cell containing the Schiff base (H_2L), whereas heteroleptic complexes [MLL′] were obtained by adding a co-ligand such as 1,1-diphenylphosphanylmethane, 2,2′-bipiridine or 1,10-phenhantroline to the reaction cell. In the [ML] homoleptic complexes the Schiff base acts as a dianionic tetradentate ligand whereas in the [MLL′] heteroleptic complexes the Schiff base behaves as a dianionic tridentate ligand. X-ray analysis of the crystal structures revealed some interesting structural features regarding the intermolecular interactions: compounds **2** and **3** exhibit two unusual and identical π–π stacking interactions between one phenyl ring and one metal-containing chelate ring.

Experimental Section

General: Cobalt, nickel, copper, zinc and cadmium (Aldrich) were used as plates (ca. 2 × 2 cm). All other reagents, including acetonitrile, 2,2′-bipyridine, 1,10-phenanthroline and 1,1-diphenylphosphanylmethane, were commercial products and were used as supplied. *N*-Tosyl-1,2-diaminobenzene and 2-(tosylamino)benzaldehyde were synthesized according to previously reported procedures.

Physical Measurements: The C, N, H and S contents of the compounds were determined with a Perkin–Elmer 240B microanalyser. IR spectra were recorded as KBr mulls with a Bruker IFS-66V spectrophotometer. The ^{1}H NMR spectrum of the ligand was recorded with a Bruker WM 350 spectrometer using [D_6]DMSO or $CDCl_3$ as solvent. The chemical shifts were recorded against TMS as internal standard. FAB mass spectra were recorded with a Micromass Autospec instrument using 3-nitrobenzyl alcohol (3-NBA) as the matrix material. Solid-state electronic spectra were recorded with a Shimadzu UV 3101 PC spectrophotometer. EPR measurements were recorded with a CW-X-band EMX Bruker spectrometer equipped with a liquid N_2 accessory for the three Cu compounds {[CuL] (**3**), [CuL(bipy)] (**6**) and [CuL(phen)]} on powder and frozen solutions. Powder samples of the two first compounds were obtained by grinding microcrystals and the third sam-

Table 5. EPR Parameters obtained by spectral simulation.[a]

Physical state	EPR parameters	[CuL] (**3**)			[CuL(bipy)] (**6**)			[CuL(phen)]		
		x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Solid	*g*	2.0500	2.0685	2.2095	2.0721	2.0734	2.2230	2.0710	2.0940	2.2380
	Lw [MHz]	63.0	63.0	150.0	60.0	60.0	480.0	40.0	145.0	345.0
Frozen solution	g_1	2.0550	2.1200	2.2600	2.0525	2.1124	2.2820	2.0475	2.0642	2.2535
	A_1 [MHz]	97.2	83.4	515.3	91.6	92.9	425.6	108.4	108.4	472.3
	Lw_1 [MHz]	155	160	170	235	235	235	180	180	180
	g_2	2.0307	2.0890	2.2275	2.0570	2.1800	2.1114	–	–	—
	Lw_2 [MHz]	49.1	127.6	823.0	49.0	49.0	49.0	–	–	–

[a] g_1 and g_2 correspond to the two spectral components existent in frozen solution. Lw is line width.

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ple was precipitated. Measurement conditions: microwave frequency 9.4340 GHz, modulation amplitude 0.4 mT, time constant 20.48 ms, time conversion 81.92 ms, solid sample room temperature, frozen solution 120 K.

Preparation of 2-(Tosylamino)-*N*-[2-(tosylamino)benzylidene]aniline (H_2L): The Schiff base was prepared by heating an ethanolic solution of equimolar amounts of 2-(tosylamino)benzaldehyde (0.95 g, 10 mmol) and *N*-tosyl-1,2-diaminobenzene (2.63 g, 10 mmol) at reflux. The water produced in the reaction was removed by using a Dean–Stark trap and the resulting solution was concentrated. The resulting yellow crystals, which were suitable for X-ray studies, were filtered off, washed with diethyl ether and dried under vacuum; yield 70%. IR (KBr): $\tilde{\nu}$ = 3298 (m), 2924 (w), 1615 (s), 1596 (m), 1573 (m), 1510 (m), 1483 (s), 1391 (m), 1335 (vs), 1296 (s), 1209 (m), 1184 (m), 1169 (vs), 1153 (vs), 1120 (m), 1090 (s), 952 (m), 887 (m), 818 (s), 760 (vs), 674 (vs), 662 (vs), 574 (s), 541 (vs) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 11.44 [s, 1 H, NH (amide-Ph-C)], 9.63 [s, 1 H, NH (amide-Ph-N)], 8.27 (s, 1 H, HC=N), 7.78–6.86 (m, 16 H, aromatic), 2.28 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3) ppm. ^1H NMR ($CDCl_3$): δ = 10.80 [s, 1 H, NH (amide-Ph-C)], 9.85 [s, 1 H, NH (amide-Ph-N)], 8.20 (s, 1 H, HC=N), 7.77–7.12 (m, 16 H, aromatic), 2.35 (s, 3 H, CH_3), 2.15 (s, 3 H, CH_3) ppm. MS (FAB): *m*/*z* = 519 $[H_2L]^+$. $C_{27}H_{25}N_3O_4S_2$ (519.63): calcd. C 62.41, H 4.85, N 8.09, S 12.34; found C 61.98, H 4.77, N 8.05, S 11.89.

Electrochemical Synthesis: The complexes were prepared by following a previously reported electrochemical procedure.[7] The cell consisted of a 100 mL tall-form beaker fitted with a rubber bung through which the electrochemical leads entered. An acetonitrile solution of either the ligand or the ligand/co-ligand (1,10-phenanthroline·monohydrate, 2,2′-bipyridine or 1,1-diphenylphosphanylmethane) mixture containing tetraethylammonium perchlorate (ca. 10 mg) (***Caution****: perchlorate compounds are potentially explosive and should be handled in small quantities and with great care*) as a current carrier was electrolysed by using a platinum wire as the cathode and a copper plate suspended from another platinum wire as the sacrificial anode. Direct current was supplied by a purpose-built d.c. power supply. Applied voltages of 5–15 V allowed sufficient current flow for smooth dissolution of the metal. In all cases, hydrogen was evolved at the cathode. The cell can be summarized as $Pt^{(-)}/CH_3CN + LH_2 + L'/M^{(+)}$, with H_2L representing the Schiff-base ligand, L′ is the additional ligand and M is either Co, Ni, Cu, Zn or Cd. After electrolysis, the resulting solutions were filtered to remove any particles of metal and then left to concentrate. This procedure yielded crystalline products. The solids were washed with acetonitrile and diethyl ether and dried at room temperature.

[CoL]: Electrochemical oxidation of a cobalt anode in a solution of the ligand H_2L (0.199 g, 0.38 mmol) in acetonitrile (50 cm^3) at 14.9 V and 10 mA for 2 h caused 22.4 mg of cobalt to be dissolved, E_f = 0.51 mol F^{-1}. IR (KBr): $\tilde{\nu}$ = 2922 (w), 1612 (s), 1597 (s), 1553 (m), 1477 (s), 1443 (w), 1398 (w), 1384 (w), 1298 (s), 1259 (vs), 1232 (w), 1232 (w), 1133 (vs), 1087 (s), 1018 (w), 962 (s), 895 (m), 844 (m), 812 (m), 754 (m), 743 (m), 708 (m), 665 (s), 561 (s) cm^{-1}. MS (FAB): *m*/*z* (%) = 1153 (11) $[CoL]_2^+$, 576.1 (41) $[CoL]^+$, 422 [CoL – Ts]$^+$, 267 (26) [CoL – 2Ts]$^+$. $C_{27}H_{23}CoN_3O_4S_2$ (576.55): calcd. C 56.25, N 7.29, H 4.02, S 11.12; found C 55.90, N 6.73, H 4.25, S 11.03.

[CoL(bipy)]: Electrolysis of a solution of the ligand (0.147 g, 0.28 mmol) and 2,2′-bipyridine (0.044 g, 0.28 mmol) in acetonitrile (50 cm^3) at 10 V and 10 mA for 1.5 h dissolved 16.0 mg of cobalt from the anode, E_f = 0.48 mol F^{-1}. IR (KBr): $\tilde{\nu}$ = 2933 (w), 1598 (s), 1554 (w), 1475 (s), 1439 (m), 1384 (w), 1297 (m), 1259 (vs), 1180 (w), 1141 (vs), 1087 (s), 1018 (w), 956 (m), 888 (m), 840 (m), 810 (m), 762 (m), 734 (w), 709 (w), 664 (m), 589 (w) cm^{-1}. MS (FAB): *m*/*z* = 733 [CoL(bipy)]$^+$, 576 [CoL]$^+$, 422 [CoL – Ts]$^+$, 267 [CoL – 2Ts]$^+$. $C_{37}H_{31}N_5O_4S_2Co$ (732.74): C 60.65, N 9.56, H 4.26, S 8.75; found: C 60.44, N 8.95, H 4.05, S 8.64.

[CoL(phen)]: A solution of the ligand (0.150 g, 0.29 mmol) and 1,10-phenanthroline (0.057 g, 0.29 mmol) in acetonitrile (50 cm^3) was electrolysed at 8 V and 10 mA for 1.5 h and 17 mg of cobalt metal was dissolved from the anode, E_f = 0.51 mol F^{-1}. Air-concentration of the mother liquor gave brown crystals of [CoL(phen)] suitable for X-ray studies. IR (KBr): $\tilde{\nu}$ = 1608 (m), 1594 (m), 1554 (w), 1516 (m), 1495 (w), 1477 (m), 1423 (m), 1384 (w), 1297 (m), 1272 (m), 1261 (s), 1180 (w), 1141 (vs), 1087 (s), 956 (s), 890 (w), 851 (m), 809 (w), 726 (m), 663 (s), 589 (w), 550 (s) cm^{-1}. MS (FAB): *m*/*z* = 757 [CoL(phen)]$^+$, 602 [CoL(phen) – Ts]$^+$, 576 [CoL]$^+$, 422 [CoL – Ts]$^+$. $C_{39}H_{31}CoN_5O_4S_2$ (756.76): calcd. C 61.90, N 9.25, H 4.13, S 8.47; found C 61.87, N 9.55, H 4.14, S 8.38.

[NiL]: A solution of the ligand H_2L (0.199 g, 0.38 mmol) in acetonitrile (50 cm^3) was electrolysed at 11 V and 10 mA for 2 h and 22.1 mg of nickel was dissolved from the anode, E_f = 0.50 mol F^{-1}. The reaction mixture was concentrated and [NiL] was obtained as a crystalline brown solid suitable for X-ray studies. IR (KBr): $\tilde{\nu}$ = 1598 (s), 1550 (w), 1475 (s), 1445 (w), 1401 (m), 1306 (s), 1256 (s), 1238 (m), 1137 (vs), 1118 (s), 1088 (vs), 971 (m), 901 (w), 847 (w), 811 (m), 754 (vw), 663 (s), 563 (s) cm^{-1}. NMR ($CDCl_3$): δ = 8.60 (s, 1 H, CH=N), 8.00–6.86 (m, 28 H, aromatic), 2.40 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3) ppm. MS (FAB): *m*/*z* = 576 [NiL]$^+$, 421 [NiL – Ts]$^+$, 266 [NiL – 2Ts]$^+$. $C_{27}H_{23}N_3NiO_4S_2$ (576.33): calcd. C 56.27, N 7.29, H 4.02, S 11.13; found C 55.52, N 6.65, H 4.64, S 10.66.

[NiL(bipy)]: Electrolysis of a solution of the ligand (0.146 g, 0.28 mmol) and 2,2′-bipyridine (0.043 g, 0.28 mmol) in acetonitrile (50 cm^3) at 8 V and 10 mA for 1.50 h dissolved 17 mg of nickel, E_f = 0.52 mol F^{-1}. IR (KBr): $\tilde{\nu}$ = 2916 (w), 1601 (s), 1562 (vw), 1552 (vw), 1494 (s), 1473 (s), 1294 (m), 1269 (m), 1250 (vs), 1135 (vs), 962 (m), 846 (w), 812 (m), 760 (m), 743 (vw), 734 (w), 659 (m), 579 (m), 557 (s) cm^{-1}. MS (FAB): *m*/*z* = 732 [NiL(bipy)]$^+$, 576 [NiL]$^+$, 421 [NiL – Ts]$^+$, 266 [NiL – 2Ts]$^+$. $C_{37}H_{31}N_5NiO_4S_2$ (732.51): calcd. C 60.67, H 4.27, N 9.56, S 8.75; found C 60.33, H 4.19, N 9.49, S 9.07.

[NiL(phen)]: In a similar experiment to those described above, the ligand (0.109 g, 0.21 mmol) and 1,10-phenanthroline (0.041 g, 0.20 mmol) in acetonitrile (50 cm^3) was electrolysed at 10 V and 10 mA for 1.15 h and 12.8 mg of nickel metal was dissolved from the anode, E_f = 0.51 mol F^{-1}. IR (KBr): $\tilde{\nu}$ = 2922 (w), 1589 (s), 1552 (w), 1518 (m), 1476 (m), 1427 (m), 1299 (m), 1252 (vs), 1178 (m), 1162 (m), 1134 (vs), 1051 (m), 964 (m), 846 (m), 752 (w), 727 (m), 658 (m), 557 (s) cm^{-1}. MS (FAB): *m*/*z* (%) = 756 (23) [NiL(phen)]$^+$, 600 [NiL(phen) – Ts]$^+$, 576 [NiL]$^+$, 421 [NiL – Ts]$^+$, 265 [NiL – 2Ts]$^+$. $C_{39}H_{31}N_5NiO_4S_2$ (756.54): calcd. C 61.92, H 4.13, N 9.26, S 8.48; found C 62.09, H 4.65, N 8.64, S 7.85.

[NiL(dppm)]: Electrochemical oxidation of a nickel anode in a solution of the ligand (0.132 g, 0.25 mmol) and dppm (0.099 g, 0.25 mmol) in acetonitrile (50 cm^3) at 14 V and 10 mA for 1.4 h caused 15 mg of nickel to be dissolved, E_f = 0.49 mol F^{-1}. The resulting solution was slowly evaporated at room temperature to give red-brown crystals of [NiL(dppm)] suitable for X-ray studies. IR (KBr): $\tilde{\nu}$ = 2920 (w), 1599 (m), 1546 (w), 1470 (vs), 1435 (s), 1389 (m), 1307 (m), 1270 (m), 1246 (m), 1141 (vs), 1125 (s), 1086 (m), 1070 (m), 1030 (m), 962 (m), 833 (m), 810 (m), 785 (m), 745 (m), 699 (m), 560 (s) cm^{-1}. MS (FAB): *m*/*z* = 960 [NiLdppm]$^+$, 575 [NiL]$^+$, 421 [NiL – Ts]$^+$. $C_{52}H_{45}N_3NiO_4P_2S_2$ (960.72): calcd. C

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65.01, N 4.37, H 4.72, S 6.45; found C 64.92, N 4.59, H 4.66, S 6.56.

[CuL]: A similar experiment to those described above (10 V, 5 mA, 1.25 h) with H_2L (0.125 g, 0.24 mmol) in acetonitrile (50 cm^3) led to the dissolution of 15 mg of metal, E_f = 1.01 mol F^{-1}. From the mother liquor, brown crystals of [CuL] suitable for X-ray studies were obtained. IR (KBr): $\tilde{\nu}$ = 1600 (m), 1548 (m), 1474 (s), 1391 (w), 1322 (m), 1300 (m), 1280 (s), 1245 (m), 1150 (vs), 1116 (m), 1087 (vs), 1051 (m), 959 (m), 852 (m), 758 (m), 665 (s), 564 (vs), 549 (m) cm^{-1}. MS (FAB): *m*/*z* = 581 $[CuL]^+$, 426 $[CuL – Tos]^+$. $C_{27}H_{23}CuN_3O_4S_2$ (581.16): calcd. C 55.80, N 7.30, H 4.31, S 10.70; found C 55.61, N 7.23, H 3.99, S 11.03.

[CuL(bipy)]: A similar experiment to those described above (10 V, 10 mA, 1 h) with H_2L (0.194 g, 0.37 mmol) and 2,2′-bipyridine (0.058 g, 0.37 mmol) in acetonitrile (50 cm^3) led to the dissolution of 23 mg of metal, E_f = 0.97 mol F^{-1}. The resulting solution was slowly evaporated at room temperature to give brown crystals suitable for X-ray studies. IR (KBr): $\tilde{\nu}$ = 2922 (w), 1605 (s), 1595 (s), 1474 (vs), 1441 (w), 1297 (s), 1275 (vs), 1240 (m), 1142 (vs), 1068 (s), 956 (s), 894 (m), 847 (m), 810 (m), 768 (m), 760 (m), 734 (w), 680 (m), 561 (s), 549 (s) cm^{-1}. MS (FAB): *m*/*z* = 737 $[CuL(bipy)]^+$, 581 $[CuL]^+$, 425 $[CuL – Tos]^+$. $C_{37}H_{31}CuN_5O_4S_2$ (737.35): calcd. C 60.27, N 9.50, H 4.24, S 8.70; found C 59.98, N 9.61, H 4.30, S 8.50.

[CuL(phen)]: A similar experiment to those described above (12 V, 5 mA, 1.20 h) with H_2L (0.130 g, 0.25 mmol) and 1,10-phenanthroline (0.049 g, 0.25 mmol) in acetonitrile (50 cm^3) led to the dissolution of 15 mg of metal, E_f = 1.05 mol F^{-1}. IR (KBr): $\tilde{\nu}$ = 2924 (w), 1593 (m), 1548 (w), 1514 (m), 1474 (m), 1426 (m), 1295 (s), 1273 (s), 1239 (m), 1139 (vs), 1086 (s), 956 (s), 849 (m), 727 (m), 707 (m), 664 (s), 573 (m), 552 (m) cm^{-1}. MS (FAB): *m*/*z* = 761 $[CuL(phen)]^+$, 581 $[CuL]^+$, 425 $[CuL – Tos]^+$. $C_{39}H_{31}CuN_5O_4S_2$ (761.37): calcd. C 61.52, N 9.20, H 4.10, S 8.42; found C 60.95, N 9.43, H 4.15, S 8.32.

[ZnL]: A similar experiment to those described above (15 V, 10 mA, 2 h) with H_2L (0.196 g, 0.38 mmol) in acetonitrile (50 cm^3) led to the dissolution of 25.4 mg of metal, E_f = 0.52 mol F^{-1}. IR (KBr): $\tilde{\nu}$ = 2931 (w), 1612 (s), 1596 (s), 1553 (m), 1475 (vs), 1394 (m), 1298 (vs), 1275 (vs), 1257 (vs), 1142 (vs), 1089 (s), 968 (s), 847 (m), 834 (m), 812 (m), 709 (m), 663 (s), 563 (s), 551 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.76 (s, 1 H, CH=N), 7.98–6.82 (m, 28 H, aromatic), 2.30 (s, 3 H, CH_3), 2.16 (s, 3 H, CH_3) ppm. MS (FAB): *m*/*z* = 581 $[ZnL]^+$, 427 $[ZnL – Ts]^+$. $C_{27}H_{23}N_5O_4S_2Zn$ (611.01): calcd. C 55.63, N 7.21, H 3.98, S 11.00; found C 55.43, N 7.17, H 3.90, S 11.23.

[ZnL(bipy)]: A similar experiment to those described above (15 V, 10 mA, 1.5 h) with H_2L (0.149 g, 0.29 mmol) and 2,2′-bipyridine (0.045 g, 0.29 mmol) in acetonitrile (50 cm^3) led to the dissolution of 19 mg of metal, E_f = 0.52 mol F^{-1}. IR (KBr): $\tilde{\nu}$ = 2931 (w), 1614 (m), 1597 (w), 1475 (m), 1440 (m), 1299 (m), 1274 (m), 1261 (m), 1248 (m), 1143 (vs), 1121 (s), 1108 (m), 1089 (s), 965 (m), 858 (m), 845 (m), 765 (m), 750 (w), 734 (w), 663 (m), 549 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.98 (m, 2 H, $H^{6,6'}$), 8.53 (s, 1 H, CH=N), 8.11 (m, 2 H, $H^{3,3'}$), 7.92–6.77 (m, 28 H), 2.30 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3) ppm. MS (FAB): *m*/*z* = 738 $[ZnL(bipy)]^+$, 582 $[ZnL]^+$, 427 $[ZnL – Ts]^+$. $C_{37}H_{31}N_5O_4S_2Zn$ (739.18): calcd. C 60.12, N 9.47, H 4.23, S 8.67; found C 60.17, N 9.52, H 4.19, S 8.66.

[ZnL(phen)]: A similar experiment to those described above (15 V, 10 mA, 1.7 h) with H_2L (0.163 g, 0.31 mmol) and 1,10-phenanthroline (0.062 g, 0.31 mmol) in acetonitrile (50 cm^3) led to the dissolution of 21 mg of metal, E_f = 0.51 mol F^{-1}. IR (KBr): $\tilde{\nu}$ = 2931 (w), 1614 (s), 1555 (w), 1517 (m), 1476 (s), 1425 (m), 1385 (m), 1294 (m), 1254 (vs), 1133 (s), 1087 (m), 963 (m), 894 (m), 850 (m), 810 (m), 757 (m), 725 (m), 663 (s), 551 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 9.33 (d, ^3J(1H–1H) = 3.1 Hz, 2 H, $H^{2,9}$), 8.70 (s, 1 H, CH=N), 8.38 (d, ^3J(1H–1H) = 7.9 Hz, 2 H, $H^{5,6}$), 8.11 (d, ^3J(1H–1H) = 7.9 Hz, 2 H, $H^{3,8}$), 7.95–6.78 (m, 28 H), 2.29 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3) ppm. MS (FAB): *m*/*z* = 763 $[ZnL(phen)]^+$, 608 $[ZnL(phen) – Ts]^+$, 582 $[ZnL]^+$, 427 $[ZnL – Ts]^+$. $C_{39}H_{31}N_5O_4S_2Zn$ (763.21): calcd. C 61.38, N 9.18, H 4.09, S 8.39; found C 61.17, N 9.30, H 4.06, S 8.16.

[CdL]: Electrolysis of a solution of the ligand (0.157 g, 0.30 mmol) in acetonitrile (50 cm^3) at 8 V and 10 mA for 1.6 h dissolved 33 mg of cadmium from the anode, E_f = 0.49 mol F^{-1}. IR (KBr): $\tilde{\nu}$ = 2926 (w), 1613 (s), 1596 (m), 1555 (m), 1480 (s), 1444 (m), 1303 (s), 1251 (s), 1170 (w), 1133 (s), 1119 (vs), 1080 (vs), 983 (s), 892 (m), 842 (w), 804 (m), 757 (m), 705 (m), 663 (m), 556 (s) cm^{-1}. MS (FAB): *m*/*z* = 631 $[CdL]^+$. $C_{27}H_{23}CdN_3O_4S_2$ (630.02): calcd. C 51.47, H 3.68, N 6.67, S 10.18; found C 50.98, H 3.61, N 6.64, S 9.99.

[CdL(bipy)]: Electrolysis of a solution of the ligand (0.154 g, 0.30 mmol) and 2,2′-bipyridine (0.050 g, 0.32 mmol) in acetonitrile (50 cm^3) at 8 V and 10 mA for 1.5 h dissolved 31 mg of cadmium from the anode, E_f = 0.49 mol F^{-1}. IR (KBr): $\tilde{\nu}$ = 2923 (w), 1615 (m), 1594 (s), 1475 (s), 1438 (s), 1385 (m), 1296 (m), 1282 (m), 1253 (vs), 1136 (vs), 1086 (s), 1018 (m), 975 (s), 888 (m), 842 (m), 829 (m), 811 (m), 760 (s), 735 (w), 663 (s), 547 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.79 (m, 2 H, $H^{6,6'}$), 8.62 (s, 1 H, CH=N), 8.04 (m, 2 H, $H^{3,3}$), 7.87–6.79 (m, 1 H, aromatics), 2.29 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3) ppm. MS (FAB): *m*/*z* = 786 $[CdL(bipy)]^+$, 632 $[CdL]^+$, 477 $[CdL – Ts]^+$. $C_{37}H_{31}CdN_5O_4S_2$ (786.20): calcd. C 56.52, H 3.97, N 8.91, S 8.16; found C 56.89, H 3.73, N 8.23, S 8.12.

[CdL(phen)]: A solution of the ligand (0.156 g, 0.30 mmol) and 1,10-phenanthroline (0.061 g, 0.31 mmol) in acetonitrile (50 cm^3) was electrolysed at 8 V and 10 mA for 1.5 h and 33 mg of cadmium metal was dissolved from the anode, E_f = 0.52 mol F^{-1}. IR (KBr): $\tilde{\nu}$ = 2926 (w), 1617 (m), 1594 (m), 1517 (w), 1475 (s), 1427 (s), 1297 (m), 1255 (s), 1153 (m), 1135 (vs), 1087 (s), 974 (m), 854 (m), 727 (m), 651 (m), 550 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 9.14 (d, ^3J(1H–1H) = 4.4 Hz, 2 H, $H^{2,9}$), 8.70 (s, 1 H, CH=N), 8.30 (d, ^3J(1H–1H) = 7.9 Hz, 2 H, $H^{3,8}$), 7.97–6.80 (m, 28 H), 2.29 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3) ppm. MS (FAB): *m*/*z* = 811 $[CdL(phen)]^+$, 656 $[CdL(phen) – Ts]^+$. $C_{39}H_{31}CdN_5O_4S_2$ (810.23): calcd. C 57.81, H 3.86, N 8.64, S 7.91; found C 57.72, H 3.98, N 8.04, S 7.76.

X-ray Crystallographic Studies: Intensity data sets for compounds **1**, **2**, **3** and **6** were collected by using a MACH3 Enraf–Nonius diffractometer (Cu-K_α radiation; λ = 1.54184 Å) equipped with a graphite monochromator. The ω and ϕ scan techniques were employed to measure the intensities of these crystals. Intensity data for compounds **4**, **5** and **7** were collected by using a Smart CCD-1000 Bruker diffractometer (Mo-K_α radiation, λ = 0.71073 Å) equipped with a graphite monochromator. The ω scan technique was employed in these cases. All crystals were studied at 293 K. Decomposition of the crystals was not detected during data collection. The intensities of all the data sets were corrected for Lorentzian and polarization effects. Absorption effects in compounds **1**, **2**, **3** and **6** were corrected by using semi-empirical ψ scans; the absorption effects in compounds **4**, **5** and **7** were corrected by using the SADABS program.[73] The crystal structures of all the compounds were solved by direct methods. Crystallographic programs in the SHELX97 collection were used for structure solution and refinement.[74] Scattering factors were those provided with the SHELX programme system. Missing atoms were located in the difference Fourier map and included in subsequent refinement cycles.

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The structures were refined by full-matrix least-squares refinement on F^2. Hydrogen atoms were placed geometrically and refined by using a riding model with U_{iso} constrained at 1.2 (for non-methyl groups) and at 1.5 (for methyl groups) times U_{eq} of the carrier C atom. For all structures non-hydrogen atoms were anisotropically refined and in the last cycles of refinement a weighting scheme was used, with weights calculated using the formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, in which $P = (F_o^2 + 2F_c^2)/3$.

Table 6. Summary of the crystallographic data and refinement for compounds.

	H_2L	[NiL]	[CuL]	[NiL(dppm)]
Empirical formula	$C_{27}H_{25}N_3O_4S_2$	$C_{27}H_{23}N_3O_4S_2Ni$	$C_{27}H_{23}N_3O_4S_2Cu$	$C_{52}H_{45}N_3O_4S_2P_2Ni$
Formula mass	519.62	576.31	581.14	960.68
Crystal size [mm]	$0.40 \times 0.24 \times 0.16$	$0.24 \times 0.16 \times 0.12$	$0.48 \times 0.48 \times 0.12$	$0.30 \times 0.27 \times 0.07$
Temperature [K]	293(2)	293(2)	293(2)	293(2)
Wavelength	1.54184	1.54184	1.54184	0.71073
Crystal system	orthorhombic	triclinic	triclinic	triclinic
Space group	$Pca2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions				
a [Å]	20.3993(6)	8.535(2)	8.5316(10)	9.046(2)
b [Å]	7.1230(4)	10.9738(19)	11.0240(3)	10.438(3)
c [Å]	17.5386(7)	13.735(4)	13.7471(13)	25.400(6)
α [°]	90.00	94.36(3)	95.373(4)	82.552(4)
β [°]	90.00	99.532(17)	100.113(11)	82.566(4)
γ [°]	90.00	98.80(3)	98.568(4)	87.945(4)
Volume [Å^3]	2548.43(19)	1247.0(6)	1249.09(19)	2357.7(10)
Z	4	2	2	2
μ [mm^{-1}]	2.216	3.028	3.136	0.617
F(000)	1088	596	598	1000
Reflections collected	2632	5209	5213	26039
Independent reflections	2631	4989	4993	7836
	[R(int) = 0.1842]	[R(int) = 0.0769]	[R(int) = 0.2260]	[R(int) = 0.0888]
Data/restraints/parameters	2631/1/326	4989/0/334	3939/6/223	7836/336/689
Goodness-of-fit	1.041	0.990	1.060	1.001
Final R indices	R_1 = 0.0396	R_1 = 0.0615	R_1 = 0.0902	R_1 = 0.0536
[$I > 2\sigma(I)$]	wR_2 = 0.0931	wR_2 = 0.1530	wR_2 = 0.2251	wR_2 = 0.1148
R indices (all data)	R_1 = 0.0803	R_1 = 0.1497	R_1 = 0.1036	R_1 = 0.1076
	wR_2 = 0.1088	wR_2 = 0.1926	wR_2 = 0.2405	wR_2 = 0.1366
Largest diff. peak and hole [e Å^{-3}]	0.198 and –0.253	0.702 and –0.871	2.387 and –1.865	0.461 and –0.614

	[CoL(phen)]	[ZnL(phen)]	[CuL(bipy)]
Empirical formula	$C_{39}H_{31}N_5O_4S_2Co$	$C_{39}H_{31}N_5O_4S_2Zn$	$C_{37}H_{31}N_5O_4S_2Cu$
Formula mass	756.74	763.18	737.33
Crystal size [mm]	$0.57 \times 0.23 \times 0.07$	$0.20 \times 0.10 \times 0.03$	$0.20 \times 0.20 \times 0.12$
Temperature [K]	293(2)	293(2)	293(2)
Wavelength	0.71073	0.71073	1.54184
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
Unit cell dimens.			
a [Å]	18.030(4)	18.171(8)	37.287(6)
b [Å]	12.778(3)	12.764(5)	12.359(3)
c [Å]	16.791(3)	16.927(7)	17.05(3)
α [°]	90.000	90.000	90.000
β [°]	116.245(4)	116.855(7)	107.093(14)
γ [°]	90.000	90.000	90.000
Volume [Å^3]	1141.6(4)	3502(2)	7509(13)
Z	4	4	8
μ [mm^{-1}]	0.665	0.870	2.220
F(000)	1564	1576	3048
Reflections collected	21180	19890	6331
Independent reflections	7077	4268	6227
	[R(int) = 0.0856]	[R(int) = 0.1981]	[R(int) = 0.0532]
Data/restraints/parameters	7077/0/460	4268/0/461	6227/0/442
Goodness-of-fit	1.085	1.001	1.001
Final R indices	R_1 = 0.0774	R_1 = 0.0772	R_1 = 0.0611
[$I > 2\sigma(I)$]	wR_2 = 0.1860	wR_2 = 0.1600	wR_2 = 0.1149
R indices (all data)	R_1 = 0.1954	R_1 = 0.2172	R_1 = 0.2040
	wR_2 = 0.2656	wR_2 = 0.2168	wR_2 = 0.1294
Largest diff. peak and hole [e·Å^{-3}]	1.041 and –0.684	0.514 and –0.505	0.358 and –0.632

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In compound **4** both 4-toluenesulfonate groups and one phenyl ring on the uncoordinated phosphorus atom were found to be disordered over two positions (occupancies: 75:25, 50:50 and 50:50, respectively). Disorder was typically handled by introducing split positions for the affected groups into the refinement of the respective occupancies. Compound **6** contains a severely disordered molecule of acetonitrile in a void of the crystal lattice. This solvent was removed by using the Squeeze program[75] implemented in Platon.[76]

Compound **7** is a very weak diffractor and did not give detectable diffraction above $\theta = 22°$. Thus, the bond lengths and angles for this structure are of lower precision than the parameters obtained for the rest of the crystal structures.

Pertinent details of the data collections and structure refinements are summarized in Table 6. Further details regarding the data collections, structure solutions and refinements are included in the Supporting Information. ORTEP3 drawings[77] with the numbering schemes used are shown in Figures 1–6.

CCDC-805162 (for **1**), -805163 (for **5**), -805164 (for **3**), -805165 (for **6**), -805166 (for **2**), -805167 (for **4**), -805168 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see the footnote on the first page of this article): The crystal packing of the ligand and FAB mass spectra of the metal complexes are described, hydrogen-bonding parameters for compounds **1**–**7** (Table S1), π–π stacking interactions for compounds **2**, **3**, **5**–**7** (Table S2), crystal structure of [NiL] showing C–H···O interactions (Figure S1), ORTEP diagrams of the molecular structures of [CoL(phen)] and [ZnL(phen)] (Figures S2 and S3).

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